DOE Methods

for Evaluating Environmental and Waste Management Samples

October, 1994 U.S. Department of Energy Assistant Secretary
for Environmental Restoration and Waste Management

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DOE Methods for Evaluating Environmental and Waste Management Samples

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Abstract

DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods) is a resource intended to support sampling and analytical activities for the evaluation of environmental and waste management samples from U.S. Department of Energy (DOE) sites. *DOE Methods* is the result of extensive cooperation from all DOE analytical laboratories. All of these laboratories have contributed key information and provided technical reviews as well as significant moral support leading to the success of this document. *DOE Methods* is designed to encompass methods for collecting representative samples and for determining the radioisotope activity and organic and inorganic composition of a sample. These determinations will aid in defining the type and breadth of contamination and thus determine the extent of environmental restoration or waste management actions needed, as defined by the DOE, the U.S. Environmental Protection Agency, or others. The development of *DOE Methods* is supported by the Analytical Services Division of DOE.

Methods are prepared for entry into *DOE Methods* as chapter editors, together with DOE and other participants in this program, identify analytical and sampling method needs. Available resources are typically used to fill these needs. These resources include private corporations, contacts at other DOE facilities, and the *DOE Procedures Database* (located at the Los Alamos National Laboratory, Los Alamos,

New Mexico), which incorporates sampling and analytical procedures submitted from DOE laboratories.

Unique methods or methods consolidated from similar procedures in the *DOE Procedures Database* are selected for potential inclusion in this document. Initial selection is based largely on DOE needs and procedure applicability and completeness. Methods appearing in this document are one of two types, "Draft" or "Verified." "Draft" methods that have been reviewed internally and show potential for eventual verification are included in this document, but they have not been reviewed externally, and their precision and bias may not be known. "Verified" methods in *DOE Methods* have been reviewed by volunteers from various DOE sites and private corporations. These methods have delineated measures of precision and accuracy. All pertinent reviewer comments are addressed by the author of the method so as to meet technical approval by the reviewers. Once all comments are satisfactorily resolved, the method is incorporated as fully verified.

DOE Methods is a "living document." As new and better procedures become available, they should be submitted to Dr. S.C. Goheen (Pacific Northwest Laboratory, Box 999, Mail Stop P8-08, Richland, Washington 99352) for entry into the database for evaluation and potential inclusion in this document.

Acknowledgments

DOE Methods has been assembled at Pacific Northwest Laboratory with the assistance of numerous authors, editors, and reviewers. The editors of this edition of the document coordinated the preparation and technical editing of the chapters and methods. Wayne C. Cosby provided nontechnical editorial support, and Georgia K. Ruebsamen, desktop publisher, created the design. Michael H. Carter and David W. Bottrell have coordinated this program within the U.S. Department of Energy (DOE). W. Patrick Brug has also contributed significantly to this program by managing the *DOE Procedures Database* at the Los Alamos National Laboratory. Method contributors are indicated in each published method.

In addition, many individuals contributed their time and efforts to submit procedures to the database. These contributors are too numerous to list, but we appreciate their efforts and their support of this project. Funding for this project has been provided by the Department of Energy, Analytical Services Division.

We also thank those who continue to provide valuable input to each edition of *DOE Methods*.

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Introduction

The U.S. Department of Energy's (DOE's) environmental and waste management (EM) sampling and analysis activities require that large numbers of samples be analyzed for materials characterization, environmental surveillance, and site-remediation programs. The present document, *DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods)*, is a supplemental resource for analyzing many of these samples. Laboratories frequently use methods contained in the U.S. Environmental Protection Agency's (EPA's) laboratory manual, *EPA Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW-846)*; statements of work (SOW) for the EPA Contract Laboratory Program (CLP); or other EPA standard methods, such as those developed for assessing water pollution in drinking water. *DOE Methods* complements these established documents by combining information from existing DOE activities, thus providing a resource with enhanced visibility and combined quality control (QC) information. This process enhances method verification for EM sampling and analysis activities. Field sampling methods are included as well as methods for radioactive and other unique samples encountered in conducting many of the DOE/EM programs.

In this document, methods are distinguished from procedures in that procedures are generally site-specific documents, giving a level of detail that might refer, for example, to specific instruments. Methods are more generic, but specific enough to be reproducible. Methods are included in *DOE Methods*.

To help readers quickly identify changes made since the April 1994 addendum, this revision (October 1994) includes highlighted text and (occasionally) a "Draft" designation at the top of the page. These markings indicate modifications made to the April 1994 addendum. The methods chapters {Chapter 7 (Sampling Methods), Chapter 8 (Organic Methods), Chapter 9 (Inorganic Methods), and Chapter 10 (Radiochemistry)} were extensively rewritten for this issue (Revision 2) of *DOE Methods* to make them more consistent in style and content. Therefore, these chapters are designed as "draft." Changes in tables are indicated by thick brackets (**[]**). All draft designations will be removed in the April 1995 addendum. New modifications will be similarly identified at that time.

Background and Scope

DOE Methods provides methods for supporting EM sampling and analysis activities that are unique to the DOE complex. Many sites have independently developed their own procedures for sampling, sample analysis, quality assurance (QA), and QC to ensure sample and data integrity in support of EM programs. These new methods have been developed for three prominent reasons: 1) to apply technological advances, 2) to implement waste reduction, and 3) to analyze components of complex matrices. The intent of *DOE Methods* is to pull these methods together into one document for use by other analysts. This program is designed to expedite technology transfer, reduce costs, and

improve the guidance needed to perform sampling and analytical work for EM.

DOE Methods also provides associated guidelines for method selection and use. These guidelines can be used to address conventional as well as unique EM sampling and analysis challenges found at sites throughout the DOE complex.

In the current version of *DOE Methods* (Rev. 2) the order of the first 5 chapters has been revised. The old Chapter 5 (Sampling and Analysis Plan) has been revised and placed near the front of the document. The new chapter, "Guidance for Effective Project Planning", is now Chapter 1. Chapters 1 through 5 have been renumbered to accommodate this change.

Need for New Methods

The focus of *DOE Methods* is to provide methods that fulfill needs not met by other standard methods.

Modifications, alternatives, and additions to current standard procedures are a common practice at laboratories providing analytical chemistry support for the more unique sampling and analysis needs encountered under DOE/EM programs. Evaluating samples from complex matrices (e.g., matrices containing high radioactivity, interfering contaminants, and/or unidentified matrix effects) may require specialized equipment, facilities, and procedures not currently covered by standard methods. For example, to protect analysts from the more radioactive samples, sample sizes may need to be reduced to maintain personnel exposure and equipment contamination "as low as reasonably achievable" (ALARA). Hot cells or gloveboxes may also be needed. Highly radioactive tank waste must be collected using specialized and shielded equipment. Sampling plans based on random sampling may inadequately identify concentrated

contaminants in secondary containers (e.g., glass bottles in 55-gal drums). Environmental samples obtained from the vadose zone or underlying groundwater of DOE waste sites may also be very complex, and, therefore, require specialized procedures as well.

Proposed Action to Fill Needs

DOE Methods is intended to meet some of the more challenging sampling and analytical capability needs brought about by implementing EM programs at DOE sites. Both verified and nonverified ("draft," as defined in Appendix A) methods have been included. Verified methods contain adequate QC data and have been extensively reviewed. Draft methods, which are to be used at the user's own risk, have not yet been reviewed externally and may or may not contain QC data. It is the intent of the editors of *DOE Methods* to obtain adequate QC data from draft methods and subsequently to process these methods through a rigorous external review to verify them. Once verified, the "draft" designation of the methods will be removed, and they will be reissued with other updated sections of *DOE Methods*. *DOE Methods* will be maintained as a "living document," with new information entered in subsequent revisions as additional or more complete data are obtained.

To develop *DOE Methods* and to provide interested parties with quick access to available procedures, laboratory personnel from DOE sites were contacted to obtain the procedures they use for analyzing radioactive and other hazardous waste samples. Upon receipt, information from each procedure was entered into a database called the *DOE Procedures Database* (or database). The database is maintained as an information resource available to any interested party. The goal is to increase information flow and

technology transfer and to decrease duplication of effort. These procedures were originally gathered in hardcopy form and were transformed into text and image files that are now stored electronically. The database currently contains approximately 2,000 full-text procedures, most of which are procedures for radiochemical analyses. The database is being updated continuously as new and revised procedures are provided by labs across the DOE complex. The database is accessed through the SEARCHmate® system, which permits full text searching of each procedure and allows the user to find the procedures of interest quickly. Additionally, the user may search for procedures by analyte, matrix, and detection limit. The database can be accessed externally through a modem once access has been granted. For access, contact W. Patrick Brug {(505)-665-7409; e:Mail address - brug@lanl.gov} at the Los Alamos National Laboratory.

DOE Methods and the *DOE Procedures Database* are being assembled in cooperation with one another as components of the DOE Methods Compendium program. Procedures have been and will continue to be selected or combined from the database where applicable. Methods are generated, selected, or consolidated according to the process described in Appendix A. Methods are then prepared to conform to a standard format, and are included in *DOE Methods* with a draft status. If the draft methods contain appropriate QC data and are approved by peer reviewers, they are included in *DOE Methods* as verified methods. Where applicable, some of these verified methods are also submitted to EPA for inclusion in SW-846.

DOE Methods now includes alternative performance requirements for selecting or generating methods and for designing a sampling and analysis program (see Appendix B). Performance requirements specify acceptable precision and accuracy criteria as well as reliable quantitation limits and range for an analysis.

They also allow the analyst flexibility in achieving that performance level. Analysts may use a method or modify it to achieve the desired level of performance they need—i.e., methods or procedures should be documented to meet the data requirements of the project according to the guidelines in Appendix B.

The methods in *DOE Methods* include step-by-step instructions with performance data (if verified). These methods are provided as a guide. They have been proven to be effective for DOE waste and/or environmental analysis. Such methods may be useful as written, or may need to be modified to meet analytical needs. It is appropriate to demonstrate that data obtained from a method that resembles one of those in this document will be comparable to the data obtained using these or other documented or approved methods (e.g., ASTM, EPA, etc.). A more detailed description of the mechanism for demonstrating that a new or revised method can be used appears in Appendix B. Such consistency in analytical results ensures that data obtained from across the DOE complex are comparable when data quality objectives (DQOs) are comparable. That is our goal.

Structure and Organization of This Document

DOE Methods contains 11 chapters and 2 appendixes. The chapters are arranged as follows:

- Chapters 1 through 5 - guidance on the design of the EM sampling/analytical program.
- Chapter 6 - guidance for choosing the correct method for specific analysis needs.

- Chapters 7 through 11 - guidance for specific analyte classes and detailed methods for sampling or analysis.

Appendix A describes the process for verifying methods in *DOE Methods*, and Appendix B describes the performance-based approach to using and modifying methods.

This document has been developed using comments from a large number of reviewers. Your comments are appreciated. Please send them to

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Method Numbering System

Methods in *DOE Methods* are identified with a numbering scheme. An example from the table of contents is given below:

- The first two letters designate classes of methods, as indicated in Table 1.
- Each method is given a distinct number (the next three digits).
- Organic and inorganic methods designed for use with radioactive samples have an "R" at the end of the number.

OG015R
1 2 3

Major Nonhalogenated Volatile
Organics in Radioactive Aqueous
Liquids Analyzed by Direct
Aqueous Injection Gas
Chromatography (DAI-GC)

Table 1. Numbering System for DOE Methods

S	Sampling	M	Inorganics
SAxxx	Air Sampling	MSxxx	Screening
SWxxx	Water Sampling	MPxxx	Sample Prep
SSxxx	Soil Sampling	MAxxx	AA Methods
SDxxx	Drum Sampling	MBxxx	Immunonological Assays
STxxx	Tank Sampling	MCxxx	Ion Chromatography
		MLxxx	ICP Methods
O	Organics	MMxxx	ICP-MS Methods
OSxxx	Screening	MVxxx	Uncategorized Methods
OGxxx	Cleanup		
OPxxx	Sample Prep	R	Radionuclides
OGxxx	GC Determinative/Various Detectors	RFxxx	Field Screening
OHxxx	HPLC Determinative/Various Detectors	RPxxx	Sample Prep
OMxxx	GC-MS or LC-MS Determinative	RIxxx	Instrumentation
OIxxx	IR or GC-IR Determinative	RAxxx	Miscellaneous Radiochemistry
OVxxx	UV-Vis Determinative		
OXxxx	TOC, TOX	X	Miscellaneous Methods

Acronyms Used in Table

AA - atomic absorption	MS - mass spectrometry
GC - gas chromatography	TOC - total organic carbon
HPLC - high-performance liquid chromatography	TOX - total organic halides
ICP - inductively-coupled plasma	UV - ultraviolet
IR - infrared	Vis - visible
LC - liquid chromatography	

Chapter 1

Guidance for Effective Project Planning

Scope and Application

The purpose of this chapter is to provide general guidance for designing an environmental and/or waste-management project plan. The chapter also addresses implementing the plan and assessing project data against requirements defined in the plan. Establishing well-defined data quality objectives (DQOs) for a specific project is a prerequisite for designing an effective project plan.

Data quality objectives are determined based upon implementation of a DQO process. The guidance for completing the DQO process contained in this chapter is based upon the U.S. Environmental Protection Agency's (EPA's) data quality objectives planning process (DQOPP) and the U.S. Department of Energy's (DOE's) enhancement of this process to meet DOE's environmental restoration and waste management (EM) needs. Both the DQOPP and the DOE adaptation of this process, known as the Streamlined Approach for Environmental Restoration (SAFER), are tools to effectively define data needs to tie them to decision making. For simplicity, we will use the DQOPP to represent any planning process.

General Considerations

Quality assurance project plans (QAPPs), frequently referred to as project plans, implement the outputs of the DQOPP. This chapter provides a brief description of each step to be followed through the DQOPP (EPA 1991; EPA 1992a; EPA 1992b; EPA 1993a; EPA 1993b; Blacker 1993). The original guidance was replaced by these documents.

A complete project plan provides 1) a clearly defined project scope, 2) a set of project DQOs, and 3) a roadmap for achieving those DQOs. It also provides a plan for assessing the quality of the data to ensure that those data meet project requirements. The plan

- provides a description of the project and its scope and objectives
- identifies project participants and their roles
- defines any temporal or spatial requirements pertaining to the project, such as sampling schedules and site descriptions
- defines how the data will be used, what decisions will be made based on the data, and the acceptable error tolerances for those decisions
- defines the quality assurance/quality control (QA/QC) required to demonstrate that the needed data quality is achieved

- documents the sampling design and statistical considerations used to formulate the sampling strategy
- provides instructions or identifies procedures or methods for sampling, handling, and analyzing waste or environmental samples
- defines any subcontracting needs
- describes data handling and records requirements
- defines strategies for minimizing pollution and for safety
- provides a schedule for conducting sampling and analysis activity
- provides requirements for assessing project performance against original quality objectives.

The DQOPP is distinguished from the more traditional view of data quality in the following way:

Traditional data quality focuses on the question: "How good do those individual pieces of data need to be?" Individual data descriptors, such as precision, accuracy, representativeness, completeness, and comparability {i.e., the PARCC (precision, accuracy, representativeness, completeness, comparability) parameters}, are used to gauge the quality of a single data point or a data set. In contrast, the DQOPP focuses on how the data will be used. It acknowledges that data are collected and analyzed not because the data have intrinsic worth, but because the data are needed to make decisions or to make estimates of population parameters. The DQOPP asks the question, "How good does this decision need to be?" Most data-collection activities will involve

something less than a 100%, completely accurate sample result. Decisions based on incomplete or imprecise data will lead to decision errors. Poor data quality and few samples will lead to increased decision errors. The DQOPP says that data quality can be established only after limits on (the probability of) decision errors are established.

Federal agencies charged with setting data quality guidelines are currently re-evaluating their support for the traditional approach. As new guidelines are finalized, the emphasis will probably shift from the more traditional definitions of data quality to those more consistent with the DQOPP. Several DOE federal facilities compliance agreements are explicitly calling out the requirement that all project plans must be based on the DQO process. A considerable body of experience is accumulating on applying the DQO process. Training videos on the DQO process are available, and DQO applications are appearing in many publications.

Generally, the description of a DQOPP involves seven steps. Several seven-step processes have been introduced over time and by different groups; no single, unique DQO process exists. The individual steps or their order is not as important as the philosophy of the DQO process.

The first six of the DQOPP steps address planning issues, project objectives, and desired decision-error tolerances. These steps serve to define the problem, set priorities, define a decision rule, and focus on possible answers and decisions. The final step addresses operational issues (i.e., how many samples to take, where to take the samples, what sampling equipment to use, what analytical procedures to use) and optimization (i.e., how close can we come to our desired decision-error tolerances, yet stay within a fixed sampling and analysis budget?). Working through this process will provide the framework needed to write a QAPP. The basic tenet

of the DQO process is that only those data that are required to answer the questions being posed and make decisions among alternative actions should be collected and analyzed.

The DQOPP stresses active involvement of all stakeholders. Key decision-makers, regulators, sample-collection staff, and sample-analysis staff should be actively involved in project planning to avoid costly replanning once the project has entered its data-collection phase. Thus, team members, including regulators, should be present in the same place during the DQOPP. Without understanding the DQOPP concepts, much of the project budget may be expended before a project that meets the needs of all stakeholders is defined, leaving insufficient money and time to finish the job properly. Inclusion of all stakeholders on the DQOPP team will ensure that the required balance between data needs and available resources will be achieved. It will also ensure that the appropriate quality of data is generated to support decisions.

Each EM project will have a different objective and scope, so flexibility in applying the DQOPP is appropriate. Projects with limited scopes may not require the rigorous application of each step within the DQOPP whereas large, complex projects may require considerable time to work through the DQOPP in more detail. Similarly, projects that involve safety issues where making a decision error could have serious consequences require a more rigorous DQOPP. Recent applications of the DQO process have shown that in some situations, insufficient information exists, and decision makers cannot arrive at a consensus about what constitutes acceptable decision-error rates. In these situations, the information is not available to allow the team to work

through all seven steps of the DQO process, and flexibility must be maintained. As an example of the flexibility required, a DQO application at a DOE site addressed three categories of limited-scope DQOPPs. Included were "estimation-only" and "preliminary" DQO studies^(a).

The DQOPP is an iterative process, and it is entirely appropriate that, if one step of the DQOPP indicates that the results of a previous step need to be reevaluated/redefined, then the previous step(s) should be repeated. This iterative process helps to ensure that decisions appropriate to the project are identified during the planning stage so the active sampling and analysis stages of the project will proceed smoothly, without costly repeats. After working through the DQOPP steps, it may happen that due to cost constraints or unacceptable "achievable" decision-error probabilities, the scope of the problem must be reduced. However the stakeholders choose to resolve the issues, the final goal is to have a QAPP that is grounded in the drivers for the data collection (i.e., the decisions to be made based on the data). Table 1 shows the DQOPP steps that should be followed.

Definitions

Data Quality Objectives (DQOs) - Qualitative and quantitative statements that specify the quality of data required and that are based on the end uses of the data to be collected. In general, DQOs are expressed in terms of accuracy, precision, representativeness, comparability, and completeness. They are often determined by the nature of the test being carried out. For example, DQOs for screening purposes may allow less stringent precision and accuracy require-

(a) Draft report entitled *TWRS Data Quality Objectives Implementation Guidance: Requirements, Content and Style Guide* by B. A. Pulsipher, D. Michael, D. Neptune, R. Ryti, P. Black, and S. Redus. WHC-SD-WM-DWO-005. Prepared for the U.S. Department of Energy by Westinghouse Hanford Company, Richland, Washington.

Table 1. Project Plan Development-DQOPP Steps

Steps	Description
1	State the problem to be resolved
2	Identify the decision(s) required for successful completion of the project
3	Identify inputs to the decision
4	Define the study boundaries
5	Develop a decision rule
6	Specify limits on decision errors
7	Optimize sampling and analysis activities

ments than those imposed on analyses performed in support of federal or state regulations.

Data Quality Objectives Planning Process (DQOPP) - A total quality management (TQM) tool developed by the EPA to facilitate the planning of environmental data-collection activities. The DQOPP asks planners to focus their planning efforts by specifying the use of the data (the decision), the decision criteria, and their tolerance to accept an incorrect decision based on the data. The products of the DQOPP are the DQOs.

Data Quality Assessment (DQA) - Process used to determine the adequacy of the data to meet the degree of certainty, i.e., risk of making a wrong decision, accepted during project planning to make an environmental decision.

Quality Assurance Project Plan (QAPP) - "Quality Assurance Project Plan" and "Project Plan" are synonymous terms referring to an orderly assemblage of detailed QA, QC, sampling, and analytical procedures designed to produce data of sufficient quality to meet the DQOs for a specific data-collection activity.

Project Plan Development—Steps Before Initiation of DQOPP

Before formal initiation of the DQOPP, the project manager should evaluate the size of the project and estimate how much time should be devoted to each of the DQOPP steps. Also, the project manager should understand the available resources and relevant deadlines. Usually, the DQOPP should be initiated after the project manager has studied historical information relevant to the project and has understood enough about the project to begin helping the DQOPP team members to work through the process. Any available screening or laboratory data should be evaluated. Based on a careful review of relevant information, an initial attempt should be made to define the problem concisely and unambiguously. An initial determination should be made of who should lead and who should participate in the DQOPP.

Project Plan Development—DQOPP Steps

Step 1—State the problem to be resolved.

The problem about which a decision must be made should be defined concisely and unambiguously. To come to agreement on the problem to be resolved, all stakeholders need to present their concerns, perceptions, biases, and requirements. Understanding the problem(s) being addressed by the project clarifies how the sampling and analysis effort relates to resolving the overall project problem. Step 1 provides team members the opportunity to meet together and ensure that all issues, such as public concerns, regulatory threshold levels, resources available to the project, and relevant deadlines, are addressed before they are asked to agree upon a statement of the problem. This step allows the DQOPP team members to come to a consensus on why the work is being planned. During Step 1, it should become apparent whether the right team was initially chosen to participate in the DQOPP. If it becomes apparent that team members have been chosen who cannot contribute effectively to the process, the team makeup should be adjusted accordingly. If, on the other hand, it becomes clear that other input is needed for the process, these individuals should be added to the DQOPP team when the need is identified. Similarly, if Step 1 reveals that resources allocated to the project are insufficient to answer the problem, the team should agree upon a reduced scope problem, or they should obtain the required additional resources.

Complex projects should be broken into smaller pieces to allow the DQOPP to go forward. If the project can be better defined in terms of multiple problems, the DQOPP should be performed for each identified problem.

The initial output from Step 1 is a statement of the problem as a question. It is important that all DQOPP team members agree upon the exact wording of this statement of the problem. An example statement of the problem could be, "Is the underground tank leaking?" Agreement upon the statement of the problem should be documented by a written statement of the problem with signatures of all those on the team.

Additional outputs from this step are a list of DQOPP team members and a summary of available resources and relevant deadlines.

Step 2—Identify the decision(s) required for successful completion of the project.

The purpose of this step is to identify the action-based decision(s) that will address a specific problem using data generated as a result of this planning exercise. Multiple problems should be addressed in order of descending priority. Possible answers to the questions posed by the problems should be described, agreed upon, and documented. These answers should be stated so choices between alternate actions based on the data collected are documented. For example, the possible answers to the question posed in Step 1 are "Yes, the tank is leaking," and "No, the tank is not leaking." If the answer based on project data is "No," the action might be to do nothing. This proposed action should be documented. If, however, data supported the answer, "Yes," then another action(s) might be indicated. Actions that would be taken based on answers to the various questions resulting from Step 1 of the DQOPP should be described in detail and documented.

There may be secondary uses for the data to be collected in addition to supporting the decision(s) to be made. A list of secondary data uses should be developed. To the extent practical, the needs of secondary data users should be met.

The output from Step 2 is a list of possible answers to the question(s) that must be resolved with data from this study and corresponding actions to be taken depending on the answers to the question(s). Agreement with this list by all DQOPP team members should be documented by signatures of each team member.

Step 3—Identify inputs to the decision.

The purpose of this step is to identify the information that will be required to resolve the decision(s) and to list all the environmental variables or characteristics that need to be measured. The sample-collection staff and laboratory analysts should work with the DQOPP team to determine the minimal amount of data required. Most decisions will involve some contaminant concentration level (called action level) that will trigger an action to be taken. This action level may be a regulatory threshold, may be based on a risk or exposure assessment, or may come from technology limits or a reference-based standard. The information identified in this step includes the input required to determine this action level.

During this step, it is important to confirm that the variables or characteristics identified for making the key decision(s) are actually measurable with existing technology. If key inputs are not measurable, then 1) a different approach should be taken to address the decision, or 2) the DQOPP team should determine whether it is reasonable to make assumptions about the variables of interest. If no practical approach can be developed, the effort should shift to developing the research tools needed to address the problem.

Step 4—Define the study boundaries.

The purpose of this step is to clearly define the spatial or temporal boundaries of the problem. This serves to 1) specify the attributes that define the population

of interest for which a decision (based on the samples) will be made, 2) define the spatial area or volume to which the decision will apply, and 3) define the time period to which the study data and the decision (if different) will apply. This process narrows the scope of the project to ensure that the project problem is resolved.

The outputs from Step 4 should be a clear definition of any sampling constraints, a description of the geographical area relevant to the problem, a definition of temporal constraints relevant to the problem, a list of analyte measurements, and any relevant matrix constraints. These outputs should be documented and signed by DQOPP team members.

Step 5—Develop a decision rule.

A decision rule is a statement that defines how environmental data will be summarized and used to support the specific decision(s) that is the focus of the data-collection event.

The decision rule should 1) specify the parameter(s) that characterizes the population of interest and 2) specify the action level for the study. These two parts of the decision rule should be documented as an "If..., then..." logic statement. For example, in the scenario presented in Step 1, a possible decision statement might be: "If the mean soil concentration for carbon tetrachloride surrounding the tank is greater than or equal to 1 mg/kg, then the tank must be taken out of the ground, and the affected soil surrounding the tank must be disposed of as hazardous waste." The parameter of interest is a descriptive measure (such as a mean, median, range, upper percentile, or proportion) that specifies the characteristic or attribute the decision maker would like to know about the population. The action level can be an absolute regulatory threshold, it can be risk-based (based on a site-specific risk calculation), or it can be a multiple of a background standard.

The output from Step 5 is an “if..., then...” statement that incorporates the parameter of interest (e.g., average concentrations for carbon tetrachloride), the appropriate action level (e.g., 1 mg/kg), and the action(s) that would result from the decision (e.g., removal of tank and disposition of affected soil).

Step 6—Specify limits on decision errors.

While errors are an inherent part of any sampling and measurement process and cannot be eliminated, they can be explicitly identified, quantified, and, in many cases, controlled. Similarly, decisions that are made based on sample data, and estimates of population parameters based on sample data, will be subject to errors. We will never know whether we have made an error unless we take a completely accurate, exhaustive sample. This is usually not feasible. However, we can make statements about the probability of making errors and specify limits for these error probabilities. We can then design project plans that achieve these error probabilities.

Errors introduced through the sampling and analysis process can often be defined and controlled through rigorous adherence to QA/QC practices and the use of an appropriate QAPP. Errors introduced through the decision process can be defined and controlled through appropriate selection of the test statistic and the test criteria. More appropriate collection and analytical equipment can be purchased to reduce errors. Additional samples can be collected to minimize the errors in the estimates of spatial and temporal variability. More robust tests can be used to reduce decision errors.

Yet the key question remains: “What level of decision error is acceptable?” It is the stakeholders who must answer this difficult question. The answer to this question will drive the quality and quantity of data to collect. It will drive the sampling and analysis processes. In this step, stakeholders specify

the maximum level of errors they can tolerate in the decisions to be made.

Two types of decision errors are possible:

- False positive errors: deciding to take an action when the data incorrectly indicate that a problem exists.
- False negative errors: deciding not to take an action when data incorrectly indicate that a problem does not exist.

Acceptable levels for the probability of making these two types of decision errors depend on the potential consequences of making an error. Using the scenario presented in Step 1 and the example of a false negative error: If the true average concentration of carbon tetrachloride in the soil is significantly greater than the 1 mg/kg action level, but the sample data show levels below 1 mg/kg, a decision maker would (incorrectly) conclude not to remediate the site. The consequence of concluding the site need not be remediated (a false conclusion) is very severe at high concentration levels. However, if the true concentration is just slightly greater than the 1 mg/kg action level, but sample values are below 1 mg/kg, an incorrect decision will still be made, but the consequence is not so severe. The stakeholders would desire very small probabilities for false negative errors at concentrations significantly greater than 1 mg/kg and be willing to accept larger probabilities for concentrations near 1 mg/kg. In fact, when the true concentration is within a small region near the action level, the stakeholders are indifferent as to which decision is made. This region is called a “gray region” and must be specified by the stakeholders. The size of the gray region and the level of acceptable error probabilities determine the QA/QC requirements for the project. These desired limits on decision errors, including the gray region, can be expressed in the form of a decision-performance graph

or table that specifies the acceptable probability of incorrect decisions as a function of true parameter values.

The output from Step 6 is a desired decision-performance graph that depicts acceptable levels for the probability of decision errors as a function of true parameter values. This output should be agreed upon and signed by all team members.

Step 7—Optimize sampling and analysis activities.

Steps 1 through 6 solicited input from the DQOPP team. This input is now used to design a QAPP. Data collected using such a plan can be summarized and used in an operational decision rule to select between the alternative actions. If all assumptions hold true, the stakeholders can be assured of making decision errors no greater than those specified in Step 6. Step 7 is called the optimization step because stakeholders seek to optimize (come as close to achieving) the desired decision-error probabilities as possible, yet satisfy realistic project constraints, such as fixed budgets and time constraints.

Step 7 is used to assess and make trade-offs between project goals (as embodied in the DQO input) and project constraints. This optimization step requires knowledge of how the various components of the DQOPP interact. Reducing error probabilities requires increased sample sizes, reduced sampling variability (e.g., more accurate sample collection and analysis equipment) or both. Decreasing one type of decision error (say, the false positive rate) will increase the other type (the false negative rate). A very narrow “gray region” will require large sample sizes and/or very accurate and precise sampling and measurement equipment. Populations that are highly variable require large sample sizes to accurately estimate their characteristics. Some sampling designs are more efficient than others at detecting

extreme values and possible outliers. Making these trade-offs to arrive at a project plan that is defensible is not a trivial task.

Optimizing the design is an interactive process in which all stakeholders must participate. It also requires the expertise of a statistician. A model must be developed that describes the relationship of the measured value to the “true” value. The theoretical decision rule specified in Step 5 needs to be transformed into an operational decision rule. A statistical test must be found that has the power to differentiate between different “true” values of the parameter, yet is consistent with distributional assumptions about the population being sampled. A simulation model is usually required to evaluate the alternative sampling and analysis plans so that the “best” can be selected. The simulation is used to verify that the desired-error probabilities can indeed be achieved with the proposed plan.

If it is found that the desired error probabilities cannot be met with the planned sampling and analytical methods or equipment, and/or with the planned number of samples, then the DQOPP team members must either be willing to accept higher error rates or increase the project budget so that more samples can be taken and/or more sensitive and accurate equipment can be made available. If this is not possible, the problem scope must be reduced. If conservative estimates or uncertainty in estimates is causing the large sample requirements, the DQOPP team should look into initiating a pilot study to get better estimates of parameters that affect the decision to be made. The DQOPP team needs to consider the political, social, and economic consequences of decision errors when setting uncertainty constraints and making tradeoffs.

Outputs of this step include identifying

- the sampling method(s)

- the least number of samples required to answer the decision question(s)
- the least-costly analytical procedure(s) required to answer the question(s)
- the minimum QA/QC activities required to meet constraints established by the previous step
- the mechanism to draw together the DQOPP team and renegotiate the DQOs, if it becomes necessary
- an operational decision rule.

The DQOPP team should document the results of their optimization effort by signatures of all members.

Project Plan Guidance

This section should be used to help design individual required components of any project plan. Once the DQOPP has been completed to the satisfaction of all team members, the project plan for the project should be prepared. The project plan should consist of information gathered in the DQOPP. In addition, the plan should address safety and waste handling. The following provides a guideline of sections that should be included in the project plan.

Introduction

The project plan should contain an introduction that provides a brief statement of the problem and possible solutions that are based on a consensus by DQOPP team members. This introduction should include a brief summary of the DQOPP and the results of the process. It should contain a list of

DQOPP team members and participants, and it should provide dates when the DQOPP was begun and completed.

Plan Purpose

The project plan should contain a purpose statement that documents details relating to the DQOPP, the collection of data, and the decision. It should provide the requirements and framework to successfully complete the project.

Safety Considerations

Most sampling and analysis activities present some element of risk to project staff. Chapter 4, "Safety," contains further guidance applicable to project safety. Any requirements to ensure that the project is carried out safely should be documented in this section. For example, some activities may require training to specific equipment or safety regulations for project staff. Many projects require that safety meetings be held on a specified schedule. This schedule should be documented, and, if appropriate, the topics of the meetings should be detailed.

Any special safety equipment should be identified and its use explained. For example, sampling personnel may be required to wear respirators or other protective equipment. Requirements for "as low as reasonably achievable" (ALARA) and offsite sample transportation should be contained in the project plan.

Waste Handling

Waste issues, such as minimization and disposal, should be briefly described. Refer to Chapter 5, "Waste Handling," for further guidance.

Data Summary

The project plan should summarize data that will be needed to answer the decision questions. This data summary should include the acceptable error tolerances and a discussion of QC activities that will ensure that acceptable error tolerances are achieved. Refer to Chapter 3, "Quality Control," for further guidance.

Sampling

The approach for collecting samples should be provided in detail: for example, whether the sampling strategy is based on a random sampling or a grid should be documented. Any screening requirements used to develop final sampling strategies should be described. Contingency approaches should be documented in case the strategy originally agreed upon fails to produce samples that would yield the needed analytical data for the project.

All equipment required for the sampling phase of the project should be listed, and requirements regarding maintenance should be documented.

The standard operating procedures (SOPs) or methods to be used for sample collection should be documented. The bases for their selection should be provided. Any sampling QA/QC controls and their acceptance criteria should be included in this section of the project plan. Refer to Chapter 3, "Quality Control," and Chapter 7, "Sampling Methods," for further guidance.

Details regarding sample container type and size specifications, sample size, sample preservation, sample labeling, chain-of-custody documentation, shipping requirements, and decontamination activities should be provided in the project plan.

Sample Hold Times

Sample hold times appropriate for the project should be defined during the DQOPP and documented in the project plan.

Sample Preparation and Analysis

The SOPs or methods to be used for sample preparation and analysis should be documented. Refer to Appendix B, "Guidance for Selecting and for Qualifying Methods to Meet Analytical Data Quality Objectives: A Performance-Based Approach," for method/SOP qualification guidance. The bases for method selection should be provided. Any analytical QA/QC controls and their acceptance criteria should be included in this section of the project plan. Refer to Chapter 3, "Quality Control," for guidance on QC activities that should be performed. Refer to Chapter 6, "Choosing the Correct Method," for guidance on choosing sample preparation and analytical methods.

All equipment required for the analytical phase of the project should be listed, and requirements regarding maintenance should be documented.

Data Management

Any requirements pertaining to data management should be specified in this section. Records-control requirements should be documented (e.g., a requirement that analytical data be stored in a limited-access environment that protects the data from loss and destruction). It is appropriate, in this section, to identify data-review or validation requirements.

Data reporting formats should be specified so data will be made available to the decision makers in a

form that facilitates the most efficient use of the data. Turn-around times required for reporting analytical data should be specified.

Requirements for records disposition following completion of the project should be specified in this section of the project plan.

Project Plan Schedule

This section of the plan should include a task/milestone chart for collecting and analyzing samples and for any deliverables, such as reports. The chart should be realistic. Time lost through poor planning of one stage in the project usually cannot be made up during subsequent stages. For example, the analytical chemist cannot realistically be asked to compress the time s/he has been allotted to perform analytical tests. If any tasks within the project will be subcontracted, the subcontracting plan with appropriate milestones should be identified.

Project Plan Review and Approval

A section of the project plan should document plan review and approval by key people (e.g., regulators, line management, project management, etc.).

Project Plan Implementation

Once the project plan has been completed, and appropriate approval signatures have been obtained, the project plan should receive controlled distribution to all project personnel who will be called upon to use the plan. This plan will become an auditable document, so care should be exercised to ensure that changes to and deviations from the plan are documented and justified.

Data Quality Assessment

A data quality assessment (DQA) should be performed after data are collected, but before using the data. This DQA evaluates whether environmental data are sufficient to support a specific intended use. The process requires that the use of data in a decision will be carefully studied and that the level of uncertainty that can be accepted in the decision is understood. The DQA process uses statistical tools to estimate the probability of making an incorrect decision based on the data set being assessed. The DQA process examines the project DQOs, statistical design assumptions, and total error associated with the data. This process consists of six sequential steps and is described in (Daniel Michael, "Data Quality Assessment: Have You Met your DQOs?", in Proceedings of the Twentieth Annual National Energy and Environmental Quality Division Conference).

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Chapter Supplements

Sampling Strategies

See Chapter 7 for sampling guidance and methods. There are three primary approaches to sampling: random, stratified, and judgmental. In many cases, sampling strategies may employ aspects of each to accommodate information needs and to account for the relative complexity of sampling sites. The relative number of samples and associated costs follows the order judgmental<systematic<random, while the order for relative bias is reversed. The approach should be sufficiently flexible to permit adjustments in the field. The application of any one of these strategies may be highly limited based on the nature of the system to be sampled.

Error Analysis

Sampling operations can contribute significantly to both systematic and random error, which will thus

impact the ability to meet the project DQOs. A sampling plan needs to address ways to control these sources of error. Table 2 summarizes descriptions of different sample types that can be collected along with the samples of interest to help control error and improve overall data quality. Sample types consist of samples used to 1) control accuracy and precision and enhance sampling cost-effectiveness (statistical samples), 2) identify and isolate sources of contamination (blanks), and 3) validate the findings of the samples of interest (control samples). The types and numbers of the samples that are incorporated into the sampling strategy will depend on the nature of the DQOs and the nature of the sampling approach selected.

Chain-of-Custody

A sample chain-of-custody form follows.

Table 2. Sampling Types that Support Data Quality Objectives

Sample Types	Definition	Purpose
Statistical Samples	Samples collected as a basis for a statistically sound sampling design.	Used to assist in satisfying DQO requirements through improved sampling strategy.
<i>Field replicates</i>	Independent field samples collected as close as possible to the same point in space and time.	Used to confirm precision of analytical data.
<i>Field composites</i>	Combined portions of several field samples to form a single sample.	Used to improve effectiveness of sampling and analysis strategies.
Blanks	Matrices that have negligible or unmeasurable amounts of the substance of interest.	Used to detect and measure extraneous material introduced into sample collection or treatment procedures.
<i>Trip (transport)</i>	Test sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened.	Used to measure cross contamination from the container and the preservative during transport, field handling, and storage.
Field	Samples of analyte-free media similar to the sample matrix.	Used to measure incidental or accidental sample contamination during the whole process (sampling, transport, sample preparation, and analysis).
<i>Equipment (rinsate)</i>	Samples of analyte-free media that have been used to rinse the sampling equipment.	Used to document adequate decontamination of sampling equipment.
<i>Material</i>	Samples of materials (e.g., solid sorbents, construction materials) used or encountered in the sample collection process.	Used to identify artifacts generated from use of these materials.
Control Samples	Samples collected from sites adjacent to or near the site under evaluation.	Used to determine whether an analyte of interest is present in a population under study but not in similar control population.
<i>Field spike</i>	Selected field samples to which a known amount of the analytes of interest are added during their collection in the field.	Used to identify field, transportation, and matrix effects.
<i>Background (reference)</i>	Samples taken near in time and space to the sample of interest.	Used to demonstrate whether the site being sampled is contaminated or truly different from the norm.

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Guidance for Effective Project Planning

Chain-of-Custody Form

Chain-of-Custody No: _____

Surveyed (Hand Held GM): CPM _____ By: _____
Screened (Scintillation): Activity α _____ β _____ By: _____

Company Contact: _____ Telephone: _____
Samples Collected by: _____ Date: _____ Time: _____
Field Logbook No/Page: _____
Ice Chest No: _____ Offsite Property No: _____
Shipped by: _____ Date: _____
Destination: _____ Carrier/Waybill No: _____

Possible Sample Hazard Identification: _____

Shipping container internal temperature when samples sealed: _____
Shipping container internal temperature when opened in laboratory: _____

Sample Identification

<u>Sample No.</u>	<u>Brief Sample Description</u> (e.g., filtered water)	<u>Analyses Ordered</u> (or attach analytical request form)
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Chain-of-Possession

Relinquished by: _____	Received by: _____	Date/Time: _____
Relinquished by: _____	Received by: _____	Date/Time: _____
Relinquished by: _____	Received by: _____	Date/Time: _____
Relinquished by: _____	Received by: _____	Date/Time: _____
Disposed by: _____	Disposal Method: _____	Date/Time: _____

Note: This form is included as an example only. The need and format for chain-of-possession documentation should be identified and defined in the Sampling and Analysis Plan.

Chapter 2

Quality Assurance

Scope and Application

One goal of the U.S. Department of Energy (DOE) is to ensure that all data resulting from environmental sampling and analytical activities in support of the Office of Environmental Restoration and Waste Management (EM) be scientifically valid, defensible, and of known precision and accuracy. The data must be of sufficiently well-known quality to withstand scientific and legal challenges relative to their intended uses. This goal is best achieved by effectively implementing detailed quality assurance (QA) requirements and specifications. A comprehensive QA program should incorporate management policies, quality control (QC) functions, and quality-assessment functions.

The purpose of this chapter is to supplement information contained in Chapter 1, "Guidance for Effective Project Planning," and to aid organizations to develop quality assurance project plans (QAPPs) that meet the specific needs and missions of that project while maintaining compliance with requirements presented in Order 5700.6C (DOE 1991). This chapter also incorporates applicable topics presented in the U.S. Environmental Protection Agency (EPA) documents, SW-846 and QAMS 005/80. The chapter does not specify any format; rather, it is intended to function as a guidance document and is concerned with content of the QAPP. It reflects current quality principles and practices, and it uses concepts and terms that have evolved through experience.

General Considerations

Quality is the degree to which an item or process meets or exceeds the user's requirements and expectations. A QA program constitutes those actions that provide confidence that the required level of quality is achieved. The primary goal of an environmentally related QA program is to ensure that data provided to the client are of the quality needed and claimed.

A QA program provides a process for an organization to perform management review and oversight at the planning, implementation, and completion stages of environmental sampling and/or analysis activities. Management has a particularly important function in ensuring that a total quality management (TQM) culture is created and maintained in the organization. All personnel should understand that they have responsibility for achieving the desired quality.

In August 1991, DOE issued Order 5700.6C, which established department-wide QA requirements. One of DOE's goals in issuing this order was to instill a culture that aggressively pursues a rising standard of quality. This demands that process and item quality and the methods employed to achieve quality be continuously improved.

Quality Assurance Program

The QA program includes

- the overall policies
- organization objectives
- functional responsibilities, authorities, and interfaces

designed to achieve data quality goals for the sampling and/or analysis activities for which the particular project is responsible. It should encompass the management procedures and controls to generate data of acceptable quality. This program should describe lines of authority and assign responsibilities and authorities; define policies, requirements, and interfaces; and provide for the performing and assessing work to carry out requirements that apply to the work.

Program Design

Order 5700.6C reflects the philosophy that QA program criteria are broken down into three functional categories: management, performance, and assessment. These three broad functional categories are further broken down into 10 criteria. This chapter's organization is similar to that of Order 5700.6C. Because of the unique nature of some projects, some QA topics covered in the following chapter sections may not apply. The QAPP should reflect the needs of the specific project. The development of the QAPP should take into consideration risks associated with failure of the items and processes controlled by that project.

Quality Assurance Management Plan

Organization-wide quality-related issues dealing with planning, implementing, and assessing sampling and laboratory operations are described in the quality assurance management plan (QAMP). The QA program should be documented by written policies, procedures, or instructions and should be carried out in accordance with those policies, procedures, or instructions. The concept of quality improvement should be stressed. Consideration should be given to continued improvement in the way the organization carries out its project-specific QA activities.

Quality Assurance Project Plan

Project-specific quality-related issues are often described in a QAPP that may reference the QAMP where appropriate. The QAPP should begin with a statement of the organization's policy on QA as it relates to the project. The QAPP should include a brief description of the project's mission and objectives, and it should briefly describe what types of environmental sampling and analysis activities are covered by the QAPP. It should contain a description of the organizational entities involved in sampling and analysis activities and the nature of their involvement with the project. An organizational chart showing interfaces should be included in the QAPP.

The QAPP should emphasize that line management is responsible for achieving quality and that each individual is responsible for the quality of his/her work. The QAPP should be binding on all personnel, including those having responsibility for planning and scheduling. The QAPP should

- be approved by management and a representative of the organization's quality group
- describe data-quality goals
- describe the QA/QC procedures to be followed in achieving those goals
- describe the means by which the quality of sampling and/or analysis activities is verified.

Those sections of the organization's QAMP, a higher level document than the QAPP, that are generally applicable to all projects and activities within an organization and that adequately document project policies, procedures, and instructions may be referenced in the QAPP. The QAPP typically provides details regarding how QAMP requirements are to be implemented for a specific project. The QAPP may specify activities that are applicable to the project and are not addressed in the QAMP, or it may justify exceptions to the QAMP as deemed appropriate for the scope of the project. A common vocabulary that is consistent and representative of the work being performed should be adopted.

The QAPP should provide for conducting a readiness review to

- ensure that the work has been adequately planned
- ensure that all equipment and facilities are operational
- ensure that technical and QA procedures and modifications to those procedures have been reviewed for adequacy and appropriateness

- ensure that personnel have been suitably trained and qualified
- ensure that the proper equipment, material, and resources for work performance are available.

These reviews should be performed before performance of work.

Data Quality Objectives

Not all environmental programs require the same quality of data. The needs and requirements for data of specified quality levels must be reflected in the QAPP through documentation of established data quality objectives (DQOs). Defining DQOs specific to the project aids management in carrying out a cost-effective program by tailoring requirements (e.g., QA, QC, analytical methods, etc.) to the specific project and eliminating unnecessary (expensive) requirements. The DQOs developed for the project are then translated into performance objectives (i.e., data quality requirements) that reflect EM's needs. The QAPP should include a discussion of the policy to use a risk-based approach to quality management. That is, the policy for applying quality controls to a project should vary with the required degree of confidence needed in the resulting data.

Work Authority

The responsibility and authority to stop work that is failing to meet QA requirements should be delineated. Safety and quality considerations must not be overridden by planning and scheduling considerations. In the event of a stop-work order, a readiness review should be performed before restarting work.

Personnel Training and Qualification

This section of the QAPP should describe the project's process for

- establishing training requirements for sampling and/or analysis personnel
- identifying training needs
- assigning priorities to training needs
- satisfying those training requirements.

Specific, job-related requirements pertaining to education and experience of personnel involved in sampling and analysis activities should be stated and met.

Management should evaluate each job-related responsibility and determine the qualifications necessary for personnel to execute their responsibilities in a safe and effective manner. These qualifications should be documented (e.g., education, experience, training, technical knowledge, or combinations of the above). Qualifications should reflect the hazard and risk associated with a specific responsibility.

Training should be performed by qualified instructors who address potential consequences of improper work and focus attention on "doing it right the first time." Personnel performing work that requires special skills or abilities should be qualified *prior* to performing work. Documentation of qualifications for staff requiring these special skills or abilities should include demonstrated proficiency. The documentation that demonstrates the qualifications of personnel should reflect periodic evaluation to ensure that skills are maintained to meet current practice requirements.

Quality Improvement

This section of the QAPP should describe the management system for preventing and detecting quality problems and for ensuring continuing quality improvement in its environmental sampling and analysis activities. The basic goal should be to continually improve the system so that required data quality can be achieved at lower costs. The emphasis should be upon minimizing sampling and analysis errors and delays. Appropriate preventive maintenance of equipment and facilities should be performed and properly documented.

Because customer needs may change, quality improvement requires that existing quality goals be reviewed and adjusted to ensure that customer needs are continuously satisfied in the most cost-effective manner.

The quality of data in terms of meeting quality requirements should be measured and documented. Project quality requirements can best be evaluated by developing qualitative and quantitative quality indicators. These indicators should be periodically assessed by appropriate management personnel to ensure that they are still appropriate.

In spite of preventive measures, QA deficiencies and nonconformances do occur. Specific planning, sampling, analytical, and program management activities that do not meet established requirements should be identified, controlled, documented, reported, and corrected. Because identifying problems is an important step in quality improvement, a "no-fault" attitude should be encouraged so personnel do not feel threatened.

Corrective actions should include identifying primary causal factors and root causes of problems, determining if the problem is unique or has more

generic implications, and recommending procedures to prevent recurrence. The system for applying flags to denote data that are defective in some respect should be defined in the QAPP.

Documents and Records

The QAPP should identify procedures to control the timely preparation, review, approval, issuance, use, and revision of documents that specify requirements of prescribed or critical activities or serve to document the results of critical activities. The QAPP should specify documents that must be controlled. Examples of documents to be controlled include data files (various media), calculations, purchase orders, and data sheets. Management should ensure that current revisions to controlled documents are reviewed and approved by the organization that originally reviewed and approved the documents. The QAPP should define the system used to ensure that only current controlled documents are used by personnel performing work.

The QAPP should establish and implement a process to ensure that records that reflect completed work and/or fulfill any statutory requirements are specified, prepared, reviewed, approved, and maintained. Deviations from the QAPP or standard operating procedures (SOPs) should be justified and documented. The maintenance of records should include provisions for retention, protection, preservation, traceability, and retrievability.

All documents should be legible and all records traceable to the originator and the date originated. Changes to document entries should be made by lining through the entry to be changed, making the correction, signing or initialling, and dating the change. If the reason for the change is unclear, a brief explanation should be provided.

Work Process

Work Performance

Acceptance criteria for work performance should be defined. The QAPP should define the controlled conditions necessary for work performance; for example, it should identify appropriate instructions and procedures, and it should identify the types of records that should result from a sampling or analysis activity.

Identification and Control of Items

The QAPP should identify established and implemented processes used to identify, control, and maintain items (e.g., samples, analytical standards). Positive identification and control measures should be defined to ensure that test samples and other quality-affecting items are identifiable at all stages of work performance. The processes used to control items with limited shelf life and to prevent the use of incorrect or defective items affecting data quality should be documented.

Handling, Storing, and Shipping

The QAPP should identify the processes used to control the handling, storage, shipping, cleaning, and preservation of items to prevent damage, loss, or deterioration. Requirements for off-site transportation should be identified. Sample chain-of-custody requirements should be identified, if applicable. Special protective measures (e.g., hot-cell facilities) should be specified.

Calibration and Maintenance of Monitoring and Data Collection Equipment

The QAPP should specify the processes (and their frequency) used to control the calibration, maintenance, and use of measuring and test equipment

used for monitoring and data collection. The method and frequency of calibration for equipment should be defined based on the type of equipment, stability characteristics, required accuracy, intended use, and other conditions affecting measurement control. If applicable, the need for certified or traceable calibration standards should be identified. The QAPP should specify the types of equipment to be used in performing the work. Measuring and test equipment found out-of-calibration should be tagged or segregated and not used until it has been recalibrated.

Design

Data Collection Operations

The QAPP should identify controls for designing the data-collection processes. These processes include documentation of method proficiency for each analytical method. The design process should ensure that data are traceable to the sampling and analytical procedures, performance standards, analysts, and measuring and test equipment.

Sampling and laboratory activities that affect data quality and are routinely performed should be written in the form of approved SOPs.

Data collection and handling processes that should be addressed in a QAPP include but are not limited to

- quality control
- sample collection
- sampling equipment decontamination
- sample handling and custody requirements
- personnel requirements and qualifications

- health, safety, and waste disposal considerations
- reagent/standard preparation
- analytical methods
- equipment calibration and maintenance
- methods for data reduction and validation
- data interpretation and assessment of limitations on use of the data
- application of statistical methods to the data
- data reporting
- records management and archiving
- assessments/readiness reviews and corrective action.

Computer Software

The QAPP should identify controls to provide assurance that computer programs used for the project are developed using defined software-development methodology. These controls should include software-documentation requirements. They should also include a requirement for documented verification of computer programs used in the project. Verification testing should be performed before using the software and, thereafter, on a regular basis by qualified individuals who 1) do not report to the manager responsible for developing the software, and 2) were not involved in its development. Software configuration management methods should be identified to ensure that changes to computer software that affect quality are properly controlled and approved. Computer software results should be traceable to the version(s) of software used. The

controls should provide assurance that the computer environment is controlled to allow the computer software to operate correctly. The QAPP should identify the policy and procedures that will ensure the security of the software against loss and unauthorized use.

Procurement

The QAPP should identify the system used to ensure that purchased items and services meet established requirements and perform as expected. The system should ensure that applicable technical and administrative requirements, such as specifications, codes, standards, tests, and inspections, are invoked for procuring items and services and that procurement documents should include acceptance criteria.

Where applicable, the QAPP should identify the system to control the evaluation of prospective suppliers to ensure that only qualified suppliers are selected. This system should also provide for monitoring suppliers and, as necessary, sub-tier suppliers, to ensure that acceptable items and services continue to be supplied.

The QAPP should identify methods to be used for accepting quality-affecting purchased items and services. Nonconformances should receive proper disposition before accepting the items or services. The actual performance of the items should be compared with performance criteria.

Inspection and Acceptance Testing

The QAPP should identify the process used to specify what type of inspections are required and the frequency with which they should be conducted. Administrative controls and status indicators should be used to preclude inadvertent bypassing of required inspections and to prevent inadvertent use of the item

or process. Personnel should not inspect their own work for acceptance. The level of inspection and degree of independence of inspection personnel should be based on risk and complexity. Retesting of items or processes to determine that they meet acceptance criteria should be performed after deficiencies are corrected.

The QAPP should identify the process for evaluation and verification/validation of data. Predetermined limits should be established for data acceptability, beyond which corrective action should be initiated. The process may include inspections, QC checks, surveillances, reviews, and audits. Consideration should be given to defining a system of performance-evaluation audits.

The QAPP should identify approved procedures that are used to qualify data. The decision to qualify the data for their intended use should be based on verification that data meet defined performance objectives derived through specification of DQOs.

Management Assessment

The QAPP should identify the process for performing and documenting management assessments. These assessments should be established and implemented as a way to improve quality. The results of these assessments should be documented, and prompt action should be taken to correct deficiencies or implement system improvements. Follow-up should include an evaluation of the effectiveness of management's corrective actions.

Management assessments should also include reviews of sampling and field events. These review should include verification that sampling teams and analysts are

- following procedures specified by the QAPP

- checking to ensure that field and sampling events are complete
- examining documentation to ensure that sampling was representative (e.g., wells were properly developed, and pH checks of well-water samples demonstrated stability before sampling)
- reviewing records to ensure that anomalous field data are identified
- reviewing QC checks to ensure that they meet acceptance criteria.

Data affected by problems identified when performing these reviews should be identified and appropriately qualified.

Management assessments should include documented reviews of laboratory activities. Data should be reviewed by a second analyst or a supervisor. These reviews should ensure the

- completeness of laboratory records
- evaluation of data with respect to detection limits
- evaluation of data with respect to control limits
- review of holding times
- review of performance-evaluation studies
- correlation of data generated through related analyses (e.g., check to ensure that data resulting from purgable organic halide analyses and volatile organic analyses are not incongruous for a single sample).

If applicable, the QAPP should identify systems for submitting performance-evaluation samples to the laboratory and then evaluating the sample data.

Independent Assessment

The QAPP should identify the process for planning and performing periodic independent assessments that should focus on improving items and processes. Personnel performing independent assessments should be technically knowledgeable and should act in a management advisory function. Their role should be to monitor work performance, identify abnormal performance and precursors of potential problems, identify opportunities for improvement, report results to a level of management having the authority to effect corrective action, and to verify satisfactory resolution of problems.

Scheduling assessments and allocation of QA resources should be based on the status, risk, and complexity of the activity being assessed. Responses to assessments should include the following, as applicable:

- identification of cause of problems
- action to correct the deficiency
- actions to prevent recurrence
- lessons learned
- actions taken for improvement.

Assessment results should be tracked and resolved by management.

Reference

U.S. Department of Energy (DOE). 1991. DOE Order 5700.6C, Quality Assurance. Office of Environmental, Safety, and Health. Washington, DC.

Further Reading

For additional information related to the material presented in this chapter, consult the following publications:

American Society for Quality Control. 1991. *Quality Assurance Program Requirements for Environmental Programs*. ANSI/ASQC-E4-19xx. Draft. Energy Division, Environmental Waste Management Committee.

U.S. Environmental Protection Agency (EPA). 1980. *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans*. QAMS-005/80. Office of Monitoring Systems and Quality Assurance, ORD, Washington, DC.

U.S. Environmental Protection Agency (EPA). 1986. EPA/SW-846, 3rd Edition, Chapter 1, Rev. 0. Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

U.S. Environmental Protection Agency (EPA). 1986. EPA/SW-846, 3rd Edition, Chapter 1, Draft, Rev 1. Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Chapter 3

Quality Control

Scope and Application

Quality control (QC) consists of the overall system of technical activities that measures and controls the quality of a process, items, or service so they meet the stated needs of the user (ANSI/ASQC 1993). The goal of a well-designed QC program is to provide data of known quality that are satisfactory for their intended uses and are dependable and economical. This chapter provides an overview of QC-program components that support sampling and analytical activities, and should be used in conjunction with Chapter 1, "Guidance for Effective Project Planning," to define the QC program that should be implemented for a specific sampling and analysis task. Specific QC activities related to sample collection and to organic, inorganic, and radiochemistry determinations are included in the corresponding chapters. The information presented here is intended to serve as a guide rather than a specification of requirements; however, the recommended activities might help to document that data quality objectives (DQOs) of a project were met.

General Considerations

Analytical data are generated under a wide variety of conditions in support of DOE environmental monitoring and remediation activities. The data need to be generated in conjunction with specific QC practices to meet standards appropriate for their use.

A QC program should develop information that can be used to establish and define the quality of the data, indicate the need for corrective actions, and deter-

mine the effect of corrective actions. Information quality is established by quantifiable and qualitative indicators, such as accuracy, precision, and detection limit. Inadequacies in data quality that require corrective action can be due to many causes, including unanticipated matrix effects, equipment malfunctions, and operator error. Applied to each method, QC can quantify such impacts to data quality.

A QC program should be tailored to the specific scope of analyses required. The scope of DOE sampling and analysis activities might include hazardous samples, radioactive samples, or samples containing both radioactive and hazardous components (mixed waste). Samples may contain levels of radioactivity that require special controls or facilities to protect workers from radiation doses posing health hazards. The QC analysis needed for hazardous chemicals with low levels of radioactivity may be unchanged from those identified in the U.S. Environmental Protection Agency's (EPA's) SW-846 (1986) methods or other standard methods. The DOE promotes the health and safety related philosophy "as low as reasonably achievable" (ALARA) regarding worker exposure when dealing with radioactive or hazardous substances. Because of this philosophy, levels of QC may be reduced from those applicable to sampling and analysis of materials posing a lesser health risk. Lengthy analytical processes may also require reduced levels of QC (e.g., radiochemistry measurements with long count times). When QC is reduced, an explanation of the reason this is necessary should be contained in the method or in the Quality Assurance Project Plan (QAPP), or should be noted in records associated with the analysis.

Definitions

Various terms are defined here as they relate to QC.

Accuracy - The relative agreement between an observed value and an accepted reference value. Accuracy measurements will reflect both random errors that are responsible for the observed scatter of measured values and systematic errors. Accuracy is assessed by means of percent analyte recovery versus that present in reference samples.

Batch - The basic unit for analytical QC is the analytical batch. The batch is defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar compositions.

Bias - A systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system. Temperature effects and extraction inefficiencies are examples of the first kind. Blank contamination, mechanical losses, and calibration errors are examples of the latter kinds. Bias may be positive or negative, and several kinds can exist concurrently so that net bias is all that can be evaluated, except under special conditions.

Blind Sample - A sample submitted for analysis whose composition is known to the submitter, but unknown to the analyst. Its identification as a check sample may be known to the analyst. A blind sample is one way to test the proficiency of a measurement process.

Check Sample - A blank that has been spiked with an analyte(s) from an independent source to monitor the execution of the analytical method. The level of

the spike should be at the regulatory action level when applicable. Otherwise, the spike should be at five times the estimate of the quantification limit. When sensible, the matrix used should be phase matched with the samples and well characterized; for example, reagent-grade water is an appropriate blank matrix for an aqueous sample.

Comparability - A qualitative parameter expressing the confidence with which sample measurement data can be compared with measurement data for similar samples and sample conditions.

Completeness - The amount of valid data obtained from a sampling and analysis program compared to the amount that was expected to be obtained under correct, normal operations. Completeness is usually expressed as a percentage.

Control Chart - A graphical plot of test results with respect to time or sequence of measurement, together with limits within which they are expected to lie when the system is in a state of statistical control.

Control Limit - The limits shown on a control chart beyond which it is highly improbable (typically less than 1%) that a point could lie while the system remains in a state of statistical control.

Control Sample - A material of known composition that is analyzed concurrently with test samples to prepare and evaluate the measurement processes.

Data Quality Objectives - Qualitative and quantitative statements that specify the quality of data required and that are based on the end uses of the data to be collected. They are often determined by the nature of the test being carried out. For example, DQOs for screening purposes may allow less stringent precision and accuracy requirements than those imposed on analyses performed in support of federal or state regulations.

Double Blind - A sample submitted for analysis whose composition and identification as a check sample is known to the submitter but unknown to the analyst.

Duplicate - see **Matrix Duplicate**, **Field Duplicate**, **Matrix Spike Duplicate**.

Field Duplicate - Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures.

Laboratory Control Sample - A known matrix spiked with compound(s) representative of the target analytes. It is used to document laboratory performance.

Matrix - The component, substrate, or medium (e.g., surface water, drinking water, soil) that contains the analyte of interest.

Matrix Blank - "Matrix blank" and "method blank" are synonymous terms referring to an artificial sample designed to monitor the introduction of artifacts into the sample preparation and analysis process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and, therefore, it is not always appropriate to include a solid matrix blank in a sample batch.

Matrix Duplicate - An intralaboratory split sample (duplicate sample) used to document the precision of a method in a given sample type. In cases where aliquots of sample are impossible to obtain, field duplicate samples should be taken for matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

Matrix Spike - An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs before sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample composition. It may be appropriate to direct the laboratory to use specific samples as matrix spikes. It may be necessary to provide additional samples for this purpose.

Matrix Spike Duplicates - Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs before sample preparation and analysis. They are used to document the precision and bias of a method in a given sample composition.

Method Blank - An analyte-free matrix, or a "clean sample," e.g., purified water for aqueous samples, to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank must be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte (or isotope) concentration is greater than zero. The MDL may be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation. The standard deviation is obtained from a minimum of three analyses of a matrix spike. Each matrix spike should contain the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

Number of Samples:	t-statistic
3	6.96
4	4.54
5	3.75
7	3.14
8	3.00
9	2.90
10	2.81

The MDL is estimated as follows:

The concentration value is obtained that corresponds to a) an instrument signal/noise ratio within the range of 3.0 to 5.0, or b) the region of the standard curve where a significant change in sensitivity occurs (i.e., a break in the slope of the standard curve).

The variance (V) for each analyte is determined as follows:

$$V = s^2 = \frac{1}{n-1} \left[\sum_{i=1}^n (x_i - \bar{x})^2 \right]$$

where x_i = the i^{th} measurement of the variable x and $\bar{x}$ = arithmetic mean of the x_i measurements:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i$$

The standard deviation (s) for each analyte is the square root of the variance:

$$s = V^{1/2}$$

The MDL for each analyte is determined as follows:

$$\text{MDL} = t_{(n-1, \alpha=.99)} s$$

where $t_{(n-1, \alpha=.99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine s at the 99% level.

Precision - The relative agreement among a set of replicate measurements. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may use matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV):

$$\text{RSD} = \text{CV} = 100 s/\bar{x}$$

where $\bar{x}$ = the arithmetic mean of the x_i measurements, and s = standard deviation.

Another measure of the precision, the relative percent difference (RPD), is calculated when only two samples are available as follows:

$$\text{RPD} = 100 \left[|(X_1 - X_2)| / [(X_1 + X_2)/2] \right]$$

where X_1 and X_2 are the measurement analyte concentrations of the first and second replicates, respectively.

Quality Assurance Management Plan (QAMP) - A management plan that defines administrative policies, procedures, and organizational structure on an organization-wide basis.

Practical Quantitation Limit - The reliable quantitation limit and the practical quantitation limit of a method are synonymous terms and are determined as follows: $\text{PQL} = 4\text{MDL}$.

Reagent Blank - see **Method Blank**.

Reagent Grade - The following are synonymous terms for reagents that conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS): analytical reagent (AR) grade, ACS reagent grade, and reagent grade.

Reference Material - A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

Replicate Sample - A sample prepared by dividing a sample into two or more separate aliquots. Duplicate samples are considered to be two replicates.

Representativeness - Expresses the degree to which complete data accurately and precisely represent conditions within the entire sample. A carefully planned sampling protocol and careful homogenization of a sample before aliquoting are two examples of activities that affect the representativeness of a sample.

Split Samples - Representative aliquots of a sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field-duplicate samples should be taken for the matrix-duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

Standard Addition - The practice of adding a known amount of an analyte to a sample immediately before analysis. It is typically used to evaluate interferences.

Standard Reference Material - A trademark reference material distributed and certified by the National Institute of Standards and Technology (NIST) or other certified vendor.

Surrogate - An organic compound that is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but that is not normally found in environmental samples. For some analytical methods, all samples are spiked with surrogate compounds at the start of the procedure.

Surrogate recoveries provide an estimate of accuracy for the entire analytical procedure.

Traceability - The ability to trace the source of uncertainty (or validity) of a measurement or a measured value.

Uncertainty - The range of values within which the true value is estimated to lie. It is a best estimate of possible inaccuracy resulting from both random and systematic error.

Quality Control Criteria

Quality Control in the Field

Perhaps the most critical element in an environmental project is the QAPP (refer to Chapter 1, "Guidance for Effective Project Planning"). The goals of environmental sampling and analysis are to make inferences about a parent population based upon the information contained in a sample. The QC activities associated with sampling should be designed so that, where possible, the data produced will identify sampling errors and will show that sampling errors are effectively minimized and defined. Some sampling activities in support of DOE programs require specialized QC and safety controls. For example, DOE sampling programs include collecting diverse types of samples, such as wastes from double-shell tanks potentially contaminated with low to high levels of radionuclides, inorganics, and organic contaminants; groundwater samples; and soils with various levels of contamination. Project personnel should tailor QC sampling programs to the scope of the sample-collection activity and should consider the physical state and location of the site, sampling equipment, health and safety, and maintenance of sample integrity. The QC program should consider using bottle blanks, trip blanks, field duplicate samples, and equipment-rinsate samples. Adequate

volumes of samples should be collected to ensure that the laboratory can analyze matrix spikes and the matrix duplicates that are indicated in the QAPP.

One of the primary objectives of a QAPP is to ensure collection of representative samples. Representative sampling will help to develop environmental data that are both accurate and precise relative to the sampling site. Sampling accuracy is usually achieved by incorporating some form of random selection into the sampling process. Sufficient precision, as defined in the DQO process, is most often obtained by selecting an appropriate number of samples (i.e., the least number of samples required to generate a sufficiently precise estimate of the true mean concentration of the analyte of interest). Consideration should be given to using statistical techniques to develop a confidence interval for sampling accuracy and precision.

Acceptance criteria for field activities should be described in the associated QAPP. Acceptance criteria may be qualitative or quantitative. Field events or data that fall outside established acceptance criteria may indicate a problem with the sampling process that should be documented and investigated.

Laboratory Quality Control

Guidance provided in Appendix B should be used in selecting and in qualifying analytical methods. To provide reliable data, certain minimum policies should be implemented in the laboratory. The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria associated with those QC samples should be specified in the QAPP. Information in the QAPP should include the statistical treatment of the data and the responsibility of laboratory staff and management in generating and in using the data.

Control Limits. Where applicable, protocols should be in place for establishing and updating control limits for analyses. Control limits based on the analyses of control samples should be established to evaluate laboratory precision and bias. Typically, control limits for bias are based on the historical-mean percent recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical-mean relative-percent difference plus three standard deviation units. Control charts that include control limits are effective in demonstrating laboratory statistical control of a method. Control charts should be updated periodically to reflect current laboratory capability, and consideration should be given to incorporating a system for continuously updating control charts, e.g., by using a computer-based system.

Laboratory Control Protocols. Procedures should be in place for demonstrating that the laboratory data are within control limits during each data-collection activity. Analytical data generated with laboratory control samples that fall within prescribed limits are said to be generated while the laboratory was "in control." Data generated with laboratory control samples that fall outside the established control limits are frequently judged to be generated when the laboratory was "out-of-control." Out-of-control data are considered suspect, and the method used to produce the data should be repeated, or the data should be reported with qualifiers.

Laboratory Control Samples. Laboratory control samples should be analyzed for each analytical method when appropriate for the method. A laboratory control sample may consist of either a standard matrix spiked with analytes representative of the target analytes or a certified reference material. Spiked laboratory control samples should have, insofar as possible, a matrix, volume, and other relevant characteristics of the actual samples being

analyzed. Additional control samples may be necessary to ensure that data quality meets the project-specific DQOs.

Laboratory control sample(s) should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process are in control. The results from the analysis of laboratory control sample(s) are compared to control limits established for both precision and bias to determine usefulness of the data.

A matrix blank should be analyzed with each batch of samples processed to assess contamination levels in the laboratory. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank.

Matrix Effects. Protocols should be in place for documenting the effect of the matrix on method performance. When appropriate for the method, at least one matrix blank or matrix spike and either one matrix duplicate or one matrix-spike duplicate per analytical batch should be used.

- **Matrix-Specific Bias.** Procedures should be in place for addressing the bias of the method due to the sample composition or matrix. These procedures should include preparing and analyzing matrix spikes and selecting and using surrogates for organic methods, radioactive tracers for radiochemistry, or the method of standard additions for inorganic methods. Matrix bias should be determined relative to the best available standard material. When the concentration of the analyte in the sample is greater than 0.1%, a spike is often unnecessary.
- **Matrix-Specific Precision.** The precision of the method should be assessed for the matrix of interest. Consideration should be given to per-

forming analysis of matrix duplicates and/or matrix-spike duplicates. The frequency of using these techniques should be based on the DQO for the data-collection activity.

- **Matrix-Specific Detection Limit.** The MDL for a specific matrix type (e.g., wastewater treatment sludge, contaminated soil, etc.) should be assessed. Data below established MDLs frequently have value and may be appropriately flagged and used to support the project.

Other Considerations. Analytical instrumentation and other measuring and testing equipment (e.g., pipets, balances) should be checked and/or calibrated in accordance with requirements that are specific to the instrumentation and methods employed.

Data Reporting

Reporting needs for analytical and sampling data should be specified in the QAPP. Documentation requirements for data packages should address content and reporting format. Data-reporting requirements are often dictated by factors such as sample matrix, project or regulatory requirements, and objectives of the analysis. It is appropriate to report blank values, matrix- and blank-spike recoveries, and percent difference of duplicates. The estimated uncertainty of the analytical data should be reported. Traceability of data to the test method should be documented in the data report. If appropriate, analytical results should clearly indicate whether data are reported on a wet-weight or dry-weight basis and should include percent moisture or percent solid content of the sample.

QC Samples Submitted by Outside Organizations

Submission of blind and/or double-blind QC samples by outside organizations constitutes a vital component in any comprehensive QC program. These blind samples provide a means to test the proficiency of a measurement process. Through participation in QC programs administered external to the laboratory, confidence in the authenticity of data generated within the laboratory can be evaluated and documented. Project management should also consider sending split samples to various laboratories.

Analytical laboratories should participate in one or more intercomparison programs when such programs exist for the analytes of interest. Examples of such programs include control samples prepared by the following organizations:

Radionuclides

- Environmental Monitoring Systems Laboratory (EMSL), Las Vegas
- U.S. Department of Energy Environmental Measurement Laboratory Quality Assurance Program

Organic and Inorganic Analytes

- U.S. Environmental Protection Agency Water Pollution Performance Evaluation Studies
- U.S. Environmental Protection Agency Water Supply Performance Evaluation Studies

Reference

American National Standards Institute/American Society for Quality Control (ANSI/ASQC). 1993. *Quality Assurance Program Requirements for Environmental Programs*. ANSI/ASQC-E4-19xx. Draft.

Further Reading

For additional information related to the material presented in this chapter, consult the following publications:

40 CFR Ch 1 (7-1-90 Edition) Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11.

U.S. Department of Commerce National Bureau of Standards. 1985. *Standard Reference Materials: Handbook for SRM Users*. Gaithersburg, Maryland.

U.S. Department of Energy (DOE). 1991. DOE Order 5700.6C, *Quality Assurance*, Office of Environmental, Safety, and Health. Washington, DC.

U.S. Environmental Protection Agency (EPA). 1977. *Handbook for Analytical Quality Control in Radioanalytical Laboratories*. EPA-600/7-77-088, Washington, DC.

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Chapter 4

Safety

Scope and Application

This chapter provides general guidance for safe operations at U.S. Department of Energy (DOE) facilities where radioactive and/or hazardous waste samples are analyzed. It presents basic radiation protection standards for DOE laboratories and outlines radiation protection practices that are based on recommendations and requirements from recognized authorities, such as the U.S. Nuclear Regulatory Commission (NRC), the National Council on Radiation Protection (NCRP), and the International Commission on Radiological Protection (ICRP). It also presents guidance based on the Occupational Safety and Health Administration (OSHA) laboratory standard, "Occupational Exposure to Hazardous Chemicals in Laboratories" 29 CFR 1910.1450 and DOE Order 5480.10, "Contractor Industrial Health Program" (DOE 1985).

In instances where both DOE and non-DOE environment, safety, and health (ES&H) standards are applicable and mandatory and conflicts exist between such standards, the ES&H standards providing greater protection should govern.

General Considerations

Sampling and analysis requirements for wastes are generally site specific; therefore, uniform guidance for meeting all requirements is impractical.

For those hazards that have not been precisely defined for samples, reagents, or chemicals that are

used in methods in this document, protection methods should be employed that will keep exposure levels to a minimum. The chemicals required in the methods should not be used until hazards are identified through material safety data sheets (MSDS) or other sources. The risk of exposure to any chemical should be reduced to the lowest practical level. The laboratory should ensure that procedures are reviewed and approved to identify hazards and establish appropriate controls. All staff should have received required training before exposure to hazards. Emergency procedures should be in place, and staff should be trained in their use. To ensure safety, appropriate steps should be taken that the requirements for hazard communication are met and protocols are in place for handling samples of unknown toxicity/radioactivity.

Sampling and analyzing hazardous waste can expose personnel and the environment to hazardous chemicals. When sampling and analyzing radioactive mixed waste (RMW), the sample's radioactivity, depending on the type and level, can present additional control and personnel-exposure problems. For very low-activity RMW, many of the precautions taken to eliminate the health concerns from the hazardous constituents are sufficient to provide protection from the radioactive components of the waste. However, as the amount of radioactivity increases, additional precautions must be taken to minimize the spread of contamination and to maintain exposures to personnel to levels that are "as low as reasonably achievable" (ALARA). In many cases, the precautions necessary for handling and analyzing RMW may require deviations from standard methods.

Persons working with chemicals and/or radioactive materials should receive continuing training. This training should include the use of protective clothing, spill handling, chemical compatibility, radiation safety, and others as appropriate.

Analyses of radioactive and/or hazardous waste samples conducted in a facility that does not meet the 29 CFR 1910.1450 definitions of a "laboratory" (e.g., mobile labs) should meet all applicable OSHA, DOE, NRC, NCRP, and ICRP requirements for hazardous waste and general industry, as applicable.

Definitions

Radiotoxicity - The term "radiotoxicity" signifies the relative hazard of radionuclides when deposited in the human body. Table 4.1 classifies radionuclides based on high, medium, or low toxicity. From a health standpoint, materials that are highly radioactive present the greatest relative hazard when deposited in the body. When working with radioactive material, the level of radiotoxicity should be considered when the degree of confinement is determined.

Dispersibility - The radioactive or hazardous material, its physical form, and its intended use affect the chance, and the outcome, of an accidental release. The following list of conditions of relative dispersibility aids in understanding the degree of physical containment/confinement, engineered safeguards, and administrative controls needed when working with radioactive materials.

Nondispersible conditions include

- simple wet operations
- using encapsulated or sealed sources nondestructively

- storing nonflammable, nonexplosive radioactive or hazardous materials in sealed containers specifically designed for such storage.

Limited dispersible conditions include

- normal chemistry
- using radioactive or hazardous materials strongly bound in a solid matrix or biological system
- performing operations that can result only in fractional releases of material. Evaluators should base predictions of potential releases on experience and accident analysis.

Dispersible conditions include

- risk of wet spills
- simple dry operations.

Highly or readily dispersible conditions include

- using radioactive or hazardous powders, gases, vapors, or other aerosols
- using radioactive or hazardous materials in combustible or explosive conditions
- using radionuclides in dry, dusty operations
- using pyrophoric radioactive or hazardous materials
- performing high-temperature or high-pressure operations that may increase the chance of producing radioactive or hazardous aerosols.

Criticality - Fissionable radionuclides will sustain a neutron chain reaction (criticality) under specific conditions.

Table 4.1. Classification of Radionuclides According to Toxicity^(a,b)**Group I - High Toxicity**

Actinium-227	Californium-252	Curium-246	Plutonium-241	Thorium-227
Americium-241	Californium-253	Curium-248	Plutonium-242	Thorium-228
Americium-242m	Californium-254	Lead-210	Polonium-210	Thorium-230
Americium-243	Curium-242	Neptunium-237	Protactinium-231	Uranium-230
Californium-249	Curium-243	Plutonium-238	Radium-223	Uranium-232
Californium-250	Curium-244	Plutonium-239	Radium-226	Uranium-233
Californium-251	Curium-245	Plutonium-240	Radium-228	Uranium-234

Group II - Medium Toxicity

Actinium-228	Chlorine-36	Indium-114m	Radium-224	Tellurium-129m
Antimony-124	Cerium-144	Iodine-124	Ruthenium-106	Terbium-160
Antimony-125	Cesium-134	Iodine-125	Scandium-46	Thallium-204
Barium-140	Cesium-137	Iodine-126	Silver-110m	Thorium-234
Berkelium-249	Cobalt-56	Iodine-131	Sodium-22	Thulium-170
Bismuth-207	Cobalt-60	Iodine-133	Strontium-89	Uranium-236
Bismuth-210	Europium-152	Iridium-192	Strontium-90	Yttrium-91
Cadmium-115m	Europium-154	Manganese-54	Tantalum-182	Zirconium-95
Calcium-45	Hafnium-181	Protactinium-230	Tellurium-127m	

Group III - Medium Toxicity

Arsenic-73	Dysprosium-166	Nickel-63	Rhenium-183	Technetium-97m
Arsenic-74	Erbium-169	Niobium-93m	Rubidium-84	Technetium-98
Arsenic-77	Europium-155	Niobium-95	Rubidium-86	Technetium-99
Barium-131	Gadolinium-153	Osmium-185	Ruthenium-97	Tellurium-125m
Beryllium-7	Gold-196	Osmium-191	Ruthenium-103	Thallium-202
Bismuth-206	Gold-198	Palladium-103	Samarium-151	Thallium-171
Cadmium-109	Gold-199	Phosphorous-32	Scandium-47	Tin-113
Cadmium-115	Iridium-190	Phosphorous-33	Scandium-48	Tin-125
Calcium-47	Iron-55	Platinum-191	Selenium-75	Tungsten-181
Carbon-14	Iron-59	Platinum-197	Silver-105	Tungsten-185
Cerium-141	Lanthanum-140	Plutonium-244	Silver-111	Vanadium-48
Cesium-131	Lutetium-177	Praseodymium-143	Sodium-24	Zinc-65
Cesium-136	Manganese-52	Promethium-147	Strontium-85	
Chromium-51	Mercury-197	Protactinium-233	Sulfur-35	
Cobalt-57	Mercury-203	Radon-220	Technetium-96	
Cobalt-58	Molybdenum-99	Radon-222	Technetium-97	

Group IV - Low Toxicity

Argon-37	Iodine-129	Rhenium-187	Uranium-235	Zirconium-93
Cesium-135	Krypton-85	Rubidium-87	Uranium-238	
Germanium-71	Nickel-59	Samarium-147	Uranium-NAT	
Hydrogen-3	Oxygen-15	Thorium-232	Xenon-131m	
Indium-115	Platinum-193m	Thorium-NAT	Xenon-133	

(a) Based on *CRC Handbook of Radiation Measurement and Protection*, 1982.

(b) International Atomic Energy Agency (IAEA) Radiation Protection, Safety Series No. 38, 1973

Carcinogen - A carcinogen is a chemical that has produced statistically significant experimental evidence of cancer in animals and/or epidemiological evidence of cancer in man.

Toxic Chemical - A chemical for which statistically significant evidence exists, based on at least one study conducted in accordance with standard scientific principles, that acute or chronic health effects may occur. This definition includes chemicals that are carcinogens, reproductive toxins, irritants, corrosives, sensitizers, and agents that damage the lungs, skin, eyes, or mucous membranes.

Guidelines for Selecting Laboratory Facilities

Guidelines for selecting laboratory facilities for RMW sample analysis based on gross-alpha, gross-beta, and penetrating radiation screening are described in Figure 4.1. These guidelines can be used to specify minimum radiological controls in the absence of more specific health physics procedures. In addition, this operating guide (Figure 4.1) provides guidance as to when modifications to standard methods may be required due to health physics concerns. The International Atomic Energy Agency (IAEA) recommendations for radioisotope laboratory classification have been adopted, with modifications, in these guidelines. The RMW laboratories, as well as RMW samples, are designated A, B, C, and D, in order of decreasing activity. Field screening of the collected sample for penetrating radiation should be used to determine the laboratory type required to handle the sample initially (i.e., extruding, aliquoting, visually inspecting, etc.). As aliquots of the sample are taken for analysis, the RMW laboratory requirements can be determined using Figure 4.1, based on

the dose equivalent rate and the gross-alpha and gross-beta activity of the aliquot. It should be emphasized that the activity determination referenced in the guidelines is intended only as a gross-sample-screening method and should not be used as a quantitative determination of sample activity. It should also be noted that these guidelines are not universally applicable to all radionuclides. An alternate, site-specific waste classification should be developed and justified as part of the waste-analysis plan.

The guidelines for RMW laboratory selection are based on two major radiological concerns: contamination and personnel exposure. These hazards are controlled by partially or totally containing the radioactive material when the potential for contamination is high and by remotely manipulating and shielding the material when working with samples that present high external-dose rates. Type A laboratories should be used when both contamination and external exposure potential are high. These factors are controlled by using hot cells and remote manipulation. Type B laboratories should be used when the potential for contamination is high and dose equivalent rates are low. Shielded gloveboxes should be used to reduce external exposure to levels that are ALARA as required. Type C labs provide partial containment of the radioactive material with hoods that keep the general flow of airborne radioactive materials away from the worker. Hoods in Type C labs are equipped with HEPA filters to prevent the emission of radioactive materials to the environment. Type D labs are chemical labs with approved chemical hoods. Materials recommended for use in Type D labs pose little contamination or external-exposure hazard.

Sample Handling

Safety should always be the primary consideration when analyzing samples. This chapter outlines

Note: When aliquots of a sample are taken, the facility requirements will be based on the radiological quantitation associated with that aliquot.

Laboratory Types

Type A - Radiochemical laboratory equipped with gloveboxes and hot cells with nonabsorbent floors and working surfaces. Designed specifically for handling high-activity radioactive materials. Laboratory should be isolated from surrounding offices or laboratories by change facilities or air locks. Contamination-zone clothing, such as coveralls and shoe covers, should be used. Personnel dosimetry (including extremity dosimeters as required), portable Geiger Müller (GM) and ionization survey instruments, air samplers, and other appropriate monitors should be available.

Type B - Intermediate radiochemical laboratory equipped with approved chemical hoods with high-efficiency particulate air (HEPA) filters and gloveboxes. Laboratory should be isolated from surrounding offices or laboratories by change facilities or air locks. Contamination-zone clothing, such as coveralls and shoe covers, should be used. Personnel dosimetry (including extremity dosimeters as required), portable GM and ionization survey instruments, air samplers, and other appropriate monitors should be available.

Type C - Radiochemical laboratory equipped with approved chemical hoods that are vented through HEPA filters. Face velocities at hood openings should have a minimum velocity of 100 fpm. Lab coats and personnel dosimetry should be worn. Labs should be equipped with GM survey meters and should offer other appropriate monitors.

Type D - Chemistry laboratory equipped with approved chemical hoods. The radioactivities of samples will present no external exposure or internal concern. Most procedures for handling hazardous waste samples should provide sufficient protection for employees.

Figure 4.1. Operating Guide for RMW Samples

general safety considerations. As a minimum form of protection, lab coat, gloves, and safety glasses should be worn to prevent samples from contacting the skin and eyes. Samples should be handled inside a fume hood. A respirator should be worn if hazardous vapors are present in the laboratory atmosphere above regulatory limits. A respirator should also be worn when potential for airborne radioactivity exists. The type of respiratory protective equipment to be used depends on the location and type of the hazard. Analyzing more hazardous samples may require using supplied air and additional special clothing. Face shields should be worn if the samples are corrosive. In most cases, respirators should be used only as a temporary measure until engineered controls are in place. Site-specific safety requirements should be referred to.

For handling samples that may have low-level or medium-level radioactivity, certain precautions should be taken to prevent any material from escaping into the laboratory. For example, the roughing pumps on the mass spectrometer should have HEPA filters and a venting system above the injection port to collect any vapors. As required by the DOE ALARA principle, to minimize radiation exposure and contamination of personnel and facilities, staff should follow all radiochemical laboratory procedures for handling radioactive samples and for monitoring associated with health physics issues (site-specific radiation control policies should be referred to). Chapter 5 provides guidelines for waste handling.

Radiation Protection

ALARA Philosophy

The radiation protection policy of DOE requires that occupational exposures of personnel, and radioactive material releases to the environment, be reduced

to the lowest levels practical, commensurate with sound economics and good operating practices.

Control of Exposure

The guidance in this section provides a basis for controlling personnel exposure. The recommendations here and in 10 CFR 835 "Occupational Radiation Protection," 1/13/93, reduce the chance for any person to exceed the dose equivalent limits and increase the chances for people to maintain personnel exposures ALARA.

Control of Exposure During a Job. Management should impose engineered and administrative controls during individual job operations to help keep exposures within DOE's exposure limits.

Management should specify the need for monitoring exposure levels during work in the radiation area and should control work time, as necessary, to ensure that exposures do not exceed the DOE controls. The following precautions should be taken:

- The dose rates should be listed at the work station.
- Nonuniform external exposure rates should be controlled in the short term to ensure that personnel are not excessively exposed. If the exposure rates are not subject to significant change with time, workers should wear a direct-reading pencil or an equivalent dosimeter. This dosimeter should be processed and the reading recorded at a frequency adequate to provide the necessary control.
- If external exposure rates are subject to significant change, the work may need continuous surveillance and careful timekeeping. Above exposure rates of 1 mSv (100 mrem/h) or when

working in nonuniform radiation fields, continuous surveillance is recommended.

Workers should use shielding, maintain maximum distance from the sample, and minimize time of handling and decontamination, as practical, to reduce radiation levels ALARA before and during the radiation work.

Individuals should not enter or remain within a radiation area if they suspect that conditions for exposure to radiation exceed the specified limits. Staff should immediately exit the radiation area if such conditions exist.

Individuals could receive significant skin exposure when working in areas where high radiation levels from contamination are present or when working with radioactive samples. The exposures can occur from radioactive material deposited on protective clothing. Therefore, during work under such conditions, frequent clothing surveys should be conducted. If high contamination levels exist ($500 \mu\text{Gy}$ (5 mRad)/h), workers should replace contaminated protective clothing.

Protection from Abnormal Dose Rates. Warning devices should be provided in areas that have a potential for high dose rates or airborne releases. The constant air monitor (CAM) will alert personnel of abnormal airborne releases. The radiation area monitor (RAM) will alert personnel if dose rates rise above normal operating levels. Criteria on using RAMs and CAMs for this purpose should be provided in site-specific documents.

Protection of the Unborn Child. The dose equivalent received by an unborn child as a result of occupational exposure to a female worker should not exceed 5 mSv (500 mrem) per 9-month period. Efforts should be made to avoid exceeding $500 \mu\text{Sv}$ (50 mrem)/month to the pregnant worker. Pregnant

workers should immediately notify management so that this guideline is not exceeded.

Dose Equivalent Limits, Controls, Policies, and Records

The radiation protection policies of DOE are based on ICRP and NCRP recommendations. The occupational dose equivalent limits are maximum permissible exposures. Actual operations should conform to ALARA practices.

Radiological Worker Dose Limits

The annual dose-limit guidelines (Table 4.2) should apply to persons 18 years of age and older who receive occupational exposure to ionizing radiation. The numerical values do not represent a dose above which injury will occur. Rather, they represent a dose that should not result in any significant risk of delayed effects. Maintaining exposure within the guidelines does not ensure that no risk to the individual exists. Therefore, exposure of personnel should be kept to a practical minimum.

Administrative Control Levels

Guidelines listed in Table 4.3 help ensure that personnel exposures are necessary and adequately justified, and are maintained ALARA. As the administrative dose (as described in Table 4.3) increases, the level of administrative approval that could be used to authorize additional exposure should increase. Administrative approval could be given only when

- the worker's radiation exposure status is known (his or her most recently worn dosimeter has been processed and a result obtained)

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- a legitimate need exists for the worker to exceed the administrative guideline. These needs include, but are not limited to, the following examples: 1) the unique ability or experience of the worker will minimize the collective exposure and 2) other qualified workers with lower exposures are not available.

The effective dose equivalent to the whole body is most often the limiting consideration. In most cases, skin and extremity doses follow or track the whole-body dose, and adherence to whole-body limits results in adherence to skin and extremity doses.

Table 4.2. Summary of Dose Limits

Type of Exposure	Annual Dose Equivalent Limit Sv (rem)
Stochastic effect	0.05 (5.0)
Nonstochastic effects	
Lens of the eye	0.15 (15.0)
Extremity	0.5 (50.0)
Skin of the whole body	0.5 (50.0)
Unborn child (entire gestation period) in 9 mo	0.005 (0.5)

Table 4.3. Administrative Control Levels

Maximum Dose Equivalent (Annual) in Sv. (mrem)					Approval Recommended to Exceed this Level
Whole Body	Skin and Extremity	Lens of Eye	Any Organ		
5 (500)	150 (15,000)	45 (4,500)	150 (15,000)		First level of management
10 (1,000)	225 (22,500)	67.5 (6,750)	225 (22,500)		Second level of management
15 (1,500)	300 (30,000)	90 (9,000)	300 (30,000)		Third level of management
20 (2,000)					DOE (regional office)

Levels 1, 2, and 3 denote the management structure concept at the Hanford site. This should be adjusted according to the management structure at other organizations and DOE sites.

Planned Exposure Variances. Unusual exposure conditions may require controls that have a different time basis or different dose-equivalent levels.

Dose Limitations. Special limitations on the occupational radiation exposure of an individual may be necessary. Limitations may be due to external exposure or exposure from internally deposited radionuclides.

Radiological Work Permit (RWP). Work that will yield appreciable radiation exposure should require filing in advance a document that defines protective equipment and monitoring to be used.

Persons working with radioactive material should receive continued training in radiation-control practices. This should include radiation-exposure minimization, contamination control, and protective-clothing requirements, as well as other training as appropriate.

Controls for Benchtop Work, Laboratory Fume Hoods, Sample Stations, and Gloveboxes

The following guidelines apply to radiological work in localized benchtop areas, laboratory fume hoods, sample stations, and glovebox operations located in areas that are otherwise contamination free. An RWP should be issued to control the radiological work in these areas.

The following controls should apply to work in all areas:

- Training, protective clothing, and self-survey requirements should be specified in the applicable RWP.

- Protective clothing should include laboratory coats and impermeable gloves, secured at the wrist. Shoe covers should be considered if the potential for floor contamination exists.
- Workers should periodically monitor their hands during work.
- Before leaving the area, workers should perform a whole-body survey.
- If a potential exists for splashing or airborne radioactive material, such as when taking pressurized samples, additional controls, such as the use of rubber aprons, face shields, full protective clothing, or respiratory protection, should be instituted.

The following additional controls should apply to benchtop work. Benchtop work is any work, using discrete quantities of unsealed radioactive material, that is conducted without specialized confinement (i.e., an open beaker, flask, test tube, centrifuge tube, or weighing boat). Benchtop work with unsealed material involves the potential for the staff member to inhale a small fraction of the unsealed material, resulting in some internal exposure.

The maximum allowable quantity of radioactive materials, in becquerels (microcuries), for benchtop work is given in Table 4.4. When the isotopic composition is unknown, the following maximum quantities should apply:

alpha emitters: 1.66 Bq { 4×10^{-5} μ Ci (100 dpm)}

beta-gamma emitters: 333 Bq { 8×10^{-3} μ Ci (20,000 dpm)}

It is important to note that the limits given are intended to be applied to discreet quantities of radio-

Table 4.5 presents limits on the maximum allowable amounts of radioactive materials allowed in a fume hood. If more than one radionuclide is present within the fume hood, the sum of the fractions obtained by

work in a laboratory fume hood.

The following additional controls should apply to its for benchtop work should have additional con-

tainment. Work with dispersible or potentially dispersible radioactive material in quantities greater than the limit for benchtop work should have additional con-

acceptable contamination limits. They should not be used as real concentrations. They should not be used as samples. These limits are not intended to be applied as radioactive activity contained in a given sample or set of active materials. They apply to the total amount of

Work with dispersible or potentially dispersible radioactive materials in amounts exceeding the limits for fume hoods should be within additional containment, e.g., a glovebox or hot cell.

For nondispersible conditions, these numbers should be multiplied by 10; for dispersible conditions, they should be multiplied by 0.1; and for highly or readily dispersible conditions, they should be multiplied by 0.01.

Table 4.5 values assume limited dispersibility conditions. For other dispersibility conditions, the maximum permissible values should be adjusted as follows: dividing the amount present by the allowable amount should not exceed one.

Radionuclide	Form	Allowable Quantity, Bq (μCi)
⁹⁰ Strontium	Water vapor	3.7×10^5 (1 × 10 ¹)
	Powders	3×10^2 (8 × 10 ⁻³)
	Volatile liquids	3×10^3 (8 × 10 ⁻²)
	Normal liquids	3×10^4 (8 × 10 ⁻¹)
¹²⁵ Iodine	All	3.7×10^4 (1)
	All	3×10^3 (8 × 10 ⁻²)
	Powders	1.48×10^5 (4 × 10 ⁻⁵)
	Volatile liquids	1.48×10^1 (4 × 10 ⁻⁴)
²³⁹ Plutonium	Powders	1.48×10^2 (4 × 10 ⁻³)
	Volatile liquids	1.48×10^2 (4 × 10 ⁻³)
	Normal liquids	1.48×10^2 (4 × 10 ⁻³)
	Normal liquids	1.48×10^2 (4 × 10 ⁻³)

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Table 4.5. Allowable Quantities of Radioactive Materials for Fume Hood Work Under Limited Dispersibility Conditions

Toxicity Group	Radioisotopes (Examples)	Allowable Amount Bq (Ci)
I	^{243}Am ^{239}Pu ^{226}Ra ^{230}Th ^{233}U	$< 37 \text{ MBq } (< 1 \text{ mCi})$
II	^{137}Cs ^{60}Co ^{131}I ^{90}Sr	$< 3.7 \text{ GBq } (< 100 \text{ mCi})$
III	^{14}C ^{132}I ^{32}P ^{65}Zn	$< 370 \text{ GBq } (< 10 \text{ Ci})$
IV	^3H ^{85}Kr Natural Th Natural U	$< 37 \text{ TBq } (< 1000 \text{ Ci})$

The following additional controls should apply to glovebox operations:

- Gloveboxes should be inspected for integrity and operability before use.
- Gloveboxes should be marked, or survey measurements should be posted, to identify whole-body and extremity dose rates.

Safe Handling of Hazardous Chemicals

Many of the chemicals that will be used when performing the methods provided in this document may be hazardous. The following section provides general guidance for safe handling and storage of chemicals. Refer to site-specific documents for more detailed information.

Emergency Procedures

If dangerous chemicals contact the body, any contaminated clothing should be removed, the contact area should be flushed immediately with large amounts of water for at least 15 min, and the person should report to a medical aid station.

Caution: A worker should report to a medical aid station because many dangerous chemicals, especially chemical splashes in the eyes, may not exhibit any symptoms or damaging effects until hours after the initial exposure.

Caution: Emergency washing facilities should not be used for extinguishing clothing fires unless the unit is immediately available. If clothing

should catch on fire, the fire should be smothered as quickly as possible, usually by rolling on the floor. This action keeps the flames away from the face and reduces smoke inhalation. Fire blankets should be available in installations where fire hazard to personnel is high.

Emergency washing facilities, such as safety showers and eyewash stations, should be provided within 100 ft or 10 sec from operations involving corrosive materials. The design and provision of emergency washing equipment should comply with the *American National Standard for Emergency Eyewash and Shower Equipment* (ANSI 1981), OSHA 29 CFR 1919.151(c) "medical services and first aid," and with local standards. Providing emergency washing facilities does not substitute for wearing proper protective clothing or face and eye protection. Drench hoses and personal eyewash units (bottles) may be used to supplement shower and eyewash units, but should not replace them.

Chemical Exposure Limits

To comply with OSHA requirements 29 CFR 1910.1450 (OSHA Laboratory Standard), laboratories are required to protect workers from over-exposure to hazardous substances. Air concentrations of hazardous chemicals in the laboratory should be maintained below the most stringent exposure levels in DOE Order 5480. Exposure of personnel to hazardous chemicals by all routes of entry (inhalation, skin absorption, and ingestion) should be minimized. A program should be established to monitor staff members potentially exposed to chemical hazards at or above the action level and to obtain an exposure measurement of workers believed to have the greatest exposure.

Protective Clothing

Hand Protection: Gloves are the primary method of protection. Long gloves should be worn and the cuffs turned up to prevent chemicals from running off the gloves onto the lab coat. Gloves should be impermeable to the chemicals used.

Foot Protection: Safety shoes or substantial footwear should be worn. Such footwear should provide a high degree of stability, support, and foot protection from lacerations, punctures, and moderate chemical splashes.

Eye and Face Protection: Appropriate eye and face protection should be worn by all staff and visitors in work areas throughout the laboratory where the potential exists for solid, liquid, or gaseous materials to accidentally come in contact with the eyes or face and result in injury or illness. To ensure that eye protection equipment is approved for occupational exposures, each component should bear the manufacturer's trademark and an ANSI Z87.1 identification. Safety glasses provide protection against flying particles and minor splashes of noncorrosive chemicals. Splash goggles and face shields, in addition to approved safety glasses, should be worn for protection against splashes of corrosive chemicals, such as strong acids, caustics, oxidizers, or dehydrating materials.

General Safe Practices: Protective clothing should not be worn away from the area where it is required, especially where a potential exists for spreading contamination.

Chemical Handling

Staff members who work in areas where hazardous chemicals are present should be informed of the

requirements under the Hazardous Communications Regulation 29 CFR 1910.1200. Each staff member who works with or who is potentially exposed to hazardous materials should be informed of the types of operations in his/her work area where hazardous materials are used and where he/she can obtain information regarding chemical hazards. Staff members should also receive training in the use and handling of hazardous materials. Material safety data sheets for hazardous chemicals should be readily accessible to workers. The information and training should assist staff members in conducting all chemical handling, storage, and disposal operations in full compliance with acceptable laboratory practices and all applicable procedures and protocols.

Most chemical handling operations require the use of appropriate protective clothing, such as eye protectors, lab coats, and gloves appropriate for the operation. A safety shower and an eyewash fountain should be available. The shower or fountain should be checked regularly to see if it is working properly and to ensure that stale water is flushed from the line.

Safe Practices. The following precautions are recommended to ensure adequate levels of safety:

- Inert, absorbent material should be available for cleaning up large spills or leaks. Spill kits are highly recommended. Mercury spill kits should be available in any location where mercury is routinely used.
- Protective clothing and equipment, such as lab coats, gloves appropriate for the operation, and safety glasses or goggles, should be worn whenever handling chemicals.
- Pouring should be done inside chemical fume hoods. Pouring should not be done from a carboy; siphoning is recommended.

Warning: A siphon should not be started by mouth.

- Chemical use should be restricted to well-ventilated areas.
- Work should be arranged so vapors travel away from other people in the work area.
- A worker should not be inside a fume hood.
- Chemicals should not be allowed to contact skin.
- Pipetting should not be done by mouth.
- Good housekeeping and orderly arrangement of equipment should be maintained.
- Trash receptacles that are either noncombustible (preferably metal with a lid in place) or are kept in a noncombustible covering should be used to dispose of trash.
- Chemically contaminated items should be thoroughly rinsed with water before being discarded in a trash receptacle. (Several substances, such as nitric acid, will react with cellulose materials and ignite spontaneously.)
- Water should not be poured into concentrated acids or onto solid caustics; rather, acids or caustics should be poured into water.

Transportation. Before lifting cardboard or styrofoam cases, ensure that they are not weakened by wetness or damage.

Bottles of chemicals should not be carried by the neck. Use bottle carriers and provide secondary containment for hazardous chemicals.

Incompatible Chemicals

Many chemicals are incompatible with other chemicals at normal or slightly elevated temperatures or pressures. To prevent fires, explosions, or runaway reactions, inadvertent mixing or contact of incompatible chemicals should be avoided during storage or use. For more detailed information on a specific chemical, the MSDS and/or the National Fire Protection Association's *Manual of Hazardous Chemical Reactions* (1991) may be referred to.

Flammable Solvents

Flammable and Combustible Materials

Flammable liquids are those having a flashpoint below 37.8°C (100°F) and a vapor pressure not exceeding 40 lb per sq in. (absolute) (2,068 mm Hg) at 37.8°C (100°F) and are known as Class I flammable liquids (see Table 4.6).

- Class IA liquids include those having a flashpoint below 22.8°C (73°F) and having a boiling point below 37.8°C (100°F).

- Class IB liquids include those having a flashpoint below 22.8°C (73°F) and a boiling point at or above 37.8°C (100°F).
- Class IC liquids include those having a flashpoint at or above 22.8°C (73°F) and below 37.8°C (100°F).

Combustible liquids are those having a flashpoint at or above 37.8°C (100°F). Combustible liquids are subdivided as follows (see also Table 4.6).

- Class II liquids include those having flash points at or above 37.8°C (100°F) and below 60°C (140°F).
- Class IIIA liquids include those having flash points at or above 60°C (140°F) and below 93°C (200°F).
- Class IIIB liquids include those having flash points at or above 93°C (200°F).

Solvent Substitution. In many applications, solvents with less fire hazard and toxic properties can be substituted. For example, 1,1,1-trichloromethane (methyl chloroform) might be a suitable substitute for acetone. With this substitution, the fire hazard is reduced considerably. In general, the least hazardous solvent that is appropriate for the work should be used.

Training. Users of flammable liquids should be trained in safe practices, and the training should include the hazardous characteristics of the specific flammable liquids used.

Flammable/Combustible Vapors and Mists. Many operations, such as heating flammable/combustible liquids, can result in explosive atmospheres. Proper ventilation and protective equipment and procedures should be required to control fire and

health hazards when flammable or combustible vapors or mists are generated.

Pressurized flammable or combustible liquids are a severe fire hazard if the pressure boundary fails. An atomized spray of either a flammable or combustible liquid is more readily ignitable than in its more normal form. Controls based on published flashpoints and flammability ranges of the liquids have no bearing on an atomized spray. Extra precautions are necessary for pressurized systems containing either class of liquids.

Handling. In addition to the hazards of fire and explosion, many flammable and combustible liquids are toxic. The vapors may or may not cause immediate undesirable effects, but they may have severe latent effects. Most solvents will dissolve the natural protective fats and oils of skin, and prolonged exposure may cause dermatitis.

Dispensing and Transfer. Dispensing of flammable and combustible liquids requires special safeguards to ensure that a fire or explosion does not occur. The following actions should be considered to ensure the safe dispensing and transfer of flammable and combustible liquids.

- The transfer should be made in a properly designed fume hood.
- Automatic fire sprinklers should be provided.
- Explosion or pressure suppression or venting should be provided.
- Electrical outlets and equipment should be Underwriter's Laboratory (UL) listed or Factory Mutual (FM), and designed for hazardous locations. Equipment should be in compliance with the National Electrical Code National Fire Protection Association (NFPA) No. 70, Article 501 (NFPA 1989).

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- Containers should be properly bonded and grounded during transfer and dispensing operations.
- Appropriate ventilation should be provided to prevent travel and accumulation of hazardous vapors.
- Proper drainage should be provided so that flammable and combustible liquid leakage and fire protection water are directed to a safe location.

Safety Cans: The basic purposes of an approved safety can (or approved container) are to control flammable vapors under both normal and abnormal conditions and to provide a convenient means for carrying, dispensing, and storing up to 5 gal of flammable liquids. Safety cans are not a substitute for a flammable storage cabinet. Safety cans should be UL listed or FM approved for flammable and combustible liquids. Safety cans should be labeled with their contents. A yellow band on which the contents are printed in contrasting colors is OSHA's preference.

Ventilation: Since most vapors of flammable and combustible liquids are heavier than air and can migrate along the floor to ignition sources, adequate ventilation should be maintained for vapor control. Analyses involving flammable and combustible liquids should be performed in fume hoods properly designed and constructed for working with flammable and combustible liquids.

Container Size: Table 4.7 specifies the types of containers and the maximum allowable container size for each class of flammable or combustible liquids.

Storage: When not in use, flammable and combustible liquids should be stored in approved cabinets or in specially constructed rooms or areas. Flammable

and combustible liquids outside of these areas should be limited to the amount necessary to perform the tasks for the day. At the end of the day, all flammable and combustible liquids should be returned to the proper storage.

Cabinets for storing flammable liquids should be UL listed or FM approved. Cabinet contents should not include other materials that are combustible or reactive with the flammable/combustible liquids. Compressed gasses should not be stored with flammable/combustible liquids. All containers should be capped so the container is vapor tight and unlikely to spill in the event the container is tipped over. Not more than 454 L (120 gal) of Class I, Class II, and Class IIIA liquids should be stored in any one storage cabinet. Indoor flammable liquid storage cabinets should have their vent holes plugged.

Refrigerators and freezers for storing flammable liquids should be UL listed for such use and should be labeled as suitable for flammable liquid storage. No more than 19 L (5 gal) of flammable/combustible liquids should be stored in any refrigerator or freezer.

Table 4.8 indicates the maximum quantity of flammable and combustible liquids that should be stored in cabinets in a building or fire area within the building.

Chemical Storage

Stored chemicals can be handled safely if the following practices are observed:

- Storage time for chemicals should be limited. Unused chemicals should be disposed of when either no future use for the chemical can be determined or if the integrity of the chemical becomes suspect.

Table 4.7. Maximum Allowable Size of Containers

Container Type	Flammable Liquids			Combustible Liquids	
	Class IA	Class IB	Class IC	Class II	Class III
Glass	.5 L (1 pt) ^(a)	.954 L (1 qt) ^(a)	3.8 L (1 gal)	3.8 L (1 gal)	3.8 L (1 gal)
Metal (other than DOT ^(b) drums) or approved plastic	3.8 L (1 gal)	19 L (5 gal)	19 L (5 gal)	19 L (5 gal)	19 L (5 gal)
Safety cans	7.6 L (2 gal)	19 L (5 gal)	19 L (5 gal)	19 L (5 gal)	19 L (5 gal)
Metal drums (DOT ^(b) specifications)	2.3 x 10 ² L (60 gal)	2.3 x 10 ² L (60 gal)	2.3 x 10 ² L (60 gal)	2.3 x 10 ² L (60 gal)	2.3 x 10 ² L (60 gal)

(a) Exception: Class IA and IB liquids may be stored in glass containers of not more than 1-gal capacity if the required liquid purity (such as American Chemical Society (ACS) analytical reagent grade or higher) would be affected by storage in metal containers or if the liquid is incompatible with metal containers. This does not allow larger containers to be used for convenience or procurement advantages.

(b) U.S. Department of Transportation

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Table 4.8: Maximum Storage Quantities for Flammable or Combustible Liquids				
Material	Class	Quantity, liters (gal)		
Flammable Liquid	IA	2.3 x 10 ³ L (60) ^(a)		
	IB	4.5 x 10 ² L (120) ^(a)		
	IC	6.8 x 10 ² L (180) ^(a)		
	II	9.1 x 10 ² L (240) ^(a)		
Combustible Liquid	III-A	2.5 x 10 ³ L (660) ^(a)		
	III-B	10 x 10 ⁴ L (26400) ^(a)		
(a) Quantities can be doubled in a building with a fire-protection sprinkler system.				

- All chemicals should be properly labelled, including information on the hazards associated with the chemical. Chemicals with a shelf life should be labeled with the date received.
- Chemicals should be stored on shelves so that all labels may be easily read.
- Chemicals should be stored such that incompatible chemicals are separated.
- Containers should be closed.
- Chemicals should be stored properly according to temperature, vibration, and amount of light.
- Containers should not be stored in stacks.
- Flammable liquids should be stored in approved storage cabinets.

Storage Areas

- For all storage areas, ample ventilation should be provided to dissipate toxic or other hazardous vapors.
- Oxidizers should be stored separately from reducers.
- Acids and bases should be stored below eye level and away from heat and light.

Acid and Bases

- Acids and bases should be stored in corrosion-resistant trays, such as those made of plastic or glass. The trays should be of sufficient volume to hold the contents of two of the largest bottles or 10% of the total inventory, whichever is larger.
- Acids and bases should not be stored in the same tray.
- Acids and bases should be stored below eye level and away from heat and light.

Organic Peroxides

Concentrated organic peroxides are frequently hazardous because of their high flammability and sensitivity to shock, sparks, friction, light, and strong oxidizing and reducing agents. Organic peroxides decompose at a fixed rate under fixed conditions, but decomposition may result in an explosive reaction if precautions are not observed. Organic peroxides are also corrosive, requiring appropriate protective clothing and equipment to prevent contact with the skin or eyes.

Storing Organic Peroxides. Organic peroxides should not be stored in glass bottles with screw caps or ground glass stoppers since the friction generated when opening these bottles may cause detonation. Peroxides should be stored at reduced temperatures in an explosion-proof refrigerator in accordance with the manufacturer's instructions.

Peroxides should be dated upon receipt and again upon opening the container to ensure that the manufacturer's shelf-life requirements are not exceeded.

Peroxides should be scheduled for disposal 1 year after receipt or 1 month after opening the container if no shelf life restrictions are provided. Only the quantity of peroxide necessary for the project should be kept at hand.

Handling Organic Peroxides

Warning: Toluene may cause decomposition of diacyl peroxides.

Metal spatulas or other metal implements should not be used in contact with peroxides since contamination by metals can lead to explosive decomposition. All sources of heat or ignition should be eliminated before working with peroxides. Solutions of perox-

ides in volatile solvents should be avoided under conditions where the solvent may be evaporated and the peroxide concentration increased. Dilute solutions of peroxides in inert solvents, such as aliphatic hydrocarbons, should be used to reduce the peroxides' sensitivity to shock and heat.

Peroxide-Forming Agents. Several classes of compounds are known to form organic peroxides:

- aldehydes
- ethers (Cyclic ethers especially and those containing primary and secondary alcohol groups form peroxides on exposure to air and light. Several colorimetric tests for determining levels of peroxides in ether are available. Distilling ethers is extremely hazardous.)
- compounds containing benzylic hydrogen atoms, especially if the hydrogen atoms are on the tertiary carbon atoms
- compounds containing the allylic ($\text{CH}_2 = \text{CHCH}_2\text{R}$) structure, including most alkenes
- vinyl and vinylidene compounds.

Chemicals known to readily form peroxides should be dated upon receipt and again upon opening the containers and tested to be free from peroxides.

Compressed Gases

While pressure is a common hazard of all compressed gases, each compressed gas may have one or more other hazardous properties that must be considered. Gases may also be flammable, toxic, corrosive, asphyxiating, oxidizing, pyrophoric, or unusually reactive with a variety of materials or other gases. Equipment design, procedures, and location must recognize all these aspects to ensure safe operations.

Storage: Gas cylinders not in use should be kept in a designated storage space and should be firmly secured. Protective caps should be installed over cylinder valves when cylinders are in storage. Cylinders should be stored outside of buildings and set up so that leaking gases do not enter the building. Storage should not be adjacent to exits, stairways, elevators, or other high-traffic areas. Gas cylinders should be protected from direct sunlight, weather extremes, and temperatures in excess of 51.7°C (125°F). Gas cylinders should also be kept separate from flammable and combustible liquids, vegetation, and other combustible materials, such as paper trash. Flammable gases should be kept separated from oxygen and other oxidizers (i.e., air, nitrous oxide) by a required fire barrier or a minimum of 6.1 m (20 ft). This applies to both full and empty cylinders. Cylinders should be stored in an upright position and firmly secured.

Moving Cylinders: Compressed gas cylinders should only be moved with a hand truck specifically made for transporting cylinders. The cylinders should be firmly secured in an upright position on the hand truck.

Cylinders in Use: When in general use, compressed gas cylinders should have a regulator attached and gas lines connected to operable equipment. Gas cylinders should be secured by means of chains, belts, or approved devices. Supports should be located high on the cylinder to prevent tipping over.

Lecture Bottles: When using compressed gas from a lecture bottle, its hazardous properties should be considered. Lecture bottles or small propane cylinders should be stored separately from ordinary combustibles and from flammable and combustible liquids. Lecture bottles should not be stored in flammable liquid cabinets. Lecture bottles should be stored and used so that they will not roll or fall or otherwise be subject to damage. Lecture bottles may

be stored horizontally, but they should be used in an upright position.

Hydrogen: Hydrogen has a wide flammable range and presents an extreme fire hazard. The special properties of hydrogen make it susceptible to autoignition if it is allowed to rapidly expand (such as when the cylinder valve is opened to the environment). Ignition sources, such as open flames or unapproved electrical equipment, should be kept away from the immediate vicinity of the hydrogen-use area. Hydrogen cylinders should be separated from oxidizers and other flammable or combustible materials.

Oxygen: Oxygen supports and can greatly accelerate combustion. Clothing should not be hung on oxygen cylinders because clothes can become saturated with oxygen if a leak at the valve or connecting threads occurs. Oxygen-saturated clothes will burn intensely if they come in contact with an ignition source, even a small spark. Oxygen cylinders should be kept separate from flammable gas cylinders as well as other combustible materials.

Alkali Metals

Industrial experience in handling sodium at low temperatures has demonstrated that alkali metals can be handled safely by following the proper safeguards.

Hazards. The following hazards of alkali metals arise from the high degree of reactivity of these metals with numerous materials.

- Alkali metals react violently with water and with substances containing water.
- The caustic produced by metal reacting with water is a danger to personnel.

- Splashes of alkali metal can cause clothing to catch fire either immediately or after a delayed action.
- Fires involving alkali metals may produce caustic fumes that are irritating to the eyes, nose, and throat. The recommended threshold limit value for these caustic fumes is 2 mg/m^3 of air.
- Fires can occur from handling sodium or a sodium-potassium alloy (NaK) carelessly in the open air, or by failures in alkali-metal systems.
- In addition to the caustic oxides formed by all alkali metals, potassium has the special property of forming a coating of orange superoxides after long exposure to air. Potassium in contact with its own superoxide is extremely sensitive to shock and can detonate.

Fire Control. When exposed to air, a sodium or potassium alloy may ignite spontaneously at low temperatures, depending on such conditions as humidity and metal particle size. Upon ignition, the temperature of the burning mass increases rapidly to 649°C (1200°F) and as high as 872°C (1600°F). The material continues to burn, giving off large quantities of opaque, white smoke that makes visibility very poor. No flame is visible—only a glowing mass of the alkali metal. The burning material cannot explode, but will react violently with almost all common fire-extinguishing materials. The high temperature of burning sodium or NaK on concrete causes “explosive spalling” of the concrete, spreading the fire and causing burns.

Water, carbon dioxide, Halon, and water-based extinguishers should not be used on fires involving alkali metals because they produce dangerous reactions. The material in ordinary dry chemical extinguishers is virtually ineffective except in extremely large quantities and in some cases may cause an

explosion. In most cases, a Class D fire extinguisher is effective.

For all alkali metal fires except lithium fires, displacing the surrounding atmosphere with inert gases or nitrogen is the most effective way to extinguish the fire. Fires involving sodium, potassium, or a sodium-potassium alloy can be extinguished by completely covering the fire with NaX, carbon microspheres, dry calcium carbonate, dry sand, or vermiculite. Only graphite or Lith-X can effectively smother a lithium fire. Carbon microspheres are considered the most effective extinguishing agent. Materials used for extinguishing such fires should be kept absolutely dry.

Handling Alkali Metals. Because of their dangerous reactions, it is important to observe the following precautions when handling alkali metals:

- The location of safety showers, fire extinguishers, and exits should be known. Access to all of them should be unrestricted.
- No open flames of any kind should be used in the area.
- Solid alkali metals should be handled with tongs or with impermeable gloves.
- Processes should avoid contact between alkali metals and water.
- The design of the facility should preclude formation of explosive hydrogen-air mixtures.
- Process equipment should be accessible for ready dismantling and cleaning.
- Dump tanks, reservoirs, or other design features should be provided to minimize spills and the resulting fire and cleanup problems.

- To handle spills or drips, catch trays of a sufficient size to handle the anticipated volume should be installed. Vermiculite should be added to the tray to help smother fires from leaks or spills.
- Alkali metals should be transferred at the lowest possible temperature to minimize fire and handling hazards. Liquid metals should be transferred in inert atmospheres.
- Cleaning operations should be performed in areas with sufficient ventilation to remove hydrogen, airborne alkali metal oxides, and hydroxide. Smoke should be captured and either filtered or scrubbed.
- Dry steam, followed by wet steam, followed by water, should be used for final cleanup of the equipment. In some cases, burning is satisfactory. Another cleanup method using methyl cellosolve, butyl cellosolve, or 100% ethyl alcohol may be used for small- and medium-size jobs.

Cryogenics

A cryogenic fluid has a boiling point below -75°C . These fluids are used extensively by vacuum scientists both for pumping gases and trapping contaminants.

Suffocating Effects: A leak in a liquid gas supply line can be caused by improper soldering techniques. Dense cold vapor can gradually displace air. In a confined space, without adequate ventilation, sufficient atmospheric oxygen may be displaced to cause persons in the space to suffocate, even though the gas itself may not be toxic.

Warning: A rescue should never be attempted in a confined space without proper breathing equipment.

Venting cryogenic gases from cold baffles or storage dewars can gradually diminish the oxygen content of the air in a confined space to a value below the minimal requirements for normal respiration; therefore, precautions for working in a confined space should be followed.

Over-Pressurization Hazards: Confining cryogenic fluids at low temperatures followed by the loss of insulating capacity can result in extremely high pressure buildup in vacuum-jacketed lines or vessels. Ice formation in the neck of small dewars, or cryogenic fluid trapped between valves, can also result in high pressure buildup. The working pressure of lines or containers may be exceeded.

Caution: If liquid nitrogen is the coolant, liquid air can condense in the trap and may explode.

- Proper piping fabrication and assembly techniques should be used.
- Valves should be opened carefully, as a sudden release of pressure can result in explosive expansion and severely injure any person directly in the path of the explosion.
- The capacity of containers and transfer lines should include an allowance for that portion of the cryogenic fluid that is gaseous.
- A pressure relief valve should be provided on the sorption pump.

Burns: When cryogenic fluids contact body surfaces, serious burns can occur.

If any part of the body is burned by cryogenic fluid, it should be immersed in tepid water immediately, and cold compresses should be applied.

Precautions: To reduce the potential for burns when handling cryogenics, the following precautions should be followed:

- Personnel should wear loose-fitting heavy gloves, chemical goggles with face shields, and loose protective clothing when handling cryogenic containers or piping.
- Watches or jewelry should not be worn when working with cryogenic fluids.
- Operations should be performed *slowly* to minimize boiling and splashing, i.e., when charging a warm container with liquid nitrogen.

Dewars:

Warning: Flying glass becomes a hazard if a glass dewar container breaks or implodes.

Exposed glass portions of the container should be taped. Strapping tape or cloth-type tape should be used.

Large-capacity storage containers should be constructed to withstand the weights and pressures that will be encountered. The container should be adequately vented to permit gas to escape.

Dewar vessels should be maintained so that an ice plug does not form in the neck. A loose-fitting cap should be used to prevent moisture or air from entering the vessel.

Only properly trained and authorized personnel should have access to liquefied inert gas storage areas.

A dewar should not be lifted in a manner for which it is not designed since the inner vessel of a double-walled dewar is supported by the neck, and the container could break.

Liquefied inert gas transfer lines should be constructed so that fluids do not become trapped between valves and thus increase the danger of an explosion. Lines should have safety relief valves and rupture disks.

Care should be taken when venting liquefied inert gases in storage containers or lines so that flammable, toxic, or inert gas does not accumulate in the work area.

Flammability and Explosion: Liquefied inert gases, such as liquid nitrogen or liquid helium, and also extremely cold metal surfaces, are capable of condensing oxygen from the atmosphere, which later may provide a source of concentrated oxygen.

Warning: If liquid nitrogen has a blue tint, it has been contaminated with oxygen and may explode.

Precautions: To reduce the potential for flammability or explosion, these precautions should be followed:

- Mixtures of gases or fluids should be controlled to prevent flammable mixtures from forming.
- Contaminating a fuel with an oxidant or vice versa should be avoided.
- Potential ignition sources should be eliminated.
- A monitoring system should be installed to warn personnel and to shut down a cryo-

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genic system when a dangerous condition develops.

- Flame-resistant clothing that does not generate static electricity should be worn.
- Two persons should handle liquid hydrogen containers.
- Liquid oxygen containers should be protected from shock.

Housekeeping

A clean and orderly work place should be maintained. Floors should be free from tripping hazards. Benches, tables, hoods, floors, and aisles should be clear of all materials not being used. Space around safety showers, eye wash stations, fire sprinkler heads, etc. should be kept clear at all times. Broken glass, sharp tools, needles, and syringes should be discarded in special containers marked "For Broken Glass." Protective clothing should be well maintained and hung in its proper place, not draped over equipment and benches. Frequently used apparatus kept on benches should be set well back from the edge and securely fastened.

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Chapter 5

Waste Handling

Scope and Application

If site-specific, local, or federal regulations differ from the guidance provided in this chapter, the regulations will take precedence.

The handling and disposal of radioactive and hazardous waste generated at U.S. Department of Energy (DOE) facilities should comply with all federal, state, and local requirements. The policy of DOE is to operate in a manner that minimizes the generation of waste and maximizes the concentration, recovery, and recycling of waste products to the extent economically practicable. The user should refer to all site-specific requirements for waste handling and disposal.

This chapter outlines disposal practices for radioactive and hazardous wastes, beginning with those wastes that can be recycled or reduced in volume before disposal.

Waste Minimization

Waste minimization is a three-fold concept that encompasses not producing waste, reducing the amount of waste, and recovering or recycling waste. Waste minimization is required by the Resource Conservation and Recovery Act (RCRA) for hazardous waste and radioactive mixed waste, and by DOE Orders for radioactive waste. In addition, reducing or eliminating waste increases the cost effectiveness of projects.

Radioactive Waste

To reduce the amount of radioactive waste to the smallest practicable volume, the amount of interior void space in waste containers should be minimized.

Low-Level Waste. The following steps should be considered, if practical:

- Radioactive waste should be segregated from nonradioactive waste before packaging.
- “Soft” radioactive waste such as rags, gloves, cardboard, or paper should be segregated in fiberboard boxes instead of in drums, if appropriate.
- Waste should be crushed or compacted to minimize void space.
- Void space should be filled with “soft” waste.
- Large pieces such as piping should be cut up to minimize the size of packages.

Transuranic Waste. To minimize the volume of transuranic (TRU) waste, known low-level waste (LLW) should be segregated from TRU waste whenever practicable; LLW should not be placed in TRU waste containers. When in doubt, the waste should be treated as TRU waste.

Exceptions to Waste Minimization Practices. Waste packages containing high-efficiency particulate air (HEPA) filters that could pose a hazard to personnel during filling or crushing operations may be exempt from this guidance.

In addition, when choosing between filling a waste container to prevent subsidence in a burial ground or leaving the container only partially full because of “as low as reasonably achievable” (ALARA) considerations, the container should be left partially full.

Radioactive Mixed Waste and Hazardous Waste

Waste reduction can be achieved in many ways, from improvements in housekeeping to replacing equipment that produces a high volume of waste. Waste minimization can be achieved by

- substituting chemicals used in a procedure or process with less hazardous or nonhazardous materials
- changing chemical processes so that fewer (or smaller amounts of) chemicals are used, safer chemicals are used, or chemicals are recycled directly back into the process
- improving program/task management and reducing spills, leaks, chemical makeup errors, and unnecessary experiment runs
- reclaiming, recycling, and reusing chemicals; recovering precious/toxic metals from solutions; cleaning and reusing oils and distilling solvents
- detoxifying or treating within the process where allowed by the Environmental Protection Agency (EPA), state, and locality
- improving waste management practices, including improved storage, transport, and onsite disposal.

Radioactive mixed waste should be segregated from radioactive waste for disposal. Any of the following

waste minimization techniques can be used to help minimize the generation of radioactive mixed waste:

- Where practical, lead shielding should be replaced with other shielding materials that are considered nonhazardous.
- Storage of laboratory chemicals in radiation areas should be limited and reduced.
- “Nonhazardous” scintillation liquids should be used.
- As low a volume of sample as effectively possible should be used.

Chemical Recycling Program

Unneeded or unwanted chemicals that are unopened or still usable should be recycled and used by others.

Disposal Guidance

Low-Level Radioactive Waste

Hood waste and room-generated waste comprise most of the LLW. These wastes are largely surgical gloves, plastic shoe covers, paper wipes, ducting, piping, and construction and other debris. The LLW that is mixed with hazardous waste should be considered radioactive mixed waste (RMW).

Container Recommendations. The following guidance applies to all containers:

- Containers should not have cracks, dents, holes, bulges, corrosion, or any other damage that could compromise their integrity.

- Containers should be protected from wastes that could react with or degrade the container by physical or chemical reaction.
- At least two containment barriers should be used to prevent the release of contamination. (For example, a 100-mil plastic wrap can be considered as one barrier, and the shipping container the second.)

Drums should be loaded either until they are full or until the maximum gross weight is reached. Sharp objects (such as broken glass) should be padded and taped to prevent damage to the plastic liner; large, bulky items should be blocked to prevent shifting that could damage the liner or container.

Not all LLW containers are the same; thus, the packaging and labeling instructions may vary, depending on which container is being used. The outer package should be marked with the proper warning label.

Documentation Requirements. Packages of LLW should be represented by accurate and complete records. Each radionuclide should be specified. It is not appropriate to list "mixed fission products."

Absorbed Inorganic Liquids. All liquids disposed of as LLW should be solidified, absorbed, or otherwise bound in the waste matrix by inert nonbiodegradable materials. The resultant waste matrix should not be capable of spontaneous combustion, decomposition, explosion, or corrosion, and should not affect the integrity of the containment barriers in any way. If the resultant waste matrix is capable of generating gas, the container should be vented.

If liquids are bound by absorption, the absorbent material should be placed in direct contact with the

liquid, and the quantity of absorbent material should be sufficient to absorb at least twice the volume of liquid present.

Asbestos. Asbestos material should be wetted, placed in a 4-mil or heavier plastic bag, and sealed wet using 2-in.-wide fabric-reinforced tape or an approved equivalent. The material should then be packaged in a leak-resistant packaging container that meets applicable shipping requirements. Sharp edges and corners within the package should be padded or protected to minimize damage to the plastic inner wrap during handling and shipping.

High-Level Radioactive Waste

High-level radioactive waste (HLW) is defined by the source of the waste as well as the radionuclide content. In general, HLW is the highly radioactive waste material resulting from reprocessing spent nuclear fuel that contains a combination of TRU waste and fission products in concentrations requiring permanent isolation from the biosphere. The classification of HLW includes liquid waste produced directly in reprocessing and any solid waste derived from the liquid.

To qualify as HLW, waste should meet both the source and radioactive content portions of this definition; otherwise, it is considered LLW.

Other Wastes Managed as HLW. Irradiated or spent nuclear fuel and greater-than-Class-C waste (as defined in 10 CFR part 61.55, 1992) are managed as HLW. These wastes, while not meeting the definition of HLW, are sufficiently hazardous to warrant the stringent waste management practices associated with HLW.

Disposing of HLW. At present, no approved disposal options exist for HLW. With projects that use or produce HLW, or wastes that are managed as HLW, an attempt should be made to have these wastes returned to the program sponsor. If this is not possible, plans should be made to store this waste for an indefinite time and funds should be included for storage in the program funding.

Transuranic Waste

Transuranic waste contains alpha-emitting radionuclides with the following characteristics:

- atomic number greater than 92
- half-life greater than 20 years
- concentrations greater than 100 nCi/g.

Wastes containing either ^{226}Ra isotopic sources or ^{223}U are also classified as TRU waste.

Contact-handled TRU waste (CH-TRU) is TRU waste with a surface dose rate of less than 200 mrem/h.

Remote-handled TRU waste (RH-TRU) is TRU waste with a surface dose rate equal to or greater than 200 mrem/h.

The CH-TRU waste can consist of glovebox waste (such as surgical gloves and paper wipes) and ducting, piping, and construction debris. The RH-TRU waste consists mainly of irradiated fuel or samples.

Packaging, Storing, and Disposing of TRU Waste. To dispose of TRU waste, all requirements should be followed for the container, packaging, and labeling specifications for the particular waste. Site and laboratory requirements should be referred to for specific guidance.

Free liquids should not be added to TRU waste. Liquids should be absorbed on a nonbiodegradable absorbent, and they should be neutralized and solidified, if necessary. Sludges should be packaged to prevent internal container corrosion.

Containers. Containers should be in good condition with no cracks, dents, holes, bulges, corrosion, or any other damage that could compromise their integrity.

The 55-gal galvanized metal drum, U.S. Department of Transportation (DOT) 17C, is recommended for routine disposal of TRU waste. A plastic 100-mil liner should be used inside the drum. The drum is limited to 100 g total mass of TRU and/or fissile material.

Containers for RH-TRU should be handled on a case-by-case basis because there are no approved shipping containers. Containers for CH-TRU, other than 55-gal drums, are also used for large TRU waste items on a case-by-case basis.

Temporary Storage at the Generating Site. Waste classified as TRU is usually stored at the generating site on a temporary basis, using the following guidelines:

- To avoid the commingling of TRU waste streams with HLW or LLW, TRU waste should be segregated or identified.
- In storage areas TRU waste should be protected from unauthorized access.
- Stored TRU waste should be monitored periodically to ensure that the wastes are not releasing their radioactive or hazardous constituents.
- Storage facilities for TRU waste should be designed, constructed, maintained, and operated to

minimize the possibility of fire, explosion, or accidental release of radioactive or hazardous components of the waste to the environment.

- Facilities that store TRU waste should have a contingency plan designed to minimize the adverse impacts of fire, explosion, or accidental release of radioactive or hazardous components of the waste to the environment.
- All TRU waste should be stored in such a way to maintain radiation exposures ALARA.

Hazardous Waste and Radioactive Mixed Waste

Radioactive waste that also contains hazardous waste is referred to as RMW. A hazardous waste is any unwanted, nonradioactive solid, liquid, or gas, or a mixture of substances having properties capable of producing adverse effects on human health or safety, or the environment. If a chemical substance has one or more of the following characteristics, it may be classified as hazardous:

acidic	irritating
shock-sensitive	reactive
basic	mutagenic
asphyxiant	heavy metal
pyrophoric	carcinogenic
ignitable	teratogenic
toxic	bioaccumulative
oxidizing	controlled substance

In addition, any material listed as hazardous in 40 CFR 261, subparts C and D (1991), and/or regulated as hazardous waste by EPA or State Dangerous Waste Regulations is included in this definition.

Containers. Containers should be in good condition; i.e., no cracks, dents, holes, bulges, corrosion or

other damage that could compromise their integrity. The normal size for containers of solid RMW is the 55-gal drum. Other sizes are available, but are not frequently approved. Liquid RMW and hazardous waste containers should be either glass, plastic or metal and of the appropriate size depending on the hazard associated with the waste; e.g., flammable, combustible, corrosive, etc.

Containers that could react with or degrade the container by physical, chemical, or radiological mechanisms should not be used for wastes unless protection for the container's interior has been provided.

Temporary Storage at the Generating Site

Temporary storage refers to storing the waste as it is being accumulated.

Caution: Labeling and container guidelines are different for storage than for disposal.

Facilities that generate RMW should have a room or area that is designated to store radioactive waste until it is shipped to a storage or disposal facility.

Note: Usually only 90 days are provided to move the waste to a permitted facility.

For liquid RMW and hazardous waste, an area within the room where the waste is generated should be designated as a satellite accumulation area.

Container Conditions. Containers that are in good condition and do not leak should be used for accumulating RMW. If the container leaks or is found to be in poor condition, the wastes should be transferred to a container that is in good condition.

Labeling. Each container should be labeled in a way that identifies the risk(s) associated with the contents (e.g., corrosive, oxidizer, poison, flammable, etc.). Labels that no longer apply should be destroyed or removed. The person who generates the waste should ensure that labels are not obscured, removed, or otherwise unreadable. The container should also be clearly marked as “hazardous waste” or “dangerous waste.”

The date on which waste accumulation begins should be marked on the container. Generally, the accumulation date is the date waste is first added to the container. In some special cases (satellite accumulation), the accumulation date is the date that the quantity being accumulated exceeds 55 gal of dangerous waste or one quart of acutely hazardous waste.

Note: Satellite areas are usually located at the point of waste generation. Such areas, which are used to accumulate waste, should be controlled by the operator whose process is generating the waste.

Chemical Incompatibility. Each container should be chemically compatible with the wastes stored in it. Chemically incompatible wastes should not be placed in the same container. An unwashed container that previously held a chemically incompatible waste or material should not be used for RMW.

Handling and Storage. Each container holding dangerous waste should be closed except when adding or removing waste. Such containers should not be opened, handled, or stored in a manner that may rupture the container or cause it to leak.

Containers of ignitable or reactive wastes should be stored according to the proper procedures.

Secondary Containment. If potential exists for a spill or leak of the dangerous waste to reach a drain or the environment, secondary containment should be provided for the waste container(s).

Inspections. Waste awaiting disposal should be inspected frequently for leaking containers and for deterioration of containers or any containment system caused by corrosion, deterioration, or other factors. The inspections should be documented.

Liquid Effluents

Radioactive and nonradioactive liquid effluents should be managed to ensure that the following conditions are met:

- All permit conditions regarding liquid effluents are met.
- Environmental regulatory compliance is maintained with the Clean Water Act (CWA), Resource Conservation and Recovery Plan (RCRA), Derived Concentration Guides (DCGs), and DOE Orders.
- Deliberate and accidental releases of hazardous or radioactive materials exceeding administrative limits should be prevented. Engineered controls, administrative procedures, and release-diversion systems should be used to ensure, to the degree possible, that no threat to human health and the environment exists.

Releases to liquid waste systems should be managed to meet the requirements of the system operator.

Radioactive Effluents. Liquid effluents going into sewers are regulated according to DCGs (DOE 1991). Effluent concentrations at the point of release should be limited to less than 10% of the DCGs for DOE

facilities. Normally, no further treatment at the source is necessary if effluent concentrations at the point of release do not exceed 10% of the applicable limit.

The 10% limit is necessary because the DCGs are a secondary limit and an index of performance for a single-dose pathway. It is possible for the cumulative primary dose limits to be exceeded even though all individual effluent concentration guides are being met.

Caution: No planned releases of radioactive liquid effluents to the environment should be made in concentrations exceeding the limits specified in DOE regulations. This includes releases to sewers, surface streams, or subsurface soil systems.

Liquid waste from areas where unsealed radioactive materials are used should be considered potentially contaminated unless an analysis indicates that the liquid can be released to uncontrolled systems.

Caution: Concentrated radioactive liquids should not be diluted to achieve release limits.

Sampling and measuring of potentially radioactively contaminated liquid effluents should be performed as close as possible to the point of release to the environment. The data for all such releases should be reported according to DOE and other local, state, and federal regulations.

Gross alpha and beta analyses of liquid effluent samples are frequently the only analyses that are routinely required if the most restrictive DCG for the radioactive materials handled in the facility has not been exceeded.

Continuous monitoring and sampling are recommended on effluent streams from any facility where the total inventory of radioactive material is large enough to create the potential for an effluent discharge above the applicable concentration guides. Automatic, continuous, and representative flow-measurement instrumentation should be provided for new facilities and for older facilities when they are significantly modified. The sampling should be done close to the point of entry. The type of monitoring and flow-measurement systems installed should meet the specifications provided.

Nonradioactive Effluents. Hazardous chemical constituents in liquid effluents are regulated by the EPA.

Caution: Regulated hazardous waste or hazardous materials should not be released to any sewer system.

Sinks and Drains. In areas where radioactive liquid waste could be accidentally released, all floor drains and other appropriate drains should be sealed, unless drains are connected to a radioactive liquid waste system or an approved collection tank.

In areas where quantities of hazardous chemicals could be accidentally released, all floor drains and other appropriate drains should be sealed, or sufficient spill-control-prevention measures or material should be provided to contain the spill.

Caution: Hazardous waste should not be disposed of in drains.

Sinks and associated piping in radiation areas where the potential for disposal of radioactive materials exists should not be used to dispose of radioactive material, unless connected to a radioactive liquid waste system (RLWS). When a RLWS is in place, sinks should be labeled to identify the liquid waste disposal system to which they are connected.

Sinks located in hoods used for radioactive material should be plugged, drained into a carboy, or connected to a RLWS. Carboys used to collect sink waste should be equipped with secondary containment.

Purgewater Disposal. Existing federal and state regulations and policy guidance are indeterminate regarding specific disposal criteria or standards for the handling and management of purgewater. Purgewater collection criteria are often based on 10 times Maximum Contaminant Levels (MCLs) for drinking water, or 10 times EPA's Chronic Freshwater Toxicity Levels (CFWTLs), or 10 times the Practical Quantitation Limits (PQLs) (DOE 1991). The radionuclide standards are currently based on 10 times the MCLs referenced in National Interim Primary Drinking Water Regulations except for uranium and plutonium standards, which are based on 10 times one 1/25th DCG. Tritium is not included in purgewater determinations because effective treatment technology has not yet been demonstrated.

Radioactive Liquid Waste System. Mixtures or solutions that may precipitate solids under certain chemical conditions should be tested for precipitation in water before being placed in a RLWS.

- Liquids that have a possibility for solidification in the line should be avoided; e.g., paint, plastics, liquid rubber, epoxy.
- Organics or water-insoluble solvents are generally avoided.

Sanitary Sewer. The sanitary sewer system transfers domestic waterborne waste originating from locations such as kitchen and janitorial sinks, showers and lavatories, and sinks in nonchemistry laboratories.

The following material should not be discharged into the sanitary sewer system:

- hazardous waste and hazardous materials
- oil
- radioactive materials.

Work with chemicals and radioactive materials should be separate from the sanitary sewer system, thus precluding accidental contamination of the sewer system.

Operating procedures, conspicuous posting (i.e., sink labels) and frequent inspections by facilities personnel should be performed to help ensure proper use of the sewer system.

Floor drains and janitorial sinks that discharge into the sanitary sewer system should be located so that the accidental discharge of hazardous materials is unlikely.

NPDES Discharges. Liquid effluents discharging directly to a navigable body of water should comply with the Clean Water Act requirements for a National Pollutant Discharge Elimination System (NPDES) permit. The effluent should be managed in a manner that meets the guidelines for the parameters of flow, settling solids, suspended solids, pH, and the other restrictions given in the permit.

French Drains. French drains are defined as any below-the-surface excavation, the dimensions of which are deeper than they are wide. The use of French drains is discouraged at some sites because of possible soil column contamination that may require later cleanup.

Liquid Waste in Tanks. Tanks and tank systems that store liquid waste should be properly managed according to their contents. If the contents of a tank are regulated dangerous waste, the storage limit is typically 90 days.

References

10 CFR Part 61.55. 1992. "*Licensing Regulations for Land Disposal of Radioactive Waste.*" U.S. Code of Federal Regulations.

40 CFR Part 261. 1991. "*Identification and Listing of Hazardous Waste.*" U.S. Code of Federal Regulations.

U.S. Department of Energy (DOE). 1991. "*Radiation Protection for Occupational Workers.*" DOE 5480.11, Washington, D.C.

Chapter 6

Choosing the Correct Method

Scope and Application

This chapter provides guidance in choosing the appropriate sampling and analytical chemistry methods for collecting and analyzing environmental and waste management samples. The selection will be based upon guidance provided in Chapter 1, "Guidance for Effective Project Planning".

For analyzing many U.S. Environmental Protection Agency (EPA)-listed analytes and radionuclides, procedures from Test Methods for Evaluating Solid Wastes {EPA 1986 (SW-846)} or other approved documents (e.g., EPA 1980) are recommended where appropriate. When these methods are not appropriate for sampling or sample analysis (e.g., because of sample matrix incompatibilities), alternative methods may be available in this publication. This chapter describes how to select the methods available in this document.

Methods in this document have either been prepared specifically for this book, or have been derived from a careful selection of procedures in the *DOE Procedures Database* (Database). The database contains analytical procedures that have been submitted by various U.S. Department of Energy (DOE) laboratories. Procedures in the database can be used for some applications, but caution should be exercised since procedures not represented in *DOE Methods* have not yet been reviewed for general use. Verified methods in *DOE Methods* have completed the review process. Draft methods are also included, but they might not contain adequate quality control (QC) data. Analytical methods described in *DOE Methods* may be followed as written, or comparable methods can be substituted. All methods should be

qualified according to guidance provided in Appendix B and should meet the requirements of the project (Chapter 1).

Sampling Methods

The sampling methods selected or developed for a project should meet the data quality requirements of the project (see Chapter 1). Sampling methods (see Chapter 7) are summarized in Table 6.1. Sampling methods should be designed and used to minimize sampling variability and error. The precision and accuracy associated with the sampling methods in Table 6.1 are not yet available, and the methods have not yet been verified by successful use in more than one laboratory; therefore, they are considered draft methods. When supporting information is available, it should be evaluated before specifying the needed precision and accuracy of the analytical chemistry methods.

Analytical Methods

Factors in Choosing an Analytical Method

Knowing as much as possible of a sample's characteristics helps in choosing the correct analysis sequence. For example, the matrix (water, soil, grout, sludge, etc.), radioactivity, and estimated analyte concentration will influence sample preparation needs. Other hazardous constituents in the sample may also determine the safety precautions that should be followed (see Chapter 4, Safety). This section outlines the key considerations in selecting an analytical method for a given sample.

General Considerations

The first choice of methods should be those from EPA (e.g., SW-846). If these methods are inappropriate or inadequate, guidance from *DOE Methods* should be used. It is recommended that methods should first be identified that either fit the needs of the project or come close enough so that slight modifications will suffice. Then, guidance in Appendix B should be checked to verify that the method meets program needs. After a method in this document has been used, please send your comments and QC data to the editors to help strengthen the validity of the published method. Additional considerations in selecting a method are described below.

Equipment. If methods have been identified that meet all the analyst's criteria, but for which equipment is not locally available, alternatives should be sought. The original authors of each method are provided for reference in the event that their specific lab capabilities are needed for your analyses.

Sample Hazards. For safe sample handling, refer to Chapter 4 (Safety). When handling and disposing of radioactive and/or hazardous samples, guidelines associated with hazardous chemistry and radiochemistry safety should be followed. See Chapters 4 and 5 for further discussion.

Physical State(s) of Sample. Samples may be gaseous, liquid, solid, or multiphasic. Gas-phase samples will usually be delivered to the analytical lab in a sampling bag or a pressurized container, or as a frozen cryostatic sample kept in liquid nitrogen. Liquid samples can include wastewater, groundwater, oil, other organic liquids, extracts, or biological fluids. Solid samples can include filters, soils, or biological solids. The sample matrix,

where appropriate, is indicated for each method given in this document

Analytical Objective. The project analytical objectives should be defined before applicable methods can be selected. The project plan should identify the purpose of the analysis, analytes, and sample phase or matrix (see Chapter 1—Guidance for Effective Project Planning).

Method Limitations. Guidance from Chapter 1 should be followed before selecting methods. Ideally, method detection limits (MDLs) will be less than or equal to those specified in the project plan. If not, either the method or the project plan should be modified. If the project plan specifies more requirements than the detection limits, these additional criteria should also be met by the method. Uncertainties, for example, should be clearly defined and considered in the selection process.

Potential Interferences. Interferences potentially present in the sample matrix should be taken into account when choosing a method. Many existing methods are most often used for analyzing relatively clean samples. This document attempts to address these and more challenging samples, especially complex radioactive waste. If specific components are known to interfere with a method given here, that information is stated in the method. Therefore, a method and its potential interferences should be carefully studied before it is used.

Component Concentrations. The concentrations of components (analytes, contaminants, or other components) should be considered. It is possible in many instances to adapt methods for trace analysis to the analysis of more concentrated analytes by adjusting sample size and dilution. However, samples should be large enough to represent the source appropriately. Samples may be, for example,

nonhomogeneous. This nonhomogeneity should be considered when selecting the method.

Sampling and Transport. The process of sampling and transporting materials should be carefully considered so that the uncertainties associated with these processes do not significantly exceed those of the analysis.

Analytical Method Tables

Pages 6-5 through 6-8 contain tables showing all analytical methods currently available in *DOE Methods*. The methods in these tables are either draft or verified. In each case, the type of method is indicated at the top of the table with method titles at the bottom. Method types include those designed for screening, sample preparation, or analysis. Analytes or analyte classes are also indicated. For more information, refer to Chapters 8 (Organic), 9 (Inorganic), or 10 (Radiochemistry).

Organic Methods. Methods that are available in *DOE Methods* for analyzing organic components in waste and environmental samples are summarized in Table 6.2.

Inorganic Methods. Methods that are available in *DOE Methods* for analyzing inorganic components in waste and environmental samples are summarized in Table 6.3.

Radiochemistry Methods. Methods that are available in *DOE Methods* for analyzing radioactive components in waste and environmental samples are summarized in Table 6.4.

Method Flexibility

Other Methods

To encourage the development of new methods, especially those that take advantage of emerging technologies, other methods that meet or exceed the project method requirement can be acceptable substitutes. However, these methods should be clearly identified as acceptable substitutes by demonstrating that the methods are qualified as described in Appendix B.

In some instances, methods are available in either this document, SW-846, or other documents for which MDLs are much lower than those required by the project. In those cases, smaller samples, or more dilute samples, may be used. This may also result in the possibility for reduced worker exposure to hazardous components. Nevertheless, it may still be necessary through guidance in Appendix B and the program plan to demonstrate that the dilution or sample size reduction would not influence the ability of the method to meet the project requirements.

Choice of Apparatus and Preparation of Reagents

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, substitutions of similar types for those given in these methods are encouraged when appropriate as long as the substitution does not adversely affect the quality of the analyses. However, when variations or new methods are used, results from QC standards should be compared to results obtained in the same laboratory using a standard or established method according to guidance in Appendix B.

Radiological Screening References

The history of the sample site is important in estimating levels of hazardous or radioactive contaminants. If radioactive levels cannot be adequately estimated, samples should first be screened for levels of alpha, beta, and gamma radiation appropriate for division into nonradioactive, low, and high levels of radioactivity as defined by local regulations. This will allow appropriate measures of control to be taken by laboratory staff (see Table 6.5). Chapter 10 provides methods for screening samples for radioactivity (see Table 6.4).

These estimates may be coupled with field screening to assist in categorizing the samples, as in Table 6.5. These precautions are for the safety of the sampling and analytical staff, as well as to meet guidelines for transporting samples.

U.S. Environmental Protection Agency (EPA). 1980. *Prescribed Procedures for Measurement of Radioactivity in Drinking Water*. EPA-600/4-80-032, Washington, DC.

U.S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste*, 3rd Edition, Vol. IA-IC. EPA/SW-846, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Table 6.1. Sampling Methods

	<u>Solids</u>	<u>Liquids</u>	<u>Air</u>
Drums			SA010* SA011*
Tanks	ST010*	ST010*	

Table 6.1 indicates three sampling methods that can be found in this document. The methods are all in draft form. Draft methods (*) are in a preliminary form as described in the introduction of this document. The reader is encouraged to use standard methods where appropriate. The titles for these methods are listed below:

SA010	Sampling Headspace Gas for Volatile Organic Compounds Within a TRU Waste Drum with a Sampling Manifold
SA011	Sampling Headspace Gas Within a TRU Waste Drum with SUMMA™ Canisters for Volatile Organic Compounds
ST010	General Method for Sampling Liquids and Solids in Low-Level Waste Storage Tanks

Table 6.2. Organic Methods

	<u>Field</u>	<u>Sample Prep</u>	<u>Lab. Analysis</u>
Volatile	OS030	OC010R*	OG015R
	OS040*	OP010R*	OP010R*
		OP020R	
		OP030R	
Semi-volatile	OS010		OG100R
	OS020	OP100R	OH100R*
	OS050*	OP120R	OP100R
		OG100R	
		OP130R*	OP130R*
		OP150R*	
Non-volatile		OP150R	
TOC, TOX	OS010		

Table 6.2 indicates organic methods that can be found in this document. Methods are verified (see Appendix A) unless indicated with an asterisk. Draft methods (*) are in a preliminary form as described in the introduction of this document. The reader is encouraged to use other standard methods where appropriate. The titles for these methods are listed below:

OC010R	Preparation and Cleanup of Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds
OG015R, Rev. 1	Major Nonhalogenated Volatile Organics in Radioactive Aqueous Liquids Analyzed by Direct Aqueous Injection Gas Chromatography
OG100R, Rev. 1	Analysis of Polychlorinated Biphenyls as Aroclors in Solid Radioactive Mixed Wastes
OH100R	Direct Analysis of TCLP Acidic Semivolatile Compounds in Radioactive Liquid Wastes or Leachates Using HPLC with Ultraviolet Absorbance Detection
OP010R	Remote Purge and Trap Gas Chromatography of Volatile Organics in High-Level Radioactive Wastes
OP020R	Ultrasonic Solvent Extraction for Analysis of Volatile Organic Compounds in Solid Radioactive Mixed Wastes
OP030R	Purge and Trap in a Glovebox
OP100R	PCBs in Aqueous Radioactive Mixed Wastes Using Solid Phase Extraction Disks and GC-ECD

Table 6.2. (Contd)

OP120R	Reduced-Scale Liquid-Liquid Extraction of Semivolatile Organic Compounds
OP130R	Analysis of TCLP Semivolatiles and Pesticides in Radioactive Mixed Waste Sludges
OP150R	Ultrasonic Extraction in a Glovebox or Hot Cell
OS010	Total Organic Chlorine in Oil: Field Test Kit Method
OS020, Rev. 1	Immunoassay for Polychlorinated Biphenyls in Soil
OS030	A Photoacoustic Infrared-Based Screening Method for the Detection of Selected Chlorinated Volatile Organic Chemicals in Water
OS040	Rapid Determination of Volatile Organic Contaminants in Water and Soils by Direct-Purge Mass Spectrometry
OS050	Supercritical Fluid Extraction for the Analysis of Contaminated Soils

Table 6.3. Inorganic Methods

	Field	Sample Prep.	Lab. Analysis
Metals	MS100*	MP100R	MB100
	MS110	MP110R	MM100*
	MS210*		MM210*
	MS410*		MM800*
Anions	MS100		MU012R*
	MS310*		

Table 6.3 indicates inorganic methods that can be found in this document. Methods are verified (see Appendix A) unless indicated with an asterisk. Draft methods (*) are in a preliminary form as described in the introduction of this document. The reader is encouraged to use other standard methods where appropriate. The titles for these methods are listed below.

MB100, Rev. 1	Immunoassay for Mercury in Soils
MM100	Inductively Coupled Plasma-Mass Spectrometry for Radionuclide Analysis
MM210	ICP-MS of ^{99}Tc , ^{230}Th , and ^{234}U using Flow Injection Preconcentration
MM800	Ion Chromatography and Inductively Coupled-Mass Spectrometry Determination of Uranium Concentration Isotopic Abundance in Groundwater and Drinking Water
MP100R	Solvent Extraction of Uranium and Thorium from Radioactive Liquid Wastes
MP110R	Cleanup of Transuranic Liquid Wastes using Extraction Chromatography
MS100	A Reflectometry-Based Instrument for Reading Colorimetric Test Strips
MS110	An Indicator Strip-Based Colorimetric Test for Chromate Ions (CrO_4^{2-}) in Aqueous Samples
MS210	An Indicator Strip-Based Colorimetric Test for Lead (Pb^{2+}) in Water
MS310	An Indicator Strip-Based Colorimetric Test for Nitrate Ions (NO_3^-) in Water and Soil
MS410	An Indicator Strip-Based Colorimetric Test for Nickel (Ni^{2+}) in Aqueous Samples
MU012R	Total Cyanide by Remote Microdistillation and Argentometric Titration

Table 6.4. Radiochemistry Methods

<u>Screens</u>	<u>Field</u>	<u>Sample Prep. and Analysis</u>
Alpha/Beta		RP710; RP720*
Tritium		RP720*
Gamma (gross)		RP730*
Actinides		RP725*
Gamma (spec)	RS100*	
<u>Chemical Separations</u>		
¹²⁹ I, ¹³¹ I		RP230
²¹⁰ Pb		RP280*
⁵⁹ Ni, ⁶³ Ni		RP300
^{93m} Nb, ⁹⁴ Nb		RP330*
⁸⁹ Sr, ⁹⁰ Sr		RP500; RP501*, RP510*, RP520*
⁷⁹ Se		RP530*
⁹⁹ Tc	RS551*	RP550
³ H		RP580*
Pu; Am		RP800*
<u>Instrumental Analysis</u>		
Gamma Spectroscopy		RI010*
Beta Spectroscopy - Liquid Scintillation Counting (LSC)		RI100*
Gross Alpha/Beta Analysis		RP710*
<u>Miscellaneous</u>		
Surface Analysis		RA010*
		RA020*
Total Fissile Content		RP735*

Table 6.4 indicates radiochemistry methods that can be found in this document. Methods are verified (see Appendix A) unless indicated with an asterisk. Draft methods (*) are in a preliminary form as described in the introduction of this document. The reader is encouraged to use other standard methods where appropriate. The titles for these methods are listed below:

RA010	Method for Utilization of Electret Ionization Chambers for Characterization of Gross Alpha Emission from Indoor Surfaces
RA020	Method for Utilization of Alpha Track Detectors for Characterization of Gross Alpha Emission from Indoor Surfaces
RI010	Gamma-Ray Spectrometry
RI100	Liquid Scintillation Instrumentation Method
RP230	Iodine-129 Analysis in Aqueous Solutions
RP280	Determination of Lead-210 in Water Using Extraction Chromatography
RP300	Nickel-59 and Nickel-63 Determination in Aqueous Samples

Table 6.4. (contd)

RP330	Separation of Niobium for Niobium-93m and Niobium-94 Determination
RP500	Purification of Strontium in Water Before Strontium-89/Strontium-90 Measurement
RP501, Rev. 1	Determination of Total Radioactive Strontium in High-Level Samples using Extraction Chromatography
RP510	Determination of Strontium-90 in Dissolved Environmental Samples Using a Chelating Resin
RP520	Determination of Strontium-90 in Soil, Water, and Filter Samples
RP530	Determination of Selenium-79 in Aqueous Samples
RP550	Technetium-99 Analysis using Extraction Chromatography
RP580	Water Distillation from Soil and Aqueous Matrices Using a Micro-Distillation System for Tritium Determination
RP710	Laboratory Method for Gross Alpha and Beta Activity Determination
RP720	Rapid Determination of Gross Alpha, Gross Beta, and Gross Tritium in Water Samples Using A Liquid Scintillation Counter
RP725	Group Actinide Screening Using Extraction Chromatography
RP730	Gross Gamma Screening for Environmental Matrices
RP735	Determination of Total Fissile Content by Neutron Activation Followed by Delayed Neutron Counting
RP800	Sequential Separation of Americium and Plutonium by Extraction Chromatography
RS100	<i>In Situ</i> Analysis of Gamma-Ray Emitting Radionuclides by Borehole Logging
RS551	Rapid Isolation and Measurement of Technetium-99 Using Anion-Exchange Filter Membrane

Table 6.5. Containment Considerations^(a)

Type of Radioactivity	Low Level	High Level
Alpha	Radiation bench	Hood or glovebox
Beta/gamma	Radiation bench	Hood with shielding/hot cell
Tritium	Radiation bench	Fume hood with high flow rates

(a) Typical containment for low- and high-level radioactive samples. Cutoff levels of radioactivity that will dictate the category (high, low, or nonradioactive) for a specific sample are not given, as these levels can vary with local and site-specific regulations.

Chapter 7

Sampling Methods

Scope and Application

This chapter focuses on methods that are currently used at U.S. Department of Energy (DOE) sites to collect hazardous, radioactive, and mixed-contaminant wastes and environmental samples. These methods supplement current guidance {e.g., U.S. Environmental Protection Agency's (EPA's) Characterization of Hazardous Waste Sites (EPA 1984), SW-846 (EPA 1986), Compendium of Superfund Field Operations Methods (EPA 1987), Description and Sampling of Contaminated Soils (EPA 1991), Annual Book of American Society for Testing and Materials (ASTM 1993), and Standard Methods for the Examination of Water and Wastewater (Greensburg et al. 1992)}. Emphasis is placed on 1) sampling of air, liquids (e.g., liquid waste, surface and groundwater), and solids (e.g., waste, soils, sediments), and 2) environmental and waste samples associated with different waste storage (e.g., tanks, repositories), waste treatment, and environmental contamination/disposal scenarios (waste-disposal sites, dispersed contamination, drums, waste forms, and disposal options).

Limitations

If samples are not properly collected and transported, results from their analysis may be meaningless. For example, sampling for organic constituents requires that certain rules be followed (e.g., refrigeration; in the case of volatiles, no headspace; glass containers; addition of preservatives). If such basic conditions are not met, further analysis of the sample may lead to compromised results. Sometimes, however, such

manipulations (e.g., refrigeration, which can cause phase changes in sample matrix) can also result in compromised results. The above rules are also very difficult to put into practice with samples containing high levels of radioactivity.

Definitions

See compendium glossary.

Sampling Environment and Types of Sampling

Waste and environmental sampling involves using numerous types of sampling devices and equipment within the context of a broad range of environmental settings. In this section, various sampling environments and types of sampling common at DOE sites are described. Sampling environments addressed include 1) waste disposal sites, 2) dispersed contamination, 3) tank wastes, 4) treated wastes, and 5) waste forms. The types of sampling addressed for both environmental and waste matrices include air, liquid, and solids. Tables have been constructed that list sampling devices/systems and their sampling application.

Sampling methods used for different contamination scenarios at DOE sites are summarized below. Tables that define the scope of field sampling methods are listed throughout this chapter. Sample-container, preservation, and holding-time constraints for specific analytes and chemical parameters should be addressed in the planning process.

Waste Disposal Sites

The sampling methods selected for evaluating the subsurface at waste disposal sites depend on 1) the objective of the sampling and 2) the type of analytes being evaluated. Objectives may include the need to characterize the site to support the development of remediation strategies. Sampling may be performed to determine a remediation strategy's effectiveness. Suspected contaminants may be hazardous, but not radioactive; thus conformance to standardized guidelines (e.g., guidelines established by the EPA) may be sufficient to meet regulatory compliance requirements. However, the site may contain waste, subsurface sediments, and groundwater that is highly contaminated with mixed hazardous constituents. Sampling of the waste site may require that new methods be developed, or that standard methods be adapted to ensure worker protection and sample quality. As a result, contractors prepare guidance manuals and sampling protocols to bridge the gap between available regulatory guidance and the specific operational needs associated with sampling radioactive or radioactive mixed waste sites. This section describes approaches used to obtain samples of soils, sediments, soil gas, and groundwater from waste sites. Sampling of drum wastes is also addressed.

Soil/Sediment Sampling

Sampling of soils/sediments is influenced by the depth of samples needed and, therefore, consists of deploying samplers with or without the support of drilling technology.

Surface/Near-Surface Sampling. Surface/near-surface sampling employs numerous manual techniques, some of which can be augmented with mechanical devices (e.g., auger on a tripod) so that the sampling can proceed to greater depths (Table

7.1). Depending on the nature of the subsurface materials and methods deployed, manual sampling to a depth of ~20 ft can be achieved.

Sampling at Greater Depth. For sampling at greater depths, samplers can be deployed as 1) an integral part of the drilling operation to obtain continuous samples, or 2) an independent step once drilling has reached a certain depth, and the drilling apparatus has been removed from the hole (Table 7.1). Sampling that decouples the sampler from the drilling operation (drill removed from hole in order to sample) produces samples that range in quality. Split-spoon, thin-walled, and drive-tube samplers (Table 7.1) produce undisturbed to relatively undisturbed samples, but core-barrel sampling and cable drilling using a slurry produce disturbed samples. Using a slurry in the drill operation can dramatically affect the chemistry of the sample, and no information on layering can be obtained from slurried samples. Split-spoon and drive-tube samplers have been used successfully to retrieve radioactive samples from holes. This approach is used for sampling tank wastes and soils/sediments from within and below a radioactive waste-containing crib or trench.

Soil-Gas and Soil VOC Sampling

Soil-gas sampling and sampling of volatile organic compounds (VOCs) sorbed to soils have become standard elements of waste-site characterization since VOCs are ubiquitous contaminants at DOE sites. In a field-screening mode, data from soil-gas sampling and analysis can be used to construct profiles of VOCs concentrations in the vadose-zone soil gas. These data can also be used to assist in the effective targeting of future sampling and analysis activities, including the measurement of VOCs sorbed to soils. Where possible, field analysis of samples for VOC should be considered to minimize the negative impacts of sampling and sample transport on data quality. Where this is not possible, techniques should be

Table 7.1. Soil/Sediment Sampling^(a)

	Material Types		
	Solids, dry	Solids, wet	Gas
Surface/Near Surface Sampling			
Sampling thief	X ^b		
Sampling trier	X ^c		
Hand corer	X ^d		
Punch	X ^e		
Hand Auger			
Helical	X ^f		
Spiral	X ^f	X ^f	
Gravity corer		X ^g	
Ponar grab		X ^h	
Veihmeyer sampler	X ^h	X ⁱ	
Grab	X ^j	X ^j	
Scoop	X ^j	X ^j	
Spade	X ^j	X ^j	
Shovel	X ^j	X ^j	
Soil-Gas Probe			X ^k
Greater Depth Sampling			
Dual-wall core barrel	X ^l	X ^l	
Split spoon	X ^{l,m}	X ^{l,m}	
Conventional core barrel (CCBS)	X ^l	X ^l	
Thin-walled (Shelby) tube	X ^m	X ^m	
Drive tube	X ^m	X ^m	
Cable top drilling/slurry sampling method	X ⁿ	X ⁿ	
SEAMIST TM			X ^o
<p>a See EPA 1984, EPA 1987, and EPA 1991 for guidance and/or descriptions of standard soil/sediment sampling methods</p> <p>b Most suitable for dry, granular, powdery materials</p> <p>c Works best in sticky or solid samples at >3 in. in depth</p> <p>d Collects undisturbed sample</p> <p>e Most suitable for granular material</p> <p>f Device works for most material types except cohesionless material below the water table and hard or cemented soil/sediment. Mechanically driven augers operated from tripods can achieve depths up to 20 ft.</p> <p>g Collects samples through open water</p> <p>h Works best on stony, rocky, or very wet soil/sediment</p> <p>i Sample obtained manually using a cutter and trowel</p> <p>j Areas from which the samples are taken may be gridded/surveyed. Used also for sampling soils/solid wastes in drums.</p> <p>k Active sampling from soil probes into canisters, glass bulbs, and gas sampling bags. Passive sampling on to buried adsorptive substrates.</p> <p>l Used to retrieve radioactive samples from holes.</p> <p>m Collects undisturbed samples. Works best in intermediate moist soils.</p> <p>n Runs concurrently and is a preferred method for collecting radioactive samples.</p> <p>o <i>In situ</i> collection of soil gas from membrane-lined borehole.</p>			

employed that address stability and loss during the sampling, subsampling, containerization, and transport process. Techniques to consider include using 1) devices that collect undisturbed samples and immerse them directly into methanol, 2) sample containers that directly attach to analytical instrumentation, 3) amber glass jars with teflon seals, 4) surrogates added in the field to evaluate the performance of the sampling and sample-transport process, and 5) preservatives to reduce volatile and microbial degradation. Sampling of soil gas and soil VOCs can be achieved using a number of sampling devices; however, some devices are more effective than others in helping to reduce the large spatial and temporal variations and measurement error (-100 to +25%). Potential variation is associated with the multiphase distributions of VOCs in the subsurface. Techniques for sampling soil gas include passive sampling onto buried adsorptive substrates or active sampling from soil probes into canisters, glass bulbs or gas sampling bags, and SEAMIST™. With SEAMIST™, gas samples can be pulled from discrete ports on a membrane-lined borehole via tubes to surface collectors. Samples can also be collected by attaching activated charcoal absorbers to the membrane surface to gather contaminants. Samplers most often recommended for measuring VOCs sorbed to soils include split spoon with liner (stainless steel or brass preferred), shelby tube (thin walled), hollow-stem augers, veihmeyer or king tubes with liners (stainless steel or brass preferred), piston, and zero contamination (Lewis et al. 1991).

Sampling of VOCs sorbed to soils is being directed toward techniques that minimize sample disturbance and seal the sample within the confines of the sampler (e.g., sleeve-lined split-barrel samplers) or sequester VOC volatility in the containerized sample. Other techniques under development involve the extrusion of samples from micro coring devices into specially designed jars that can be transported to the laboratory and directly attached to the measurement instrument

(e.g., purge and trap). Such approaches eliminate field handling and lab sub-sampling steps, thus improving detection-limit capabilities.

Once samples are collected, preservatives (e.g., Molecular Sieve-5A, Aluminum Silicate, and Florisil) should be considered to reduce loss due to volatility. Mercuric chloride has been shown to be an effective preservative in stabilizing soil samples against microbial activity. Sample and sample containers should be kept away from man-made sources of VOCs (e.g., hand lotion, labeling tape, vehicle and generator exhaust). Sample containers should be stored at reduced temperatures (0 to 4°C).

Drum Sampling

Drums often contain different types of media (i.e., liquid, sludge, slurries, soils); therefore, several sampling devices may be needed to effectively sample drums.

When sampling soils or sludge from drums, procedures described for soil/sediment sampling are recommended {i.e., hand corer, grain sampler, sampling trier, manual (trowel, scoop, spoon), split-spoon, and/or hand auger}. The most commonly used samplers for sampling liquid drum wastes are the composite liquid waste sampler (COLI/WASA) and glass open tube. Other methods for sampling drum liquid include dip samplers, manual pumping (peristalsis, bellows, diaphragm, siphon), and weighted bottle. When sampling from drums, the choice of a headspace sampling procedure depends on whether sampling is to address the headspace above the waste or address the headspace contained within the innermost layers of confinement. In the former case, SUMMA™ canisters connected to a multiport sampling manifold have been used. The system is equipped with a purge assembly that allows sampling manifold blanks, field reference standards, and field duplicates to be collected using the manifold.

In the latter case, a version of the manifold system with a low internal volume has been used. Alternatively, a direct-canister-headspace gas-sampling apparatus has been deployed for drums containing low-level mixed waste (see SA010 and SA011 in Table 7.6).

Table 7.2 summarizes the most common drum sampling devices. Wide-mouth glass containers are often recommended for collecting samples because they simplify transferring the sample. All samples held for organic analysis should be placed in amber or opaque containers to prevent photodecomposition.

Table 7.2. Drum Sampling^a

Samplers	Material Types		
	Solids	Liquids	Gas
Hand corer	X ^b		
Grain thief	X ^c		
Sampling trier	X ^d		
Trowel/scoop/spoon	X ^e		
Split spoon	X ^f		
Hand auger	X ^g		
COLI/WASA		X ^h	
Glass open tube		X ⁱ	
Dip sampler		X ^j	
Manual pumping			
Peristalsis		X ^k	
Bellows		X ^k	
Diaphragm		X ^k	
Siphon		X ^k	
Weighted bottle		X ^l	
Manifold (SUMMA™ cartridges)			X ^m
Direct canister (SUMMA™ cartridges)			X ⁿ
Bin headspace sampling system			X ^o

a See EPA 1984 for descriptions of standard drum sampling methods.
b Not for sandy material; produces undisturbed cores
c Not used for sticky material, particle diameters 1/4 in. or less
d Not for coarse or dry granular material
e Surface samples only, not for reproducible mass
f Requires force to drive sampler; may result in sample compaction
g Produces disrupted sample. May be difficult to remove wet or sticky material
h Composite liquid waste sampler. Most common sampler for sampling liquids in drums; however, difficult to decontaminate, not for high-viscosity fluids. Available in glass or plastic depending on nature of liquid media to be sampled.
i Versatile, though sample leaking may occur.
j Used only for grab samples
k Requires large amounts of disposable tubing that must be compatible with contaminants of interest
l Good for liquids, with the exception of high-viscosity liquids. Exterior of sampling bottle becomes contaminated.
m For sampling polybag and innermost layer headspace inside drum (transuranic (TRU) wastes, see SA010 and DOE 1991a)
n For sampling headspace gases. In the case of TRU wastes, technique is used to sample gases in the innermost layers of headspace confinement inside a drum. (See SA011 and DOE 1991a)
o System attaches to sampling ports on bins. Sampling ports contain filters to prevent radioactive materials from escaping the bin.

In general, plastic containers are recommended for storing samples targeted for inorganic analysis.

Monitoring and Surveillance

Monitoring and surveillance activities include sampling of surface contamination (soils/sediments, surface water and air), and groundwater at a distance (near field, far field) from a point source. Dispersed contamination can also be attributed to nonpoint sources. Sampling of these matrices generally falls under the purview of site-monitoring and surveillance programs where samples are collected onsite, at the site perimeter, and at sites both nearby and at distant communities. One exception could be vadose-zone or groundwater sampling associated with specific waste-site characterization programs. Samples collected may vary considerably in their chemical composition (nonhazardous to mixed contaminant) and concentration (background to above guidelines). Environmental monitoring programs follow sampling guidelines established in site environmental monitoring manuals and by regulators {e.g., SW-846 (EPA 1986)}.

Groundwater and Pore-Water Sampling

Table 7.3 summarizes groundwater sampling methods. Depending on borehole type (i.e., well or piezometers), sample collection can be done using pumps (e.g., submersible or hydrostar), bailers, or an air-lift method. Pumps and Teflon bailers are used for well sampling whereas a miniaturized bailer or air-lift method is used for sampling piezometers. When pumps are used, wells are purged until stable pH, temperature, and conductivity measurements are obtained. Sampling a dry borehole is discontinued if the borehole fails to recharge after two attempts.

An issue that continuously concerns waste management is the disposal of purgewater (water that

is withdrawn from wells as a result of purging a well before sampling). Sometimes, purgewater containing constituents at levels less than collection criteria may be discharged directly to the soil or surface waters. However, purgewater containing constituents in excess of the collection criteria is often collected, stored, and treated before disposal. Purgewater of unknown chemical composition should be disposed of as waste until base-line well-water compositions have been established (see Chapter 5). Sampling of soil pore water can be performed using SEAMIST™. The SEAMIST™ membrane with attached absorbent pads is deployed in a borehole. The pads on the outside of the membrane are pressed against the borehole wall, soaking up pore water. The pads are then retrieved and subjected to sample prep and contaminant analysis techniques. For highly unsaturated soils, pore waters can be obtained by ultracentrifugation of collected samples. Leading-edge technology, such as solid-phase extraction, is rapidly becoming accepted practice for water sampling.

Air Sampling

Accurate detection of atmospheric pollutants must take into account various topographical and meteorological (e.g., temperature, wind, precipitation, dispersion) conditions to ensure a successful air-sampling effort. Air sampling is most often continuous and involves collecting samples on filter-head assemblies (particulate collection and adsorption of radionuclides, metals, and organics on filter cartridges). Collection of contaminants on solid sorbents (e.g., Tenax-GC, polyurethane foam) is a common practice. For some radionuclide species (e.g., ⁸⁵Kr), special samplers are required (see Table 7.4). Emergency air sampling procedures are used to discern the initial extent of an airborne contaminant plume if an accidental radiological release from a site facility occurs. Sampling is done for radioactive particulates or gases and special radionuclides of site

Table 7.3. Water Sampling^a

<u>Samplers</u>	<u>Groundwater</u>	<u>Surface Water</u>
Pumps		
Submersible	X ^b	
Hydrostar	X ^b	
Bladder	X ^b	
Teflon bailer	X ^{b,c}	
Miniaturized bailer	X ^c	
Air lift	X ^{c,d}	
Continuous filtration		X ^f
Automated composite		X ^g
Grab		X ^h
SEAMIST™	X ⁱ	
Ultracentrifugation	X ^j	
Solid-phase extraction	X ^k	X ^k

a See EPA 1984 and EPA 1987 for guidance and/or descriptions of standard water sampling methods.
 b Borehole - used for well sampling. Bladder pumps are limited by their capability to lift water from deep wells.
 c Borehole - used for piezometer sampling.
 d Used for radioactive samples only because airlift method requires purging of piezometer.
 e Used without purging for collecting samples from high-volume boreholes (bailers impractical for purging high-volume boreholes). Under these circumstances, the sample can be used only for the analysis of non-volatile and non-reactive species (e.g., tritium and nitrate).
 f Pumped through filters in series (rough filtration, sock, fiberglass-Millipore; mixed-bed ion exchange).
 g Samples composited over time (e.g., 1-wk intervals).
 h Manually or with a suitable sampling device, such as pump, vacuum, Kemmerer bottle or dipper device constructed of inert material.
 i *In situ* collection of pore waters from membrane-lined borehole.
 j Collection of pore water from highly unsaturated soils.
 k Collection of contaminants (organics and metals) from water onto disks containing glass fiber embedded with bonded phase or an impregnated matrix of polytetrafluoroethylene.

Table 7.4. Air Sampling^a

	<u>Material Types</u>	
	<u>Particulates</u>	<u>Air</u>
Fiber filters	X ^b	
Filter cartridges		X ^c
Kinetic impactor	X ^d	
Collection bladder/gas bulb		X ^e

a See EPA 1984 and EPA 1987 for guidance and/or descriptions of standard air-sampling methods.
 b Filter incorporated into filter-head assembly.
 c Charcoal is used to collect ¹²⁹I, ¹³¹I.
 d Silica gel is used for collecting ³H.
 Soda lime is used for collecting ¹⁴C as CO₂.
 Silver zeolite is used for collecting radiiodine for emergency sampling.
 Cartridges are incorporated into the filter-head assembly.
 d Emergency sampling of particulates for radioactivity.
 e For collection of ⁸⁵Kr.

interest (e.g., ^{131}I) with kinetic impactors and filter-collection devices, in combination with hand-held detectors {Geiger-Müller (GM) and portable alpha meter (PAM) probes} (see Table 7.4).

Surface Water and Soil Sampling

Sampling surface waters includes samples taken from rivers, irrigation canals, riverbank springs, onsite ponds, and drinking-water systems. Samples are frequently collected in continuous, composite, or grab mode. Continuous-mode sampling is used to determine average concentrations and allow for very large volumes of water needed to detect contaminants present at very low concentrations. Composite samples are collected to determine average concentrations and to provide certainty that contaminants did not flow past the sample location between sample dates. It should be noted that composite sampling may not always be an appropriate technique to deploy (e.g., when a need exists to measure analytes that are volatile or that have short holding times). Samples collected by these procedures often do not require radiation surveys. Grab samples are typically used in situations where

- water characteristics are relatively stable
- stream flow is discontinuous
- contaminant stability is a concern.

Grab samples are generally collected manually, but composite and continuous samples are collected using automatic sampling systems (see Tables 7.1 and 7.3).

Tank Waste Sampling

Radioactive mixed wastes stored in tanks at DOE sites pose significant challenges for the sampling

that must be done to support tank-waste characterization, stabilization, and remediation activities. Guidelines for this type of sampling outside the DOE laboratory system currently do not exist, and development of quality guidelines within DOE is in its infancy. Many technology gaps and technical uncertainties exist with tank-waste sampling.

Wastes are stored under alkaline (e.g., Savannah River Site, Hanford, West Valley, Oak Ridge National Laboratory) and acidic (e.g., Hanford, Idaho National Engineering Laboratory (INEL)) conditions and in carbon, carbon steel, and concrete tanks, respectively. Some wastes are also stored in a dried calcined form (e.g., at INEL). Phase composition of the waste can be simple (e.g., single liquid phase with thin layer of solids) to complex (aqueous/organic liquid phases combined with heterogeneous solid phases consisting of saltcake and soft and hard sludges).

At least eight areas of concern are involved when sampling tanks:

- sampling design adequacy
- sampling access to tanks
- sampler adequacy
- multiphase samples
- sample representativeness
- sample stability
- sample integrity
- sample archiving.

Sampling design adequacy is directly related to the flexibility of access to tanks for sampling the contents.

For example, risers (access holes in the top of tanks) on high-level waste tanks were generally constructed in configurations that are not necessarily conducive to systematic or random sampling of the contents. Existing core-sampling equipment is not effective in sampling hard salt cake or sludges, sampling the bottom 3 in. of a tank, or coping with collection of multiphase samples (e.g., samples that contain liquid and solid layers, or two immiscible liquid layers). Furthermore, current samplers are engineered to sample in areas proximate to access holes. Suggested improvements include developing angular coring and robotic devices. In tanks suspected of extensive waste heterogeneity, sample representativeness becomes important. Sample representativeness can be effectively addressed through adequate sampling design, tank access, and sampler adequacy. Sample manipulations normally considered routine in the field (e.g., compositing, in-field analysis, preservation) cannot be done based on current technology. Contaminating materials (e.g., silicone grease, normal paraffin hydrocarbons) are introduced when using some sampler designs. Sample manipulation in the laboratory (e.g., hot cell) should be minimized to avoid alterations (e.g., loss of volatiles and moisture) that affect data quality. Standardized laboratory procedures should be established for subsampling multiphase samples to ensure data representativeness. Cleaning and recycling samplers and extrusion equipment can cause cross contamination of samples. Concern has also been expressed for 1) the stability and integrity of samples as they are collected and transported to the laboratory and 2) insufficient areas for storage (shielded and ventilated) of highly radioactive samples.

Table 7.5 summarizes methods for sampling solids, liquids, and air in high- and low-level waste tanks. A thief-and-trier sampler incorporated into a dual-wall core-barrel system is used for collecting solid high-level waste samples. Cores brought to the surface are transferred to hot-cell facilities where they are

extruded, homogenized (not always done), subsampled, and placed in containers for analysis. Liquid samples are commonly collected using a dip sampling (bottle-on-a-string) method. For headspace sampling, one can choose from several methods including SUMMA™ canister technology or Occupational Safety and Health Administration (OSHA) versatile samplers.

Samplers for low-level waste liquid are used for both sample collection and screening purposes. In the screening mode, a soft-sludge sampler is used to delineate the presence and depth of an organic liquid layer. In the collection mode, some liquid samplers take advantage of access holes (e.g., vacuum pump and organic layer) while others (e.g., "Isolock" system) are "built in" to tanks where no access holes exist. Low-level-waste solid samplers focus on capabilities to sample soft and hard sludges (see ST010 in Table 7.6).

Waste Form Sampling

Across the DOE complex, a broad range of liquid and solid wastes await final disposal. These wastes include high- and low-level radioactive, hazardous and mixed (i.e., both radioactive and hazardous) materials ranging from simple to highly complex in chemical makeup. The physical form of some of the wastes (e.g., TRU low-level) can also be quite complex, consisting of discrete boxed and bagged materials (e.g., bottles of chemicals, contaminated clothing and disposal supplies, equipment, etc.) that have been randomly packed into steel drums and stored on pads or buried.

The currently preferred permanent-disposal option for high-level process waste is a form of vitrified glass (e.g., borosilicate). The processed waste will be placed in storage at selected locations throughout the DOE complex (e.g., Defense Waste Processing Facility, Savannah River, West Valley Demonstration

Project, West Valley, New York; Waste Isolation Pilot Plant, Carlsbad, New Mexico). Sampling of the high-level waste forms is needed to provide materials to test the waste form for being able to

meet waste acceptance specifications (e.g., radiological release properties, chemical and phase stability, compatibility of waste form with disposal container).

Table 7.5. Tank Sampling^a

Samplers	Material Types		
	Solids	Liquids	Gas
High-Level Wastes			
Thief and Trier Type	X ^b		
Bottle on a String		X ^c	
Cryogenic			X ^d
SUMMA® Canisters	X ^e		
Sorbent Trap			X ^f
Low-Level Wastes			
Vacuum Pump		X ^g	
Soft Sludge	X ^h	X ⁱ	
Hard Sludge	X ^j		
Organic Layer		X ^k	
Pump Module ("Isolock")		X ^l X ^m	

a. Sears et al. (1990); Winters et al. (1990); Hill et al. (1991); DOE/EA-0533 (1991b); Ligothe et al. (1993); Ligothe et al. (1994).

b. A stainless steel sampler (about 40 in. long and 1.25 in. in diameter) used to withdraw cylindrical segment (approximately 250 mL). Hydrostatic fluid (Normal Paraffin Hydrocarbons (NPH)) is added during retrieval to prevent waste from backing up into drill string. Activity leads to contamination of sample with NPH (see OC010R). Sampler cannot penetrate hard waste (e.g., saltcake, sludges) and cannot sample bottom 3 in. of tank waste.

c. A bottle (100 mL) attached to a sash cord is lowered into the tank to obtain liquid sample.

d. Headspace vapors are withdrawn under vacuum through teflon tubes to a trailer-mounted cryogenic sampling apparatus. Material concentrated in the cold trap is packaged and transported to a laboratory for mass spectrometry (MS) analysis.

e. Electropolished stainless steel canisters (0.85, 1.8 and 6 L) for collection of air samples. Currently being used to collect headspace samples from high-level waste tanks.

f. OSHA versatile sampler used for sampling tank aerosols.

g. Aqueous samples (250 mL) are collected by pumping liquid through teflon tubing (stainless steel weight at end) into pre-cleaned teflon-lined glass bottles. Used also to collect samples from thick organic liquid layer (see ST010).

h. A bottom opening (spring loaded) device capable of collecting a 15-in-long core sample. Greater sludge depths are accommodated by repetitive application of sampler at ever greater depths. Leakage can occur if seal or sampler cutting edge is damaged or solid material interferes with the seal. Sampling is repeated if sampler is less than two thirds full (see ST010).

i. Used to collect a column of liquid at the air/liquid interface to determine the presence and depth of an organic liquid layer (see ST010).

j. Manually operated sampler consists of a stainless steel pipe (barrel) with a liner, sharpened blades at the bottom, a gate valve to hold the sample in, a vented cap, and handle sections. Sampler can be assembled with either an auger-type bit (designed to minimize disturbance to core) for hard sludges or a push-type cutting end for sticky mud-consistency sludges (see ST010).

k. Stainless steel pipe with sharp machine-bevel cutting edge and threaded on opposite end to accept handle. Sampler used to collect very thick, sticky sludges. Sampler manually pushed into, twisted, and retrieved from sludge layer (see ST010).

l. A polyvinyl chloride (PVC) tube with a sealed bottom and threaded top (to receive handle) and a lateral tube for liquid intake (approximately 400 mL) near the top (see ST010).

m. Pumps and sampling compartments (Isolock System) installed on tanks where there is no access through risers. Only liquid samples are collected.

A preferred option for disposal of low-level process waste is grout. The processed waste will be disposed of in near-surface vaults at DOE sites. Sampling of low-level waste forms is needed to provide material to test waste-form stability (i.e., compressive strength and leachability) in meeting waste-acceptance criteria and the requirements of Resource Conservation and Recovery Act (RCRA) and the American Nuclear Society (ANS) {i.e., be classified a non-hazardous waste by toxicity characteristic leach procedure (TCLP) testing and meet the guidelines of ANS 16.1 for leachability index}.

Characterization of solid heterogeneous low-level waste (e.g., in steel drums) consists of drum weighing, non-destructive assay, non-destructive examination via radiography, and chemical analysis of headspace. Some selective physical sampling and analysis of the waste is done to identify dangerous waste. Information compiled from these activities is used to determine waste acceptance and shipping requirements. A high degree of waste heterogeneity and general lack of information on drum content leads to a very challenging problem in waste characterization for the purpose of segregation. Sampling and analysis is expensive and yet, no amount of sampling and analysis will produce absolute certainty of waste contents. Therefore, sampling strategies will be required that balance the costs versus the need for sampling and analysis. The chosen sampling strategy should also ensure a certain level of certainty that complies with waste acceptance and regulatory standards.

It has been decided that TRU wastes stored in drums at DOE sites are to be permanently disposed of in underground repositories. The Waste Isolation Pilot Plant (WIPP) is DOE's test repository for determining the long-term stability of TRU stored underground in bins (steel boxes measuring four feet square and three feet tall). Sampling repository solid wastes may use standard drum techniques (see

Drum Sampling section, page 7-3 and Table 7.2) incorporating protocols for safely handling, packaging, and transporting radioactive materials. One concern in storing and transporting these wastes is the presence/generation of volatile and flammable gases that could influence waste stability over the long term.

Methods have been developed for sampling VOCs inside 1) the polybag liner and innermost layers of confinement of 55-gal drums and 2) bins containing wastes stored at WIPP (Table 7.2). For sampling polybag headspace, a multiport sampling manifold equipped with SUMMA™-canisters and purge assembly is used. For sampling the innermost layers of TRU drums, two SUMMA™ canister-based systems have been developed. The first system deploys a low-internal-volume manifold similar to the manifold used for polybag headspace gas sampling. The second technique uses a direct-canister, headspace-gas sampling apparatus (see SA010 and SA011). For bin headspace sampling, a system designed to recirculate and homogenize bin headspace gas is attached to the sampling ports of the bin. Representative samples are collected in canisters following recirculation of two bin volumes.

Sampling of Separated and Treated Waste

A number of chemical constituents in nuclear process wastes influence waste-form stability (e.g., nitrate/nitrite, phosphate, chromium, organic carbon). To address this problem, options are being evaluated to separate and/or treat process wastes to eliminate or significantly reduce the levels of selected constituents in treated fractions before generation of the waste form. Sampling and analysis of treated waste streams is used to determine separation and destruction efficiencies associated with separation and treatment technology performance.

Offsite Sample Shipping

Many DOE sites transport liquid and soil samples associated with routine monitoring programs offsite to commercial laboratories for analytical services. Typically, these samples will be non-hazardous and non-radioactive. Prime contractors (i.e., DOE site contractors) for DOE should be fully aware of the regulatory restrictions regarding the transportation guidelines for shipping radioactive samples and the license restrictions of the commercial laboratory. License restrictions vary among commercial contractors and may change with some frequency, depending on renewal schedules.

For shipping, samples should be well packed and padded in coolers (i.e., hard plastic polyethylene) containing sufficient quantities of coolant (e.g., ice-water slurry) (40 CFR 136). For shipments that contain samples with volatile organic analytes, it is recommended that a maximum-minimum thermometer (non-mercury) be included to be able to account for possible temperature effects on sample integrity. Samples that contain flammable liquids (e.g., methanol) will require shipment as "flammable liquids" under Department of Transportation requirements (40 CFR 173) that include secondary containment.

Recent projections indicate that a large percentage of future analytical sample requests for DOE sites will be categorized as mixed waste. Packaging and offsite shipment of mixed-waste samples will require new packaging and monitoring guidelines (Pope et al. 1993).

Safety

Sampling tank wastes or other highly radioactive materials often requires that the samples be handled under closed and/or shielded conditions from the time of collection through the sample preparation process at the laboratory. Shielding includes, but is not limited to, polyvinyl chloride (PVC) or stainless steel sleeves on drilling rods; plastic bagging and sample containers (lead pigs and stainless steel canisters) and remote manipulation (e.g., hot cells) of samples in their preparation for laboratory chemical analysis. Gloveboxes are used in the field to assess sample radioactivity levels as a basis for properly directing samples to various laboratories for analysis. Plastic sheeting, absorbent paper, and pans are used to confine radioactive materials to areas immediately surrounding the point of sampling. Spill containment and cleanup materials should be maintained and readily available within the work area.

Sampling should be conducted using the appropriate level of protective clothing/equipment (according to federal standards) by chemical operators trained in specific areas (e.g., handling of low-level, TRU, high-level, and mixed wastes; use of respirators, project-specific procedures) required to meet their sampling objective. For radioactive and radioactive mixed waste and environmental sampling, extremity dosimeters (finger rings) should be worn by members of the sampling team that directly handle sample containers. All members of the sampling team should wear pocket meters. A Radiation Work Permit (RWP) should be prepared before sampling radioactive materials. All work should be designed and performed in accordance with guidelines provided by DOE to protect the public and the environment from the effects of radiation (DOE 1990).

The radioactive-materials sampling process should be continuously monitored by radiation-protection

personnel. In the case of tank sampling, the headspace of tanks should be evaluated for levels of explosive or toxic gases before commencement of sampling. Tank access should be continuously monitored for radioactive levels in tank headspace. It is also recommended that pre-sampling surveys be conducted (e.g., locating air, liquid, and solid interface in waste tanks) to simplify and expedite the sampling process. These practices protect workers from excessive radiation exposure and minimize environmental and laboratory contamination. Sampling of low-level or nonradioactive sites may require only safety precautions for hazardous constituents. Chapter 4 describes general safety concerns.

Quality Control

A number of factors impact sampling quality control (QC). It is important to have a clearly defined sampling objective and data quality objectives (DQOs) from which an appropriate sampling approach (i.e., strategy/design/program) can be developed. Along with the samples of interest, control samples need to be collected to assist error evaluation and to document overall data quality. Care needs to be taken to match sampling devices, containers, preservation techniques, holding times, sample volumes, analytical method(s) to be used, analytes of interest, DQOs, and sampling objective. Lastly, an adequate sample data-management system needs to be put in place. These sampling QC issues are discussed in detail in Chapter 3.

Summary of Methods

A number of techniques that represent the sampling of the above-described waste/environmental regimes have been summarized in Tables 7.1 through 7.5. Table 7.6 summarizes methods available in this

chapter. The summaries cover soil/sediment, drum, liquid, air, and tank sampling. Methods incorporated in this chapter address the problem of collecting waste and environmental samples (air, liquid, and solid) with an emphasis on application to radioactive materials. Table 7.6 (see end of chapter) summarizes Methods provided in this chapter.

Data Reporting

Sampling data to be documented falls into three categories: 1) sample labeling, 2) field notebook entries, and 3) chain-of-custody information. Data to be collected should be specified in project-specific requirement documentation (e.g., statement of work, work plans, sampling or sampling and analysis plans, quality assurance project plan). Sample data management requirements should be addressed in the planning process.

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Sampling Methods

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Table 7.6. Methods for Sampling Waste and Environmental Media

<u>Method Number</u>	<u>Title</u>	<u>Summary</u>
SA010	Sampling Headspace Gas for Volatile Organic Compounds Within a TRU Waste Drum with a Sampling Manifold	Guidance is provided for sampling headspace gases in drums containing all types of waste. Sampling involves use of a uniquely designed sampling manifold incorporating SUMMA™ passivated canisters.
SA011	Sampling Headspace Gas Within a TRU Waste Drum with SUMMA™ Canisters for Volatile Organic Compounds	Guidance is provided for sampling headspace gases in the innermost regions of waste drums (e.g., poly bags of a TRU waste drum) using SUMMA™ passivated canisters.
ST010	General Method for Sampling Liquids and Solids in LLW Storage Tanks	Guidance is provided for several different sampling devices for collecting liquids (i.e., aqueous and organic liquids) and sludges (soft and hard) from low-level waste storage tanks.

SA010(a)

Sampling Headspace Gas for Volatile Organic Compounds Within a TRU Waste Drum with a Sampling Manifold

Note:

This is a draft method and is made available for use at your discretion. The sampling method has been reviewed by the U.S. Environmental Protection Agency (EPA), and extensively reviewed by the U.S. Department of Energy (DOE) and DOE subcontractors. An automated version of this method is currently in use at Argonne National Laboratory-West at the Idaho National Engineering Laboratory near Idaho Falls, Idaho. Limited data regarding method performance have been included to validate this method; however, additional data are needed to confirm the method's performance parameters, such as precision and bias. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may have generated. Your input will assist us in verifying this method.

1.0 Scope and Application

The sampling procedure described in this section may be used to collect representative headspace gas samples from within a transuranic (TRU) waste drum. This sampling procedure is based on guidelines in EPA's Method TO-14 (EPA 1988) and guidelines in EPA's SW-846 (EPA 1986). As such, it is applicable to sampling the headspace gases in drums containing all types of waste. The method is used to sample for gases (hydrogen and methane) and specific volatile organic compounds that have a vapor-phase component at room temperature and pressure. It is based on the collection of samples in SUMMATM passivated canisters. The equipment and procedures necessary to collect samples are described below. The quality assurance (QA) requirements for this method are described in DOE's TRU Waste Characterization Quality Assurance Program Plan (QAPP) (DOE 1994).

2.0 Summary of Method

This sampling procedure employs a multipoint sampling manifold capable of collecting samples of headspace gas from within waste drums. Cleaned and evacuated sample canisters are attached to the evacuated sampling manifold. A changeable needle assembly with a valve is also connected to the sampling manifold. The needle is inserted into the headspace of the drum or poly-liner bag, and the valve is opened, allowing the headspace gases within the drum or poly-bag to expand into the evacuated sample canisters.

(a) This method was supplied by Clay McCurley of Bechtel Environmental, Inc. (San Francisco, California), and Michael Connolly of EG&G Idaho (Idaho Falls, Idaho).

3.0 Limitations and Interferences

No limitations or interferences have been identified.

4.0 Safety

Safety concerns regarding chemical and radiation exposure should be considered. Training regarding proper storage, usage, and disposal of chemicals is recommended. See Chapters 4 and 5 for a complete discussion of these issues.

5.0 Apparatus

5.1 Collecting representative samples of headspace gas from within a TRU waste drum requires the use of a variety of components. The major components required for sampling include a sampling manifold, sample canisters, pressure sensors, a thermometer, a vacuum pump, cylinders of pressurized gas, and a rotameter. In addition, the use of an organic vapor analyzer (OVA) is recommended to provide immediate indications of sampling-manifold cleanliness. Each major component of the sampling apparatus is described below.

5.2 Sampling Manifold. With the exceptions of the pressurized gas cylinders, the vacuum pump, and the OVA, all components of the sampling manifold are designed to be panel-mounted in close configuration to minimize the system's internal volume and surface area. The panel can be mounted in a standard 19-in. rack-mount cabinet on a moveable cart with the pressurized gas cylinders and vacuum pump for a mobile system, or on a wall. Figure 1 illustrates the configuration. Table 1 lists the major parts required for this configuration. The numbered components in Figure 1 correspond to the numbered components described in the text below.

5.2.1 The sampling manifold is a system with two pneumatically distinct lines: an evacuated line for collecting samples and a pressurized line for providing zero air and field-reference-standard gases.

Note: Zero air is defined as hydrocarbon-free air containing 0.01 ppmv, or less carbon monoxide, 1.0 ppmv, or less carbon dioxide, and 0.01 ppmv, or less total organic carbon (measured as methane). Nitrogen, helium, or argon may be used in lieu of zero air, depending on project needs.

Figure 1. Configuration of Headspace Gas Sampling Manifold

Table 1. Fifty-Five-Gallon Poly Bag Headspace Gas Sampling System: Listing of Major Components

Component No. ^(a)	Component Description	Purpose
Needle Assembly		
1.	1/8-in. stainless steel (SS) tubing w/sharpened tip	Pierces drum's internal poly bag
2.	Compact in-line filter (0.5 μ m sintered)	Prevents particulate contamination from entering system
3.	Full-flow quick-connect (body)	Allows multiple needle connections to be made daily
Hose Assembly		
3.	Full-flow quick-connect (stem)	Allows multiple needle connections to be made daily
4.	Manually operated bellows valve (with flow control)	Allows controlled flow of sample gases through manifold
5.	1/8 in. PFA Teflon [®] tubing	Allows movement of needle assembly
6.	Compact in-line filter (7 μ m sintered)	Provides additional particulate protection for manifold
Sampling Manifold Assembly (Evaluated Line)		
7.	Manually operated bellows valve	Isolates pressure sensor when necessary
8.	Pressure transducer	Senses pressure from 0 to 1000 torr
9.	Electronics/display unit	Controls pressure transducer and displays readings
10-15.	1/8-in. SS union tees	Provides connection ports for sample canisters
16.	Manually operated bellows valve	Isolates pump from manifold when necessary
17.	Oil-free (dry) vacuum pump	Evacuates the sampling manifold
Sampling Manifold Assembly (Pressurized Line)		
18.	Compact in-line filter (7 μ m sintered) [optional]	Provides additional particulate protection for manifold
19.	Pressurized cylinder of zero air	Provides clean air for cleaning procedures and collection of equipment blanks
20.	Pressurized cylinder of field reference	Provides known concentration of known analytes for QA/quality control (QC) purposes
21.	Two-stage SS regulator w/needle valve	Controls delivery pressure of zero air
22.	Two-stage SS regulator w/needle valve	Controls delivery pressure of helium

Table 1. (contd.)

23.	Manually operated bellows valve	Isolates humidifier from manifold when necessary
24.	250-mL SUMMA™ canister containing 100 mL of water	Humidifies pressurized gases
25.	Manually operated bellows valve (with flow control)	Controls flowrate of pressurized gases entering purge assembly
26.	Compact in-line filter (7 µm sintered) [optional]	Provides additional particulate protection for manifold
27.	1/8 in. Union Tee	Allows evacuated line to be connected to pressurized side
28.	Compact in-line filter (7 µm sintered) [optional]	Provides additional particulate protection for manifold
29.	Manually operated bellows valve	Allows pressurized line cleaning after field-reference-standard collection
30.	High-accuracy rotameter (.2 to 14 L/min)	Allows system operator to monitor excess flow
31.	Manually operated bellows valve	Isolate OVA from manifold when necessary
32.	Portable organic vapor analyzer	Provides real-time analysis for manifold cleanliness
Additional System Components^(b)		
	Blank aluminum panel (19 in. x 21 in. x 12 in.)	Allows system components to be rack mounted
	Full-range Fortin mercury barometer	Provides ambient pressure measurements
	Certified mercury thermometer	Provides ambient temperature measurements
	Resistive (heat) tape or wire	Reduces potential for analytes to adhere to internal surfaces of manifold
System Cleaning Assembly		
	Port connector (1/8 in.)	Provides tight connection to purge assembly tee (37)
	Union elbow (1/8 in.)	Connects port connector to quick-connect at 90 degrees
	Full-flow quick-connect (body)	Allows connection to evacuated line of manifold

(a) See numbered components of Figure 1

(b) Components not shown in Figure 1

- 5.2.2 The evacuated line consists of a needle assembly, capacitance manometer, six ports for attaching sample canisters, and a dry vacuum pump. The needle consists of a 6-in. tube, 1/8-in. OD, sharpened at one end and connected to an elbow fitting at the other (1). The elbow fitting is connected to a 0.5-micron filter (2), which is connected to the body portion of a quick-connect (3). The quick-connect allows the operator to easily connect a clean needle assembly between samples, thus reducing the potential for cross contamination.
- 5.2.3 A flow-regulating bellows valve (4) is connected to the stem side of the quick-connect. On the other side of valve (4) is a 7-micron filter (6) that provides additional protection against system contamination from particulate matter. Connecting valve (4) and filter (6) is flexible Teflon[®] tubing (5) that allows the needle to be moved from the purge assembly tee (27) to the 55-gal drum.
- 5.2.4 After passing through the filter (6), headspace gas passes through a tee connector before being swept past the sample canister ports and into the vacuum pump. The tee provides a pneumatic link to the transducer (8) of a capacitance-manometer pressure sensor. Closing bellows valve (7) protects the sensor from pressure shocks and overpressurization.
- Caution:** The transducer should not be exposed to pressure greater than 1200 mm Hg.
- 5.2.5 Once downstream of the pressure transducer tee, headspace gas is swept past six tees (10 through 15) that provide connection ports for the sample canisters. Each port has a permanent VCR[®] adaptor fitting for attaching the canister to the sampling manifold to circumvent potential leak problems caused by reconnecting the Swagelok[®] fitting after cleanings. If desired, valves may be placed between the ports and the canister valves to facilitate closing the ports when sample canisters are not attached.
- 5.2.6 A bellows valve (16) connects the vacuum pump (17) to the sampling manifold. When the pump is operating, opening valve (16) decreases the system pressure, and closing the valve isolates the pump. The pump exhaust is directed to the containment area through a 7-micron filter (18). This filter serves as a safety precaution to prevent contaminated particulate matter from accidentally entering the system through this port. Filter (18) is an optional component of the sampling manifold.
- 5.2.7 An OVA (32) is connected downstream of the sample port farthest from the needle assembly. The OVA's internal pump pulls zero air through the manifold to check for cleanliness. Exhaust from the OVA is directed to the exhaust port (18).

- 5.2.8 The pressurized line consists of a pressurized cylinder of zero air (19), and a pressurized cylinder of gas (e.g., nitrogen) containing field reference standards (20) metered through two-stage SS regulators (21, 22) to a purge assembly where flow rates of the pressurized gases can be adjusted and monitored with a rotameter (30). Valve (25) is a flow-regulating bellows valve for regulating flows from the gas cylinders through the rotameter. Valve (29) is a bellows valve that allows the operator to clean the system after collecting a field-reference-standard sample. Filters (26) and (28) are 7-micron particulate filters to prevent contaminated particulate matter from accidentally entering the system through the purge assembly tee (27). Filters (26) and (28) are optional components of the sampling manifold.
- 5.2.9 A bellows valve (23) connects a 250-mL sample canister (24) containing approximately 100 mL of American Society for Testing and Materials (ASTM) Type II (or equivalent) water to the pressurized line. When valve (23) is open, the water humidifies the dry pressurized gases from the pressurized gas cylinders. Closing valve (23) isolates the water from the sampling manifold. The dry pressurized gases are humidified for quality assurance/quality control (QA/QC) purposes. For QC purposes, the water vapor assists with the cleaning of the internal surfaces of the sampling manifolds. For QA purposes, the water vapor conditions the zero air and field reference standards so they are comparable to the headspace gas, which is expected to be humid. In lieu of installing the bellows valve (23) and humidifier (24), the zero-air field-reference-standard gases may be humidified by adding water directly to cylinders (19) and (2). A cylinder gas concentration of approximately 10,000 ppmv water is recommended.
- 5.2.10 With valve (29) open and the needle assembly attached to the purge assembly tee (27), valve (25) is used to adjust the flow rate through the rotameter (30). The purge assembly tee is a 1/8-in. SS tee with Teflon[®] ferrules seated by a SS nut at the needle connection port. The needle port has been drilled to 1/8-in. ID to facilitate complete insertion of the needle. The pliable Teflon[®] ferrules permit the needle to be repeatedly withdrawn from and tightened into the port. By maintaining flow through the rotameter when purging or sampling, the technician operating the system is assured that only gases from the pressurized line of the sampling manifold enter the evacuated line, thus preventing ambient air from entering the system through the rotameter, diluting the sample(s) collected, and contaminating the sampling manifold.
- 5.2.11 The only time it is necessary to remove the Teflon[®] ferrules from the purge assembly tee (27) is to facilitate attachment of the system cleaning assembly after a field-reference-standard sample has been collected. This assembly does not

have the 0.5-micron particulate filter, and a port connector is used in place of the needle assembly's 6-in. needle. This configuration allows the pressurized line, as well as the evacuated line, of the system to be evacuated, swept, and cleaned with zero air.

- 5.2.12 An additional QC provision that should be incorporated into the design of the sampling manifold, but not shown in Figure 1, is the ability to heat the sampling manifold during sampling and cleaning activities. This may be accomplished by wrapping the pneumatic lines, valves, and filters with resistive wire or tape to heat the internal surfaces of the sampling manifold (approximately 50°C is recommended). Heating the sampling manifold is recommended to reduce analyte adsorption on the sampling manifold's internal surfaces.

- 5.3 **Sample Canister.** A sample canister is a SS SUMMA™ pressure vessel that is welded and leak-free. It has a Cr-NiO-passivated interior surface, a bellows valve, and a dial pressure/vacuum gauge. All sample canisters have VCR® fittings for connecting sampling and analytical equipment. The dial pressure/vacuum gauge indicates if the canister has leaked, thereby preventing sampling-manifold contamination by exposure to a potentially contaminated sample canister. The OVA on the manifold is used, along with confirmatory equipment blanks, to check for manifold cleanliness.

SUMMA™ canisters have been used in the past for volatile organic compounds (VOCs) sample collection and have a demonstrated sample storage stability for many specific VOCs (EPA 1988; Oliver et al. 1986). Two sizes of canisters (150 mL and 250 mL) are used to collect headspace gas samples.

- 5.4 **Pressure and Temperature Measurement Apparatus.** When using the sampling manifold, the sampling manifold pressure, which is read with the capacitance manometer, is monitored and recorded. Ambient temperature is also monitored and recorded.

- 5.4.1 An accurate barometer is used to monitor ambient pressure, while a capacitance manometer is used to monitor both manifold and canister pressures. A dial pressure/vacuum gauge is used to monitor sample-canister pressure when a sampling manifold equipped with a capacitance manometer is not available.

- 5.4.1.1 **Ambient Pressure Sensor:** The ambient pressure sensor is a full-range Fortin barometer, or equivalent, with a range of approximately 500 to 800 mm Hg. It is kept in the sampling area. Its resolution is 1 mm Hg, and its calibration is traceable to National Institute of Standards and Technology (NIST) standards. A dual-scale thermometer should be provided with the barometer for temperature corrections.

5.4.1.2 **Dial Pressure/Vacuum Gauge:** This type of gauge is helium leak-tested to 1.5×10^{-7} standard cc/sec, has all SS construction, and is capable of tolerating temperatures to 125°C. The gauge is able to indicate 5 psig pressure to a vacuum of 30 in. of Hg.

5.4.1.3 **Capacitance Manometer:** The capacitance manometer is pneumatically connected to the sampling manifold. The pressure sensor consists of a pressure transducer and an electronics/display unit. The transducer is able to measure absolute pressure in the range from 0.1 mm Hg to 100 mm Hg with a usable resolution of ± 0.005 mm Hg at 0.05 mm Hg.

5.4.2 **Thermometer.** The thermometer is a NIST-traceable Hg thermometer, total immersion type, laboratory grade, with N₂ above the Hg. It has permanent stain markings in the approximate range of -30° to 50°C, with a resolution of 1°C.

5.5 **Organic Vapor Analyzer.** The OVA is a portable organic vapor analyzer that is battery powered. It is capable of measuring VOCs in air in two ranges. In the range of 0 to 200 ppm, it has a resolution of 0.1 ppm. In the range of 200 to 2000 ppm, it has a resolution of 1.0 ppm. Gas cylinders are supplied by the manufacturer for calibrating the unit.

6.0 Preplanning

Studies to characterize TRU waste require careful planning to prepare facilities, develop written documentation, secure laboratory support, and evaluate data.

7.0 Reagents, Preservation Measures, and Handling

All sampling equipment components that come into contact with the headspace-sample gases must be constructed of relatively inert materials, such as SS or Teflon®. Stainless steel components with passivated interior surfaces are recommended. Sample holding times and storage conditions should conform to the requirements specified in Table 2.

8.0 Method

8.1 **Procedures for Cleaning the Sampling Manifold:** This section describes procedures for cleaning the sampling manifold. These procedures are provided to ensure that the samples collected using this apparatus are representative. This is accomplished by reducing the possibility of contamination by manufacturing impurities and ambient air. Using these cleaning procedures will also reduce the possibility of cross-contamination between sampling operations. These procedures are as follows:

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- Section 8.1.1 is a procedure for initially cleaning and leak-checking the sampling manifold.

- Section 8.1.2 is a procedure for routine cleaning and leak-checking the sampling manifold.

- Section 8.1.3 is a procedure for cleaning the sampling manifold after collecting a field reference standard.

- Section 8.1.4 is a procedure that describes the method for needle-assembly cleaning.

- Section 8.1.5 is a procedure that describes sample canister cleaning.

Table 2. Headspace Sampling Containers and Holding Times

Parameter	Container	Minimum Turn Headspace Sample Volume ^a (mL)	Holding Temperature	Holding Time ^b (days)	Shipping Allowance Time ^c (days)	Laboratory Holding Time ^c (days)
Gases	SUMMA TM Canister	100	Ambient	4	2	28
VOCs	SUMMA TM Canister	250	0 to 40°C	4	2	28

(a) Alternatively, if available headspace is limited, a single 100-mL sample may be collected for determination of VOCs and gases.

(b) From time of headspace sample collection to shipment.

(c) This is a programmatic-based maximum holding time. Holding time begins at the validated time of sample receipt.

8.1.1

Initial Sampling Manifold Cleaning and Leak-Free Certification. After

receipt from various manufacturers and before assembly, all components of the sampling manifold that will come into contact with headspace or cylinder gases are inspected and thoroughly cleaned using this procedure. Parts received free of contamination, as stated or certified by the manufacturers, may be exempted from this cleaning procedure at the discretion of the sampling personnel.

1.

Nonmetallic components of the sampling manifold should be disassembled, rinsed with high performance liquid chromatography (HPLC)-grade deionized water, and dried in an oven at 50°C for 12 to 24 h. An evacuated oven is preferable, but not required.

2. Stainless steel parts and fittings are placed in a beaker of reagent-grade hexane in an ultrasonic bath for 15 min. This procedure is repeated with reagent-grade methanol. The SS parts are rinsed with HPLC-grade deionized water and dried in an oven at 100°C for 12 to 24 h. Stainless steel parts and fittings may also be cleaned by assembling and forcing steam through the assembly.
 3. The sampling manifold is assembled, and it is leak-checked by pressurizing it to 1700 mbar and by placing a bubble solution on all fittings and connections. For a period of 30 min, a check should be made periodically for bubble production. As an alternative, the system may be pressurized with helium and leak-checked with a helium-detection device.
 4. Fittings and connections that leak are tightened until no leaks are observed. From clean spare parts, any fittings and connections that continue to leak are replaced.
 5. The sampling manifold is evacuated to 0.13 mbar, and the pressure is monitored for 1 h. If the pressure increases by more than 0.03 mbar, steps 3 and 4 should be repeated.
 6. The sampling manifold is purged with humid zero air for 24 h.
 7. The sampling manifold is evacuated and pressurized with zero air three times.
 8. A sampling manifold blank is collected through the manifold as described in procedure 8.2.4 and analyzed for the target compounds listed in Tables 12-1 and 13-1 of the QAPP. The system is checked for cleanliness with the OVA and confirmed by analyzing the equipment blank.
 9. The sampling manifold is pressurized with zero air to 1,700 mbar when not in use.
- 8.1.2 **Routine Sampling Manifold Cleaning and Leak Check.** The following procedure assumes that a clean needle assembly (1 through 3) has been connected to valve (4) and inserted into the purge assembly tee (27). The procedure also assumes that all sampling manifold valves are closed, the vacuum pump and OVA are operating, and all regulators for the high-pressure cylinders (zero air, and field reference standards, etc.) have been properly purged and set

to a delivery pressure of approximately 1,700 mbar. Refer to Figure 1 for location of numbered components.

1. The sample canister(s) to be used for sampling should be selected, and the canister's dial pressure/vacuum gauge reading should be checked (the gauge face plate should be tapped lightly to verify the reading). The reading on the sample canister tag is recorded. The sample canister(s) is attached to the sampling manifold, and the connector(s) is tightened. A sample canister port(s) not occupied by a canister must be closed with a cap or valve. If the port to which a canister is attached has an optional valve (not shown) attached to the manifold port tee, this valve is opened before proceeding to step 2. The sample canister valve should remain closed.
2. Valves (29), (23), and (21) are opened.
3. Valve (25) is opened slowly until the rotameter (30) indicates a flow rate of approximately 2 L/min.
4. Valve (16) is opened, and then valve (4) is opened slowly until the rotameter (30) indicates a flow rate of approximately 1 L/min. The sampling manifold is now being purged with zero air. It is purged for approximately 3 min. Valves (25) and (4) should be checked periodically and adjusted, if necessary, to maintain the rotameter flow rate at 1 L/min.
5. Valve (4) is closed to evacuate the sampling manifold. After waiting 5 sec, valve (16) is closed and valve (4) is again slowly reopened to allow the sampling manifold to fill with zero air. This is repeated three to four times. This procedure is terminated by closing valve (16), opening valve (4), and allowing the sampling manifold to fill with zero air. Valve (31) is opened and the OVA (32) is allowed to pull zero air through the manifold. The OVA display should be observed for at least 10 sec. If the OVA indicates a VOC concentration of 0.5 ppmv or greater, purging is continued, and the sampling manifold is swept with zero air until the OVA indicates less than 0.5 ppmv. When the OVA indicates less than 0.5 ppmv, the internal volume between valve (7) and transducer (8) is purged by opening valve (7).

Caution: Care should be taken to slowly evacuate and fill the sampling manifold, since rapid fluctuations in manifold

pressure may damage the manometer when valve (7) is open.

6. Valve (7) is opened, and valves (4) and (31) are closed. Valves (21), (23), (25), and (29) are closed.
7. Valve (16) is opened, and the vacuum pump is allowed to reduce the pressure in the sampling manifold to 0.13 mbar, as indicated by the manometer (9).
8. Once the sampling manifold pressure has been reduced to 0.13 mbar, valve (16) is closed.
9. The manometer (9) reading is observed for 3 to 5 sec to verify that all sampling-manifold valves have been properly closed and that no observable leaks are present. If the manometer indicates a leak, sampling activities should cease, and the manifold should be leak-checked as described in steps 3 through 5 of procedure 8.1.1.
10. The sample-canister valve(s) is opened as the operator observes the nanometer (9) pressure. Pressure readings are recorded on the sample canister tags.

Note: An increase in manifold pressure greater than 0.03 mbar indicates a canister leak, and opening the remaining sample canister valves is not advised. All open valves are closed, and the exposed sample canisters are removed and replaced. Then the manifold is purged again following steps 4 through 9, above.

11. If no leaks are detected, the sampling manifold is ready for sample collection.

8.1.3 Sampling Manifold Cleaning After Field-Reference-Standard Collection.

Analytes in the field-reference-standard gas have the potential to remain in the pneumatic lines after field reference standard sample collection. To ensure that the pneumatic times are clean, this procedure is performed immediately after collecting a field-reference-standard in accordance with section 8.2.5. It assumes that the needle assembly (1 through 3) used for the field-reference-standard collection is still inserted into the purge assembly tee (27). Refer to Figure 1 for the location of numbered components.

1. Valve (23) is closed.
2. Valve (29) is closed, and valve (4) is opened.
3. The manometer (9) reading is observed until the pressure (approximately 1700 mbar) ceases to increase, and then valve (21) is closed.

Caution: Care should be taken to slowly evacuate and fill the sampling manifold, since rapid fluctuations in manifold pressure may damage the manometer when valve (7) is open.

4. Valve (16) is opened, and the sampling manifold is evacuated for a minimum of 5 sec.
5. Valve (16) is closed, and then valve (21) is opened slowly.
6. Steps 2 through 4 are repeated three more times and terminated by closing valve (16) and slowly opening valve (21).
7. Valve (4) is closed, valve (29) is opened, and valve (25) is adjusted until the rotameter (30) indicates approximately 1 L/min.
8. Valve (21) is closed.
9. The needle assembly is disconnected from the purge-assembly tee (27), and a clean needle assembly is connected to valve (4).
10. The needle assembly (1 through 3) is inserted into the purge-assembly tee (27), and the cleaning is performed as described in section 8.1.2.

8.1.4 **Needle Assembly Cleaning.** This procedure describes the steps for cleaning a needle assembly after headspace gas samples or field reference standards have been collected.

1. After samples have been collected and the sample-canister valves have been closed, the needle assembly (1 through 3) should be detached at the quick-connect (3).
2. The filter assembly is removed to an area where it can be disassembled and cleaned safely.

3. The filter's housing (2) is unscrewed, and the filter element is grasped firmly with a sturdy pair of forceps. The element is pulled firmly to dislodge it from the housing. The element should be properly discarded.
4. The Viton[®] O-ring is removed from the body of the quick-connect (3), and the O-ring is discarded.
5. The reusable parts are placed in a beaker of reagent-grade hexane in an ultrasonic bath for 15 min. This procedure is repeated with reagent-grade methanol. The parts are rinsed with HPLC-grade deionized water and dried in an oven at 100°C for 12 to 24 h.
6. A new filter element is inserted into the filter (2), and the body is screwed together tightly.
7. A new Viton[®] O-ring is placed on the body of the quick-connect (3).
8. The needle assembly and a resealable bag with zero air are purged as the needle assembly is being placed inside the bag.
9. The bag is sealed and placed in a box for storage.

8.1.5 **Sample Canister Cleaning.** Sample canisters are cleaned and certified in accordance with sections 7.3 and 11.1 of the EPA's Compendium Method TO-14 (EPA 1988).

8.2 Procedures for Collecting Headspace Gas and Quality Control Samples Using a Low Internal-Volume Sampling Manifold. Headspace gas and QC samples collected using the sampling manifold and procedures described here are as follows:

- Section 8.2.1 is a procedure for collecting headspace gas samples.
- Section 8.2.2 is a procedure for collecting field duplicates.
- Section 8.2.3 is a procedure for collecting field blanks.
- Section 8.2.4 is a procedure for collecting equipment blanks.
- Section 8.2.5 is a procedure for collecting field reference standards.

Note: Before sampling, drums are allowed to equilibrate to the temperature of the sampling area for at least 72 h.

Caution: Appropriate site radiological controls must be established before removing the drum lid.

8.2.1 **Headspace Gas Sample Collection.** Headspace gas samples are collected from within all innermost layers of confinement that meet the criteria specified in section 7.1 of the QAPP. Refer to Figure 1 for the location of numbered components of the sampling manifold. Samples are collected as follows.

1. It should be verified that the sampling manifold has been properly cleaned and leak-checked as described in section 8.1.2.
2. The drum is prepared for sampling by removing the drum lid and the internal rigid-liner lid; this should expose the poly-liner bags.
3. The needle assembly (1 through 3) is removed from the purge assembly tee (27), and the needle is pressed through the poly bag and into the headspace gas. Disturbing the bag should be avoided, if possible. However, if it is necessary to handle the bag, the operator should do so in a manner that minimizes the potential for introducing outside air into the poly bag's headspace gas.
4. The needle is held in the headspace, and valve (4) is opened. The needle should be held steady until the canister gauge indicates zero psig.
5. The sample canister valve(s) is closed.
6. The needle (1) is removed from the poly bag, and the needle assembly is disconnected from valve (4). The needle assembly is placed in a collection box for items to be cleaned, or it is discarded.
7. A fresh needle assembly is removed from its resealable bag, and the needle assembly is connected to valve (4). The fresh needle assembly is inserted into the purge-assembly tee (27), and the assembly is hand-tightened in place.
8. The sample canister(s) is removed from the sampling manifold, and the date, time, sampling manifold pressure (9), ambient pressure, and ambient temperature are logged on the sample-canister tag.

9. The sample type should be noted on a QC sample record and the sample canister should be placed in a shipping container.
10. The sampling manifold should be cleaned according to the procedure in section 8.1.2.

8.2.2 Field Duplicate Collection. Field duplicate samples are used to assess the precision of the sampling and analytical process. The measurement is expressed as relative percent difference (RPD), which is defined in section 3.2.1 of the QAPP (DOE 1994). Corrective actions should be taken when the RPD for field duplicate VOC samples exceeds ± 25 percent, and the RPD for hydrogen and methane exceeds ± 10 percent. Field duplicate samples are collected at a frequency of one for every twenty samples consecutively collected.

The procedure for collecting field duplicates is similar to that specified in section 8.2.1 for collecting headspace-gas samples. However, when collecting field duplicates, two sample canisters are attached to the sampling manifold. One canister is attached at port (10), and the other is attached at port (11). When collecting field duplicates, valves (10) and (11) are closed before opening valve (4). After opening valve (4), valve (10) is opened, and the first sample canister is filled. Then valve (11) is opened, and the second sample canister is filled. Finally, valve (4) is closed followed by valves (10) and (11).

8.2.3 Field Blank Collection. Field blanks are used to assess background levels of analytes. An air equipment blank (section 8.2.4) should be collected immediately before collecting the field blank. Also before collecting field blanks, sampling sites should use the OVA to obtain a real-time indication of sampling-manifold cleanliness. Field blanks are collected at a frequency of one for every twenty samples consecutively collected.

The following procedure is used for collecting a field blank through the sampling manifold.

1. It should be verified that the sampling manifold has been properly cleaned and leak-checked as described in section 8.1.2.
2. A drum is prepared by removing the drum lid and the internal rigid-liner lid.

3. The needle assembly (1 through 3) is removed from the purge assembly tee (27), and the needle assembly is held near the top of the drum.
4. Valve (4) is opened. The needle should be held steady until the manometer (9) indicates ambient pressure, or ceases to show an increase in pressure. It should be verified that the canister gauge indicates zero psig.
5. The sample canister(s) valve(s) should be closed.
6. The needle assembly is disconnected from valve and placed in a collection box for items to be cleaned or discarded.
7. A clean needle assembly is removed from its resealable bag attached at the quick-connect (3). The clean needle assembly is inserted into the purge assembly tee (27) and the assembly is hand-tightened in place.
8. The sample canister(s) is removed from the sampling manifold, and the date, time, sampling-manifold pressure (9), ambient pressure, and ambient temperature are logged on the sample canister tag.
9. The sample type should be noted on a QC-sample record as a field blank, and the sample canister should be placed in a shipping container.
10. The sampling manifold should be cleaned according to the procedure in section 8.1.2.

8.2.4 **Equipment Blank Collection.** Equipment blanks are used to assess the cleanliness of the sampling manifold. An equipment blank is collected and analyzed before the sampling manifold is first used, then at a frequency of one in every twenty samples consecutively collected. The following procedure is used for collecting equipment blanks. Refer to Figure 1 for the location of numbered components.

1. It should be verified that the sampling manifold has been properly cleaned and leak-checked as described in section 8.1.2.

2. With the needle assembly (1 through 3) connected to the purge assembly tee (27), valve (25) is adjusted until the rotameter (30) indicates a flow rate of approximately 10 L/min of zero air.
3. Valve (4) is opened to allow the sample canister to fill as quickly as possible without reducing the flow indicated by the rotameter (30) to zero.

Note: If rotameter (30) indicates zero flow, the sampling-manifold blank is invalidated, and the sampling manifold is cleaned (section 8.1.2) before collecting another sampling-manifold blank.

4. Zero air should be drawn continually from the purge assembly tee (27) until the manometer (9) indicates ambient pressure or ceases to show an increase in pressure. It should be verified that the sample-canister gauge indicates zero psig.
5. Valve (4) and the sample-canister valve are closed when the manometer indicates ambient pressure.
6. Valve (25) is adjusted to reduce the flow rate through the rotameter (30) to less than 1 L/min (to conserve zero air).
7. The sample canister is removed from the manifold.
8. The date, time, manifold pressure (9), ambient pressure, and ambient temperature are logged on the sample canister tag.
9. The sample type should be noted on a QC-sample record as an equipment blank, and the canister should be placed in a shipping container.

8.2.5 Field Reference Standard Sample Collection. Field reference standards are used to assess the accuracy of the sampling-and-analysis process. The measurement is expressed as relative percent accuracy (RPA), which is defined in section 3.2.1 of the QAPP (DOE 1994). Corrective actions should be taken when the relative percent accuracy exceeds $\pm 30\%$ for VOCs and/or exceeds $\pm 10\%$ for hydrogen or methane. A field reference standard is collected and analyzed before the sampling manifold is first used, then at a frequency of one in every twenty samples consecutively collected. Refer to Figure 1 for the location of numbered components.

1. It should be verified that the sampling manifold has been properly cleaned and leak-checked as described in section 8.1.2 and that canister port (11) is closed.
2. Valves (23) and (29) are opened. Valve (25) is opened slightly and then valve (22) is opened to initiate flow of the field-reference-standard gas to the purge-assembly tee (27).
3. With the needle assembly (1 through 3) connected to the purge-assembly tee (27), valve (25) is adjusted until rotameter (30) indicates a flow rate of approximately 10 L/min.
4. Valve (4) is opened to allow the sample canister(s) to fill as quickly as possible without reducing the flow indicated by rotameter (30) to zero.

Note: If rotameter (30) indicates zero flow, the field reference standard is invalidated, and the sampling manifold is cleaned (section 8.1.3) before collecting another field-reference-standard sample.
5. Field-reference-standard gas should be drawn continually from the purge-assembly tee (27) until the manometer (9) indicates ambient pressure or ceases to show an increase in pressure. It should be verified that the sample-canister gauge indicates 0 psig.
6. Valve (4) and the sample-canister valve should be closed when the manometer indicates ambient pressure.
7. Valve (25) is adjusted to reduce the flow rate through rotameter (30) to approximately 1 L/min. Valve (22) is then closed.
8. Valve (21) is opened, and valve (25) is opened and closed a few times to facilitate purging residual field-reference-standard gas from the pneumatic lines. This step is terminated with valve (25) adjusted to deliver approximately 1 L/min of zero air through rotameter (30).
9. The sample canister is removed from the sampling manifold.
10. The date, time, manifold pressure (9), ambient pressure, and ambient temperature are logged on the sample-canister tag.

11. The sample type should be noted on a QC-sample record as a field-reference standard, and the sample canister should be placed in a shipping container.
12. The sample canister port is closed, and then the sampling manifold is cleaned as described in section 8.1.3.

8.3 Calculations

8.3.1 The potential exists for sampling or analytical personnel to find, after receiving a canister, that the dial pressure gauge on the sample canister does not indicate the same pressure as the last one logged on the sample-canister tag. Changes in the sample-canister-gauge pressure may be the result of four possible occurrences: 1) a leak in the sample canister or sample-canister component (valve, gauge, etc.), 2) damage to the sample-canister gauge during storage or transportation, 3) an ambient pressure difference between the sampling and analysis location, and 4) an ambient temperature difference between the sampling and analysis location.

8.3.2 The procedures in section 8.3.3 below should be followed to determine the sample-canister-gauge pressure change expected if ambient pressure and temperature differences exist between the sampling and analysis locations. If the change in sample-canister-gauge pressure can be accounted for using the procedures in section 8.3.3, then the integrity of the sample has been maintained. If, however, the sample-canister-gauge pressure change cannot be accounted for by considering ambient pressure and temperature changes, the canister must be leak-checked and re-certified for use.

8.3.3 Calculations to Compute Expected Sample-Canister-Gauge Pressure Changes

8.3.3.1 Temperature change at constant ambient pressure: Sample-canister-gauge pressure changes resulting from a temperature change can be explained by Equation (1):

$$P_2 = \frac{P_1 T_2}{T_1} \quad (1)$$

where

P_1 is the sample-canister internal pressure (ambient pressure plus gauge pressure in in. of Hg) at the time of sampling

P_2 is the sample-canister internal pressure (ambient pressure plus gauge pressure in in. of Hg) at the time of analysis, if the ambient temperature changes from T_1 to T_2 at constant ambient pressure

T_1 is the ambient temperature (degrees Kelvin) at the time of sampling

T_2 is the ambient temperature (degrees Kelvin) at the time of analysis.

According to this equation, increasing the temperature of the canister ($T_2 > T_1$) will increase the internal canister pressure, and decreasing the canister temperature ($T_2 < T_1$) will decrease the internal canister pressure.

8.3.3.2 Ambient pressure change at constant temperature

A sample canister's dial gauge is expected to indicate a change in pressure if the canister is transported from a high elevation to a lower elevation, or vice versa. The expected change in canister-gauge pressure should be the same as the difference in ambient pressure between the high-elevation site and the low-elevation site, or vice versa.

Changes in sample-canister-gauge pressure that result from changes in temperature and ambient pressure are additive. Care, however, must be taken to ensure that the signs (positive or negative) of the calculated gauge-pressure changes are accurately assigned.

9.0 Quality Control

9.1 Specific sampling steps to ensure that the headspace gas samples are representative include

- Sample-canister cleaning and leak-checking
- Use of sample canisters with a passivated internal surface
- Use of low-internal-volume sampling apparatus
- Use of small sample volume: low sample volume to available headspace gas-volume ratio

- Careful pressure regulation in sample canister
- Performance audits
- Collection of field blanks, field reference standards, equipment blanks, and field duplicates.

9.2 Quality Control for Pressure and Temperature Measurements. This section pertains to the calibration and certification of equipment and instrumentation used for temperature and pressure measurements. All information related to the calibrations of the pressure and temperature sensors should be recorded.

9.3.1 Certification Check of the Ambient-Pressure Sensor. The ambient-pressure sensor is certified by the manufacturer using standards or equipment traceable to the NIST. The pressure indication of the sensor is corrected in accordance with temperature, indicated by a dual-scale thermometer attached to its casing, if necessary.

9.3.2 Calibration of the Capacitance Manometer. The capacitance manometer is certified using standards or equipment traceable to the NIST.

9.3.3 Calibration of Sample-Canister Pressure Gauge. The dial pressure gauge of each sample canister is certified using standards or equipment traceable to the NIST. Each canister gauge is recertified once per month, or as necessary.

9.3.4 Calibration of the Hg Thermometer. The Hg thermometer is certified using standards or equipment traceable to the NIST.

9.3.5 Calibration of the Organic-Vapor Analyzer. Cylinders of calibration gases, certified using standards traceable to NIST, are supplied by the manufacturer of the organic-vapor analyzer for calibrating the unit.

10.0 Method Performance

Since 1991, Argonne National Laboratory-West has been collecting headspace gas samples from drums of TRU waste in accordance with this method. Although the data set is limited, sufficient data have been collected to begin to assess the precision and accuracy with which the headspace-gas sampling manifold collects samples.

Precision

Precision for the manifold method was determined by collecting duplicate samples of headspace gas as specified in section 8.2.2. For each pair of canisters, the RPD for each analyte detected was calculated as follows:

$$\text{RPD} = [(X_1 - X_2)/X] 100$$

where

X_1 = concentration for sample 1 of duplicate pair

X_2 = concentration for sample 2 of duplicate pair

X = average of sample 1 and 2

The RPDs were then averaged. For analytes found in three or more duplicate samples, the standard deviation (STD) of the RPDs was calculated as follows:

$$\text{STD} = \left[\sum (x_{\text{mean}} - x)^2 / (n - 1) \right]^{0.5}$$

where

STD = standard deviation

n = number of observed or calculated values

x = individual observed or calculated value

x_{mean} = mean of all observed or calculated values

The results are summarized in Table 3. All average RPDs were within the method's precision limit of ± 25 percent, with the exception of 1,1 dichloroethane, which was found in only one duplicate sample. Additional data collection and evaluation will further verify and validate the method.

Table 3. Method Precision for the Sampling Manifold

Analyte	No. of Duplicate Samples	Average RPD $\pm$ STD ^(a)
Benzene	1	12
1,1, Dichloroethane	1	26
1,1 Dichloroethene	1	7
Methylene chloride	4	9 $\pm$ 7
Toluene	6	13 $\pm$ 5
1,1, Trichloroethane	7	11 $\pm$ 7
Trichloroethene	2	10
Cyclohexane	1	7
Bromotrifluoromethane	1	7
Oxygen	6	2 $\pm$ 2
Argon	6	1 $\pm$ 2
Nitrogen	6	1 $\pm$ 2

- (a) RPD - average relative percent difference between duplicate samples.
 STD - standard deviation of the RPDs. Standard deviation is not calculated for fewer than three samples.

Accuracy

Recovery for the manifold method was determined by collecting samples of field reference standards as specified in section 8.2.5. Compressed gas cylinders certified to contain known concentrations of known VOCs and gases were used as the field reference standards. The percent recoveries for each analyte were calculated as follows:

$$\text{percent recovery} = (Y/A) \cdot 100$$

where

T = sample concentration

A = certified cylinder concentration

The percent recoveries were then averaged for each analyte, and the STD of the percent recoveries was calculated (see STD calculation for precision). Then the relative percent accuracy was calculated by subtracting the percent recovery from 100.

The results are presented in Table 4. All average percent recoveries for the VOCs were within the method's accuracy limit of $\pm 30\%$, and hydrogen and methanol were within the method's accuracy limit of $\pm 10\%$. Additional data collection and evaluation will further verify and validate the method.

Table 4. Method Accuracy for the Sampling Manifold

Analyte	Number of Field Reference Standard Samples Collected	Average %R $\pm$ STD ^(a)	RPA ^(b)
1,1 Dichloroethane	10	96 $\pm$ 16	4
1,2 Dichloroethane	10	104 $\pm$ 11	-4
1,1 Dichloroethene	10	106 $\pm$ 10	-6
cis 1,2 Dichloroethene	10	99 $\pm$ 6	1
Tetrachloroethane	10	95 $\pm$ 11	5
Hydrogen	9	104 $\pm$ 7	-4
Oxygen	5	99 $\pm$ 1	1
Nitrogen	6	107 $\pm$ 6	4
Ethane	5	107 $\pm$ 1	-7
Methane	5	103 $\pm$ 4	-3
Propane	5	103 $\pm$ 1	-3
Carbon monoxide	4	102 $\pm$ 3	-2
Carbon dioxide	4	101 $\pm$ 3	-1
Argon	4	102 $\pm$ 3	-2

(a) %R - percent recovery of a surrogate standard
STD - standard deviation

(b) RPA - relative percent accuracy = $100 - \%R$

11.0 References

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Drum Sampling

U.S. Environmental Protection Agency (EPA). 1988. "Compendium Method TO-14, The Determination of Volatile Organic Compounds (VOC) in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic Analyses". May 1988, Quality Assurance Division, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina.

SA011(a)

Sampling Headspace Gas Within a TRU Waste Drum with SUMMA™ Canisters for Volatile Organic Compounds

Note: This sampling method has received extensive review by the U. S. Environmental Protection Agency (EPA), the U. S. Department of Energy (DOE), and DOE subcontractors. This method is currently in use at the Argonne National Laboratory-West at the Idaho National Engineering Laboratory near Idaho Falls, Idaho.

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

The sampling procedure described in this section may be used to collect representative headspace gas samples from the poly bags within a transuranic (TRU) waste drum. This sampling procedure is based on guidelines in EPA's Method TO-14 (EPA 1988) and guidelines in EPA's SW-846 (EPA 1986). As such, it is applicable to sampling the headspace gases in drums containing all types of waste. The method is used to sample for gases (inorganic and hydrocarbon) and specific volatile organic compounds (VOCs) that have a vapor-phase component at room temperature and pressure. It is based on the collection of samples in SUMMA™ passivated canisters. The equipment and procedures necessary to collect samples are described below.

2.0 Summary of the Method

This headspace sampling procedure employs a SUMMA™ canister sampling system to collect headspace samples for analysis and quality control (QC) purposes. Sample canisters are evacuated to 0.07 mbar before use and attached to a changeable filter and needle assembly capable of puncturing poly bags. Field duplicates are collected in the same manner and use the same type of sampling apparatus as used for collecting headspace samples. Field blanks are samples of room air collected in the headspace sampling area in the immediate vicinity of the

(a) This method was supplied by Clay McCurley of Bechtel Environmental, Inc. (San Francisco, California), and Michael Connolly of EG&G Idaho (Idaho Falls, Idaho).

waste drum. Equipment blanks and field reference standards are collected using a purge assembly. These samples are collected from the needle tip through the same components (e.g., needle, filter) that the headspace sample passes through.

The sample canisters, needle assembly, and headspace sample volume requirements ensure that a representative sample is collected. When an estimate of the available headspace volume can be made, less than 10% of that volume should be withdrawn.

3.0 Limitations and Interferences

No limitations or interferences have been identified.

4.0 Safety

- 4.1 Safety concerns regarding chemical and radiation exposure should be considered. Training regarding proper storage, usage, and disposal of chemicals is recommended. See Chapters 3 and 4 for a complete discussion of these issues.
- 4.2 Using the direct canister sampling apparatus requires that sample canisters be transferred into and out of a sampling area that may be contaminated by radionuclides. The following steps are general guidelines for this transfer.

Note: Each sampling site must obtain approval from appropriate operations and/or transportation personnel for proper radiological controls.

1. Sample canisters to be sent into a contaminated area are prepared by taping all external surfaces, except for the valve handle, with duct tape.
2. Each sample canister is placed in a plastic bag and taped for sealing.
3. After a sample is collected, the plastic covering of the sample canister is wiped, and a radiation level reading is obtained.
4. Contaminated plastic and tape should be properly discarded.

5.0 Apparatus and Materials

- 5.1 **SUMMA™ Canister Headspace Gas-Sampling Apparatus:** Figure 1 illustrates the direct canister sampling equipment. The numbered components in Figure 1 correspond to the numbered components described in the text below. This figure shows a 1/8-in. stainless steel (SS) needle (1) fitted via a reducer (2) to the 1/4-in. inlet of a 0.5-micron sintered metal filter (3). This filter is connected to the Swagelok® fitting on the

SUMMA™ canister (5) valve via a Swagelok® to VCR® adapter (4). The VCR® fitting, with its disposable metal gasket, makes an ideal reusable connector. The combined low internal volume of these components should ensure that a representative headspace gas sample is collected. A dial pressure/vacuum gauge is mounted on each sample canister used for direct canister sampling. The direct canister sampling apparatus components are listed in Table 1.

Figure 1. Direct Canister Headspace-Sampling Apparatus

- 5.2 Sample Canister.** A sample canister is a leak-free welded SS SUMMA™ pressure vessel with a Cr-NiO-passivated interior surface, bellows valve, and dial pressure/vacuum gauge. All sample canisters have VCR® fittings for connecting to sampling and analytical equipment. A dial pressure/vacuum gauge on a sample canister indicates if the canister has leaked.
- 5.3** SUMMA™ canisters have been used in the past for collecting VOC samples and have a demonstrated sample storage stability for many specific VOCs (EPA 1988; Oliver et al. 1986). Two sizes of canisters (150 mL and 250 mL) are used to collect headspace gas samples.

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Table 1. Direct Canister Sampling Apparatus: List of Major Components		
Component	Component Description	Purpose
1	1/8-in. SS tubing w/sharpened tip	Pierce innermost layer of confinement
2	1/4-in. to 1/8-in. reducer	Adapt needle to filter
3	Compact in-line filter (0.5- μ m sintered SS)	Prevents particulate contamination from entering sampling apparatus
4	1/4-in. Swagelok® to VCR® adapter	Allows repetitive leak-tight connection using disposable metal gasket
5	SUMMA™ canister with bellows valve and dial vacuum/pressure gauge	Sample container

5.4 Pressure and Temperature Measurement Apparatus. When using the SUMMA™ canister sampling method, sample canister pressure and ambient pressure are monitored and recorded during sampling operations. Ambient temperature is also monitored and recorded.

5.4.1 Pressure Gauges. A Fortin barometer is used to monitor ambient pressure, while a dial pressure/vacuum gauge is used to monitor sample canister pressure.

5.4.1.1 Ambient Pressure Sensor. The ambient pressure sensor is a full-range Fortin barometer, or equivalent, with a range of approximately 500 to 800 mm Hg. It is kept in the sampling area. Its resolution is 1 mm Hg, and its calibration is traceable to National Institute of Standards and Technology (NIST) standards. A dual-scale thermometer should be included on the barometer case for temperature corrections.

5.4.1.2 Dial Pressure/Vacuum Gauge. This type of gauge is helium leak tested to 1.5×10^{-7} standard cc/sec, has all stainless steel construction, and is capable of tolerating temperatures to 125°C. The gauge is able to indicate 100 psig pressure to a vacuum of 30 in. of Hg.

5.4.2 Thermometer. The thermometer is a NIST-traceable mercury thermometer, total immersion type, laboratory grade, with N₂ above the Hg. It has permanent stain markings in the approximate range of -30° to 50°C, with a resolution of 1°C.

6.0 Preplanning

Studies to characterize TRU waste require careful planning to prepare facilities, develop written documentation, secure laboratory support, and evaluate data.

7.0 Reagents, Preservation Measure, and Handling

All sampling equipment components that come into contact with headspace sampling gases must be constructed of relatively inert materials, such as SS or Teflon®. A passivated interior surface on the SS components is recommended. Sampling holding times and storage conditions should conform to the requirements specified in Table 2.

Table 2. Headspace Sampling Containers and Holding Times

Parameter	Container	Minimum Drum Headspace Sample Volume ^(a) (mL)	Laboratory Field Holding Temperature	Holding Time ^(b) (days)	Shipping Allowance (days)	Holding Time ^(c) (days)
Gases	SUMMA™ Canister	100	Ambient	4	2	28
VOCs	SUMMA™ Canister	250	0 to 40°C	4	2	28
NO _x ^(d)	SUMMA™ Canister	100	Ambient	4	2	28

(a) Alternatively, if available headspace is limited, a single 100-mL sample may be collected for determination of VOCs and gases.

(b) From time of headspace sample collection to shipment.

(c) This is a programmatic-based maximum holding time. Holding time begins at validated time of sample receipt.

(d) A separate headspace sample will not be required if mass spectrometry is used for inorganic gas analysis.

8.0 Method

8.1 Procedures for Cleaning the SUMMA™ Canister Sampling Apparatus. Procedures for cleaning the sampling apparatus are provided to ensure that the sample is representative. This is accomplished by reducing the possibility of contamination from manufacturing impurities or ambient air. Using these cleaning procedures will also reduce the possibility of cross-contamination between sampling operations. These procedures are as follows:

- Section 8.1.1 is a procedure for cleaning the individual components of the sampling apparatus before assembly.
- Section 8.1.2 is a procedure for cleaning the needle and filter between samples.

Note: Needles and filters may be discarded after each sampling operation.

8.1.1 Initial Sampling-Apparatus Cleaning and Leak-Check. Before assembly, components of the sampling apparatus are inspected and thoroughly cleaned, using the following procedure.

Note: Parts received free of contamination, as stated or certified by the manufacturer, may be exempted from this cleaning procedure at the discretion of sampling personnel.

1. Stainless steel parts and fittings are placed in a beaker of reagent-grade hexane in an ultrasonic bath for 15 min. This procedure is repeated with reagent-grade methanol. Stainless-steel parts and fittings may also be cleaned by assembling and forcing steam through them. The SS parts are rinsed with high performance liquid chromatography (HPLC) grade water and dry parts in an oven at 100°C for at least 12 h.
2. The sampling apparatus is assembled and then leak-checked by pressurizing to 1700 mbar and by placing a soap solution on all fittings and connections. For a period of 30 min, a check should be made periodically for bubble production. The sampling apparatus may also be pressurized with helium and leak-checked with a helium detection device.
3. Fittings and connections that leak are tightened until no leaks are observed. From clean spare parts, any fittings and connections that continue to leak should be replaced.

The sampling apparatus is purged with humid zero air, and open connections are capped for storage.

8.1.2 Needle and Filter Cleaning. This procedure describes the steps for cleaning the needle and filter after headspace gas samples or field reference standards have been collected. With slight modifications, this procedure can also be used to batch clean the needle and filters before use. In lieu of cleaning, the needle and filter may be discarded after collecting headspace gas samples or field reference standards. Refer to Figure 1 for the location of numbered components of the direct canister sampling apparatus.

1. After headspace gas samples or field reference standards have been collected, the needle (1) and filter (3) are detached at the VCR[®] fitting (4), and the VCR[®] gasket is discarded.

Caution: The needle and the filter may be radiologically contaminated.

2. The filter assembly should be removed to an area where it can safely be disassembled and cleaned.
3. The housing of the filter is unscrewed, and the filter element is grasped firmly with a sturdy pair of forceps. The element is pulled firmly to dislodge it from the housing. The element should be discarded properly.
4. The reusable parts are placed in a beaker of reagent-grade hexane in an ultrasonic bath for 15 min. This procedure is repeated with reagent-grade methanol. The needle assembly may also be cleaned by screwing the filter housing together again and forcing steam through the entire assembly. The parts are rinsed with HPLC-grade water and dried in an oven at 100°C for at least 12 h.
5. A new filter element is inserted into the filter, and the body is screwed together tightly.
6. The needle and filter are purged with zero air as the needle and filter are being placed into a zero-air-filled resealable bag.
7. A Teflon[®] plug is pressed over the tip of the needle, and the resealable bag is closed and placed in a box for storage.

8.2 Procedures for Collecting Headspace Gas and QC Samples using the Direct-Canister Sampling Apparatus. Headspace gas and QC samples are collected using the following procedures:

- Section 8.2.1 is a procedure for collecting headspace gas samples.
- Section 8.2.2 is a procedure for collecting field duplicates.
- Section 8.2.3 is a procedure for collecting field blanks.
- Section 8.2.4 is a procedure for collecting equipment blanks.
- Section 8.2.5 is a procedure for collecting field reference standards.

Note: Before sampling, drums are allowed to equilibrate to the temperature of the sampling area for at least 72 h.

Caution: Appropriate site radiological controls must be established before removing the drum lid.

8.2.1 SUMMA™ Canister Headspace Gas-Sample Collection. The sampling method described below employs the SUMMA™ canister sampling apparatus (see Figure 1) to collect headspace gas samples from within poly bags. Sample canisters are evacuated to 0.07 mbar before collecting samples.

1. It should be verified that the sample canister is evacuated by observing the dial vacuum/pressure gauge on the sample canister until the gauge indicates a vacuum of 30 in. Hg.
2. An area is located within the poly bag from which a headspace gas sample can be withdrawn. Care should be taken to avoid placing the tip of the needle in an area where solid material or particulate matter might fill or clog the needle.
3. The cap is removed from the tip of the needle, and the needle is pressed through the poly bag and into the headspace gas. Disturbing the bag should be avoided, if possible. If pulling on the bag is necessary, this should be done in a manner that minimizes the potential for introducing outside air into the poly bag's internal gas space.

4. While holding the needle in the bag's headspace, the sample canister valve is opened to allow headspace gas to expand into the canister.
5. The vacuum gauge on the sample canister should be observed while the sample is being collected. When the gauge indicates zero psig, the sample-canister valve is closed, and the needle is withdrawn from the bag.
6. The date, time, sample canister pressure, ambient pressure, and ambient temperature should be logged on the sample canister tag.
7. It should be noted on the QC sample record that the sample canister contains a headspace gas sample, and the sample canister should be placed in a shipping container.

8.2.2 **SUMMA™ Canister Field-Duplicate Collection.** The following procedure describes the use of the SUMMA™ canister sampling apparatus (see Figure 1) for collecting field duplicate samples. These samples are used to assess the precision of the sampling and analytical process. The procedure for field duplicate collection is similar to that specified in Section 8.2.1 for collecting headspace gas samples. However, when collecting field duplicates, two sample canisters are filled sequentially with headspace gas from within the same poly bag.

8.2.3 **SUMMA™ Canister Field-Blank Collection.** The following procedure describes the use of the SUMMA™ canister sampling apparatus (see Figure 1) for collecting field blanks. Field blanks are used to assess background levels of analytes. Field blanks are collected at a frequency of one per day.

1. A sample canister should be placed near the poly bags; the cap is removed from the tip of the needle, and the sample-canister valve is opened.
2. The sample canister is allowed to equilibrate to ambient pressure; then the canister valve is closed.
3. The date, time, sample-canister pressure, ambient pressure, and ambient temperature are logged on the canister tag.

4. It should be noted on the QC sample record that the sample canister contains a field blank, and the sample canister should be placed in the shipping container.

8.2.4 **SUMMA™ Canister Sampling-Equipment Blank Collection.** The following procedure describes the use of the SUMMA™ canister sampling apparatus for collecting sampling equipment blanks. These samples are used to assess the cleanliness of the sampling apparatus. An equipment blank is collected and analyzed before the SUMMA™ canister sampling apparatus is first used, then at a frequency of one per day. Sampling equipment blanks can be collected by the purge-assembly method described. The purge assembly can be constructed in the laboratory and used to collect equipment blanks for direct-canister sampling. The essential components of a laboratory purge assembly are illustrated in Figure 2.

Figure 2. Purge Assembly Method Schematic

The compressed gas cylinders supply zero air for collection, and the humidifier conditions this gas before collection. The rotameter indicates gas flow rate and is monitored to assure that ambient air is not drawn into the sample canister during

equipment blank collection. The tee in the purge line is adapted for leak-tight connection to the 1/8-in. needle of the direct-canister sampling apparatus.

The following procedure assumes that all valves are closed and that the regulator on the zero-air cylinder has been purged and set to a delivery pressure of 1700 mbar.

1. A sample canister with attached needle and filter to be used for equipment blank collection should be selected (the gauge face plate should be tapped lightly to verify the reading). The reading should be entered on the sample-canister tag.
2. The sampling apparatus needle is inserted into the purge assembly, and the fitting is tightened.
3. The valve on the zero air cylinder is adjusted until the rotameter indicates a flow rate of approximately 1 L/min.
4. The line is purged for several minutes.
5. The valve on the zero-air cylinder is adjusted until the rotameter indicates a flow rate of approximately 10 L/min.
6. The sample canister valve is opened to allow the sample canister to fill as quickly as possible without reducing the flow indicated by the rotameter to zero.

Note: If the rotameter indicates zero flow during this process, then the sample is invalidated.
7. Zero air is continually drawn from the purge assembly until the sample canister pressure gauge indicates zero psig.
8. The sample canister valve is closed.
9. The valve on the zero-air cylinder is closed.
10. The sampling apparatus needle is disconnected from the purge tee.
11. The date, time, sample-canister pressure, ambient pressure, and ambient temperature are logged on the sample-canister tag.

12. It should be noted on the QC sample record that the sample canister contains a blank for sampling equipment, and then the canister is placed in a shipping container.

8.2.5 **SUMMA™ Canister Field-Reference-Standard Collection.** The following procedure describes the use of the SUMMA™ canister sampling apparatus for collecting field reference standards. These samples are used to assess the accuracy of the sampling and analysis process. A field reference standard is collected and analyzed before the sampling apparatus is first used, then at a program-specified frequency. Field reference standards can be collected by the purge-assembly method. The purge assembly can be constructed in the laboratory and used to collect direct-canister field reference standards. The essential components of a laboratory purge assembly are illustrated in Figure 2.

The following procedure assumes that all valves are closed and that the regulator on the reference-standard gas cylinder has been purged and set to a delivery pressure of 1700 mbar.

1. A sample canister with attached needle and filter should be selected to be used for collecting field reference standards (the gauge face plate should be tapped lightly to verify the reading). The reading should be entered on the sample-canister tag.
2. The sampling-apparatus needle is inserted into the purge-assembly tee, and the fitting is tightened.
3. The valve on the reference-standard gas cylinder is adjusted until the rotameter indicates a flow rate of approximately 1 L/min.
4. The line is purged for several minutes.
5. The valve on the reference-standard gas cylinder is adjusted until the rotameter indicates a flow rate of approximately 10 L/min.
6. The sample canister valve is opened to allow the sample canister to fill as quickly as possible without reducing the flow indicated by the rotameter to zero.

Note: If the rotameter indicates zero flow during this process, then the sample is invalidated.

7. Reference-standard gas is continually drawn from the purge assembly until the sample-canister pressure gauge indicates zero psig.
8. The sample canister valve is closed.
9. The valve on the reference-gas cylinder is closed.
10. The sampling apparatus needle is disconnected from the purge tee.
11. The date, time, sample-canister pressure, ambient pressure, and ambient temperature are logged on the sample-canister tee.
12. It should be noted on the QC sample record that the sample canister contains a field-reference standard, and then the canister is placed in a shipping container.

8.3 Calculations

- 8.3.1 When they receive a sample canister, sampling or analytical personnel might discover that the dial pressure gauge, if present on the sample canister, does not indicate the same pressure as the one last logged on the sample-canister tag. Changes in the sample-canister gauge pressure may be the result of four possible occurrences: 1) a leak in the sample canister or sample-canister component (valve, gauge, etc.), 2) damage to the sample-canister gauge during storage or transportation, 3) an ambient pressure difference between the sampling and analysis location, and 4) an ambient temperature difference between the sampling and analysis location.
- 8.3.2 The procedures in section 8.3.3 below should be followed to determine the sample-canister-gauge pressure change expected if ambient pressure and temperature differences exist between the sampling and analysis locations. If the change in sample-canister gauge pressure can be accounted for using the procedures in section 8.3.3, then the integrity of the sample has been maintained. If, however, the sample-canister-gauge pressure change cannot be accounted for by considering ambient pressure and temperature changes, the canister must be leak checked and re-certified for use.

8.3.3 Calculations to Compute Expected Sample-Canister-Gauge Pressure Changes

8.3.3.1 Temperature Change at Constant Ambient Pressure. Sample-canister-gauge pressure changes resulting from a temperature change can be explained by Equation (1):

$$P_2 = \frac{P_1 T_2}{T_1} \quad (1)$$

where

P_1 = the sample-canister internal pressure (ambient pressure plus gauge pressure in in. of Hg) at the time of sampling

P_2 = the sample-canister internal pressure (ambient pressure plus gauge pressure in in. of Hg) at the time of analysis, if the ambient temperature changes from T_1 to T_2 at constant ambient pressure

T_1 = the ambient temperature (degrees Kelvin) at the time of sampling

T_2 = the ambient temperature (degrees Kelvin) at the time of analysis.

According to this equation, increasing the temperature of the canister ($T_2 > T_1$) will increase the internal canister pressure, while decreasing the canister temperature ($T_2 < T_1$) will decrease the internal canister pressure.

8.3.3.2 Ambient Pressure Change at Constant Temperature. A sample canister's dial gauge is expected to indicate a change in pressure if the canister is transported from a high elevation to a lower elevation, or vice versa. The expected change in canister-gauge pressure should be the same as the difference in ambient pressure between the high-elevation site and the low-elevation site, or vice versa.

Changes in sample-canister gauge pressure that result from changes in temperature and ambient pressure are additive. Care, however, must be taken to ensure that the sign (positive or negative) of the calculated gauge pressure changes is accurately assigned.

9.0 Quality Control

9.1 To prevent cross contamination, the needle and filter of the direct canister apparatus are disposed of or, if reused, cleaned between sample collections according to the procedure in section 8.1.2. As a further QC measure, the needle and filter, after cleaning, are purged with zero air, nitrogen, or helium and capped for storage to prevent sample contamination by VOCs present in the ambient air. Field duplicates are collected to assess sampling and analytical precision. Field blanks and field reference standards are also collected.

9.2 Specific sampling steps to ensure that the headspace gas samples are representative include

- Sample-canister cleaning and leak-checking
- Use of sample canisters with a passivated internal surface
- Use of low-internal-volume sampling apparatus
- Small sample volume: low sample volume to available headspace-gas-volume ratio
- Careful pressure regulation in sample canister
- Performance audits
- Collection of field blanks, field reference standards, equipment blanks, and field duplicates.

9.3 **Quality Control for Pressure and Temperature Measurements.** This section pertains to the calibration and certification of equipment and instrumentation used for temperature and pressure measurements. All information related to the calibrations of the pressure and temperatures sensors is recorded.

9.3.1 **Certification Check of the Ambient Pressure Sensor.** The ambient pressure sensor is certified by the manufacturer, using standards or equipment traceable to the NIST. The pressure indication of the sensor is corrected in accordance with temperature indicated by a dual-scale thermometer attached to its casing, if necessary.

9.3.2 **Calibration of Sample-Canister Pressure Gauge.** The dial pressure gauge of each sample canister is certified using standards or equipment traceable to the NIST. Each canister gauge is recertified once per month, or as necessary.

9.3.3 **Calibration of the Mercury Thermometer.** The mercury thermometer is certified using standards or equipment traceable to the NIST.

10.0 Method Performance

Headspace gas sampling in accordance with this procedure is currently underway at the Idaho National Engineering Laboratory. Performance data will be provided as they become available.

11.0 References

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U.S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3rd Edition, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

U.S. Environmental Protection Agency (EPA). 1988. "Compendium Method TO-14, The Determination of Volatile Organic Compounds (VOC) in Ambient Air Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic Analyses." May 1988, Quality Assurance Division, Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina.

ST010(a)

General Method For Sampling Liquids and Solids In Low-Level Waste Storage Tanks

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. If you use this method, please provide the editors of *DOE Methods* with comments.

1.0 Scope and Application

- 1.1 This method is used to sample radioactive liquid (aqueous and organic) and sludge materials (soft and hard) from low-level waste storage tanks with limited access (e.g., 3-in.-diameter access pipe).

- 1.2 A pre-sampling activity is performed to 1) determine the location of air-liquid and liquid-sludge interfaces, 2) determine which sampling activities will be performed, 3) determine the nature of sampling equipment/materials to be used, and 4) make qualitative estimates of radiation levels (inactive tanks only).

- 1.3 The scope and decision-making aspects of applying the method are summarized in Figure 1.

- 1.4 The method has been applied to waste concentrate stored in Melton Valley Storage and the Evaporator Concentrate Storage Tank (MUST) facility and the evaporator service facility located at Oak Ridge National Laboratory. The method has also been applied to inactive waste tanks. Collected samples were used to determine waste chemistry {i.e., major chemical constituents, radionuclides, organics, and possible constituents listed as hazardous under Resource Conservation and Recovery Act (RCRA)}, and general waste characteristics.

2.0 Summary of Method

- 2.1 This method employs several different sampling devices for collecting liquids (i.e., aqueous liquids and organic liquids less dense than water) and sludges (soft and hard) from low-level waste storage tanks.

(a) Points of contact for this method are Mildred Sears (Chemical Technology Division) and Wayne Griest (Analytical Chemistry Division) of Oak Ridge National Laboratory, Oak Ridge, Tennessee).

Figure 1. Scope of Method

- 2.2 For liquids {i.e., aqueous liquids and aqueous liquids in contact with organic liquids > 25 cm (10 in.) thick}, a vacuum pump sampling system is used to pull liquid by suction through teflon tubing directly into precleaned glass jars (250 mL) that contain teflon-lined lids.
- 2.3 When it is expected that an aqueous layer is in contact with a thin {< 25 cm (10 in.)} organic layer less dense than water, a bottom opening sampler is used to identify the thickness of the organic layer. A specifically designed organic layer sampler consisting of a polyvinyl chloride (PVC) tube with sealed bottom and a lateral tube for liquid intake near the top is used to collect samples {the sampler is specifically designed for MUST and it requires a minimum of 61 cm (24 in.) aqueous or fluid sludge under the organic layer to function properly}.
- 2.4 Soft-sludge samples are collected using a bottom-opening sampler tube. The sampler is capable of collecting a 51-cm (20 in.)-long core sample. For shallow-sludge layers, composite samples are collected and sonicated to obtain sufficient amounts of material.
- 2.5 Hard-sludge samples are collected with a commercial "auger-type bit" device (custom made by Arte Manufacturing and Supply), steel pipe (barrel), sharpened blades at the bottom, a gate valve to hold the sample in, a vented cap, and handle sections. Alternatively, a backup to the commercial device can be used for collecting very thick sticky sludges. The sampler consists of a stainless steel pipe that has a sharp, machine-bevel cutting edge on one end and is threaded at the other end so that it can attach to a handle.
- 2.6 In general, containerized samples are placed in plastic bags, sealed with tape, and placed in a shielded container (as needed) for transport to analytical laboratories or storage
- 2.7 Equipment should be decontaminated before and after sampling to prevent contamination of samples and to reduce radiation exposure to personnel.

3.0 Limitations and Interferences

- 3.1 The high-efficiency particulate air (HEPA) filter may hamper the reciprocating pump's suction capability (although this has not been observed for lifts of 3.1 m to 5.5 m (10 to 18 ft) when collecting liquid samples {waste solutions are viscous, and the sample must be lifted by suction a height of 3.7 m (12 ft) or more}. In such cases, the pump has been operated without the filter (see section 2.2).
- 3.2 Components of the method are currently designed to sample only organic liquids that are less dense than water. (Note: In tanks with sludge, dense organic liquids, if present, are sampled with the sludge. In the absence of sludge, dense organic liquids may be obtained in a liquid tank-bottom sample.)

4.0 Safety

- 4.1 Sampling shall be conducted during dry weather unless proper shelter is provided.
- 4.2 Proper training is important. Training should include 1) handling low-level, transuranic (TRU), and mixed wastes, 2) using respirators, and 3) knowing project-specific procedures.
- 4.3 For handling radioactive wastes, trained chemical operators should wear protective clothing while conducting sampling activities.
- 4.4 Pencil dosimeters and finger rings are recommended for all project team members who directly handle the filled sample containers.
- 4.5 Sampling activities should be continuously monitored by radiation protection personnel. Air sampling is recommended.
- 4.6 Plastic sheeting, absorbent paper, and pans should be used to confine the radioactive materials and prevent contact with clean surfaces. Waste wipes and materials used to wipe down handles and sampler assemblies should be placed in a plastic bag. Appropriate spill containment and clean-up materials should be maintained and readily available within the work area.
- 4.7 The pump for sampling liquids (section 2.2) was arranged with a safety surge bottle as backup if an overflow should occur, thus minimizing the potential for contaminating the pump. A small cartridge-type HEPA filter was installed on the pump as a precautionary measure, although no airborne radioactive emissions have been detected by air-monitoring personnel when the system has been used without a filter.

5.0 Apparatus and Materials

- 5.1 A Markland Model 10 Sludge Level Detector
- 5.2 A vacuum-pump liquid sampling system consists of the following components (Figure 2):
 - 5.2.1 Reciprocating vacuum pump with attached small cartridge HEPA filter (standard respirator type).
 - 5.2.2 Wide mouthed bottles {250 mL pre-cleaned and, if necessary, fit in standard lead pig (e.g., I Chem bottles)} with Teflon[®]-lined lids. Surge bottles are 4 L (1 gal) in size and are reused. Additional bottles may be necessary if 1) replicate samples are required, 2) more of the same sample is needed, and 3) more than one level in the tank is being sampled.

Figure 2. Liquid Sampling System

- 5.2.3 Rubber stoppers (two-hole, replaced each time tubing is changed) are needed to interconnect system components and link system to teflon sampling tube.
- 5.2.4 A valve placed between pump and safety surge bottle to vent system.
- 5.2.5 A pan (e.g., lid of big can) with blotter paper to contain the sample bottle. A pan (e.g., a big can) for the safety surge bottle.

- 5.2.6 Premarked and cut Teflon[®] tubing {6.3 mm (1/4 in.) with stainless steel pipe nozzle 1 cm (3/8 in.) OD x 10 cm (4 in.) long}; stainless Swagelock fitting to attach nozzle to teflon (see section 6.5) and associated stainless steel weight for each sample to be collected.
- 5.3 A sampler (designed for MUST tanks; may not be suitable for all tanks) for collecting a thin organic layer (Figure 3).
- 5.4 A soft-sludge sampling device (Figure 4) for collecting soft sludges and for detecting a thin organic-liquid layer.
- 5.5 A commercial hard-sludge sampling device (Figure 5) for collecting hard sludge or sludge with a sticky-mud consistency.
- 5.6 A sampling device for collecting samples of sludges that are very thick and sticky (if insufficiently sticky, sample will fall out of sampler).
- 5.7 Wipes for wiping off sampling equipment.
- 5.8 Plastic bags (clear plastic and custom made with heat-sealed bottoms for soft-sludge samples), PVC containers (auger-bit sampler only), tape and labels for packaging samples and disposing of solid waste. Cans for soft-sludge samples custom made by welding two paint cans together.
- 5.9 Pigs, paint cans, and shielded (if necessary) stainless carriers for sample transport.
- 5.10 Packaging material (as appropriate) to stabilize samples in pigs and cans.
- 5.11 Detergent cleaner and deionized water for precleaning and decontaminating equipment.

6.0 Preplanning

- 6.1 If wastes have recently been transferred into the storage tank, the tank's contents should be aerated to agitate and mix the liquid wastes before sampling. The air spargers should be left on for at least 24 h (1 day). After mixing, the air spargers should be turned off, and the solids should be allowed to settle for at least 6 days before measuring interfaces or collecting samples.
- 6.2 A presampling survey should be conducted at least 1 day in advance of collecting samples. During the survey, the air-liquid and the liquid-sludge interfaces should be located using a Markland sludge-level detector, thus establishing the depth of the supernatant liquid. Specific steps in conducting the survey are as follows:

Figure 3. Organic Layer Sampler

- 6.2.1 Tank access is opened. Radiation levels should be monitored as the access is opened. (Note: Other requirements may exist based on the specific nature of the tank.)

Figure 4. Soft sludge Sampler (Sears et al. 1990)

Figure 5. Hard Sludge Sampler (Sears et al. 1990)

- 6.2.2 To measure the air-liquid and air-sludge interface, the sludge level detector (Markland) should be raised and lowered slowly and carefully to minimize disturbing the liquid-sludge interface and any stratified liquid layers. Also, a check should be made for the presence of immiscible or stratified layers (e.g., organic layers), and any interfaces that are observed should be measured (device "beeps" when it passes an interface, at which time depth is noted from cable or tape markings).
- 6.2.3 The distance from the top of the tank opening to the liquid surface and the distance from the top of the tank opening to the liquid-sludge interface should be recorded in the log sheet. If immiscible or stratified layers are observed, the distance from the top of the tank opening to the interface should be recorded.
- 6.2.4 The detector head and cable should be wiped down with cleaner and wipes as described in section 8.9.1.1.
- 6.2.5 The tank access should be closed. Note: Requirement is tank specific (i.e., in some cases, the access can be left open overnight for sampling the next morning).
- 6.3 The information from the survey should be evaluated, and final plans should be made for collecting samples. This should include a review of the radiation protection measures needed.
- 6.4 **Preparation of Sampling Equipment.** From the liquid depth as determined in step 6.2.3, teflon tubing should be cut to the lengths specified by the distance from the supernatant liquid to the sample bottle plus depth (for a thick organic layer sample, the depth is the midpoint of the organic layer). The pieces of tubing should be premarked with tape to indicate when the appropriate level has been reached in the tank. A stainless steel weight (or nozzle) should be attached to the zero end (end going into the tank) of the tubing. The sample bottles should be labeled
- 6.5 Sampling equipment must be cleaned and allowed to dry before each use as described in section 8.10.
- 6.6 Electrical power (110V) should be provided at the site.
- 7.0 **Reagents, Preservation Measures, and Handling**
 - 7.1 Care should be taken to keep the samples upright during handling and transport.
 - 7.2 Based on sampling constraints, safety factors, and analytical measurements to be made, preservation needs and holding times should be reviewed for applicability.

8.0 Procedure

- 8.1 Radiation levels should be monitored as the tank access is opened and work is performed. The radiation level at the tank access should be recorded on the data-collection form.
- 8.2 Samples should be collected in the order 1) aqueous liquid samples, 2) organic layer samples (if present), and 3) sludge samples. Note: Sampling in this order minimizes the potential for contaminating the aqueous phase with particulates from the sludge or an organic emulsion.
- 8.3 **Liquid Sampling (aqueous and thick organic liquid layer)**
- 8.3.1 A vacuum pump sampling system will be used to take liquid samples from the waste tanks.
- 8.3.2 The Teflon[®] tubing should be lowered slowly (see section 6.4 for sample tubing/ bottle preparation) into the tank to the predetermined level. The top end of the tubing must be plugged to prevent tank liquid from seeping into the tubing while it is lowered to the predetermined sampling level. The stainless steel weight attached to the lower end of the tubing should keep the tubing vertical during sampling.
- 8.3.3 When the tubing has reached the predetermined depth (for a thick organic layer sample, the depth is the midpoint of the organic layer), the cap is removed from the top of the tubing, the sample bottle is attached, and the vacuum pump is turned on. When the 250-mL sample bottle is nearly full, the pump is turned off and the vacuum remaining in the system is released through the vent valve (see Figure 2). The sample bottle is disconnected and capped. Note: Additional samples are collected based on the nature of the samples (e.g., level of radioactivity) and sample needs.
- 8.3.4 After the required samples have been taken, any remaining liquid in the tubing should be allowed to drain back into the tank. The tubing and weight assembly are removed from the tank and placed in a plastic bag along with the absorbent paper to absorb any residual free liquid. Bags containing the apparatus are sealed and disposed of according to specific U.S. Department of Energy (DOE) site guidelines. The process is repeated for each tank sampling.
- 8.3.5 The exterior of sealed sample bottles should be wiped off to remove any spilled liquid or possible loose contamination. The sample should be prepared for transport according to instructions in section 8.7.1.1. This process is repeated for each tank sampling.

8.4 Detecting and Sampling Thin Organic Layer {<25 cm (10 in.)}

- 8.4.1 The bottom-opening sampler (also known as the soft- sludge sampler) (Figure 4) is used to measure the thickness of and collect a column of liquid at the air-liquid interface to determine whether a relatively thin organic layer is present over the aqueous layer. Before sampling, the plastic bags and the can that will be used to package the sample should be labeled.
- 8.4.2 The sampler sections should be assembled, and the sampler alignment should be checked to ensure that the sampler operates properly. With the handle in position A (Figure 4), the sample collection tube should be sealed by depressing the handle completely until it contacts the locking hole lug. (**Note:** The handle must always be depressed when moving from position A to prevent damage occurring to the gasket at the bottom of the sample collection tube.) The sample collection tube should be opened by turning the handle to position B and raising the handle until hole A aligns with the locking hole. The small Allen screw should be checked to ensure that it is removed from the vent hole at the side of the PVC sample collection tube.
- 8.4.3 The opened sampler should be submerged until the bottom is approximately 20 cm (8 in.) below the liquid surface. If an organic layer more than 10 cm (4 in.) thick is suspected, the sampler should be submerged until the bottom is approximately 13 cm (5 in.) below the organic-aqueous interface and not more than about 48 cm (19 in.) below the air-liquid interface. The bottom of the sampling tube should be sealed. The soft sludge sampler is then raised to the surface. The sample should be visually inspected for immiscible phases. If an immiscible (i.e., organic) layer is observed on the top of the aqueous supernate, the thickness of the organic layer in the sample collection tube should be inspected and recorded. If no immiscible phase is present, the sampler should be returned to the tank at the point where it was pulled; then the liquid should be released, and the sludge should be sampled.
- 8.4.4 If an organic phase is present, the outside of the sampler tube should be wiped, the Allen screw put back into position, the handle removed, and the top of the sampler tube capped.
- 8.4.5 The sample should be prepared for transport according to instructions in step 8.7.1.2.
- 8.4.6 A second (larger) sample of the organic phase should be collected using the special organic sampler (Figure 3). The handle of the sampler is the same as that used with the soft-sludge sampler (Figure 4). The handle should be premeasured

and marked with tape the appropriate distance for the lateral tube to reach the liquid organic surface. The cap should be removed from the lateral tube and the Allen screw from the side. The plastic bags and the can that will be used to package the sample should be labeled.

- 8.4.7 The sampler should be lowered until the lateral tube reaches the liquid surface. The sampler is held in that position for 30 sec to ensure that the sampler has filled with liquid. After 30 sec, the sampler should be carefully removed from the tank, maintaining the sampler in the vertical position. The lateral tube is capped with a 2.5-cm (1 in.) national pipe thread (NPT) pipe cap, and the sampler is wiped down as it is removed from the tank. The sample collection tube is unscrewed from the handle. A 2.5 cm (1-in.) NPT pipe cap is placed on the top of the collection tube, and the Allen screw is replaced in the side of the collection tube.
- 8.4.8 The sample should be prepared for transport according to instructions in step 8.7.1.2.
- 8.4.9 If the height of the organic phase is less than one third of the length of the organic sampler tube, a second sample should be taken. (Note: This may be required to meet the sample needs of the analytical lab.)
- 8.4.10 The handle should be decontaminated as described in step 8.9.4.

8.5 Soft-Sludge Sampling

- 8.5.1 The instructions in steps 8.4.1 and 8.4.2 should be followed for preparing the bottom-opening sampler to sample sludges. {Note: If the sludge depth is suspected to be more than 48 cm (19 in.), or if the sampler has been lowered 48 cm (19 in.) from the top of the sludge without reaching the bottom of the tank, an attempt should not be made to collect more than a 51 cm (20 in.) core with the first sample. One or more additional samples will be required in the same or adjacent hole (see section 8.5.6)}.
- 8.5.2 The sampler should be lowered slowly to the bottom of the tank. After the sample has been taken, the sample collection tube should be sealed by raising the sampler assembly approximately 3.2 mm to 6.4 mm (1/8 to 1/4 in.), completely depressing the handle, rotating to position B, and raising the handle until hole B aligns with the locking hole. The locking pin should be reinserted.
- 8.5.3 While radiation levels are monitored continuously (survey meter should be placed near components as they are withdrawn) the sampler should be carefully

removed from the tank, maintaining the sampler in the vertical position. As they are withdrawn, components should be sprayed with a hand-held sprayer containing de-ionized water, allowing the residue to drain back into the waste tank. The outside of the sampler components should be wiped down as they are removed from the tank. Wipes should be placed in a plastic bag.

- 8.5.4 The sample collection tube should be unscrewed from the handle, and the small Allen screw in the side of the sampling tube should be replaced. A 2.5-cm (1-in) NPT pipe cap that has been prelabeled should be placed on the top of the sample collection tube.
- 8.5.5 The sample should be prepared for transport according to instructions in 8.7.2.
- 8.5.6 In the event that sludge depth is >48 cm (19 in.), a second sample is collected according to the following guidelines:
 - 8.5.6.1 With the sampler tube in the closed position, the sampler is lowered until its bottom tip is approximately 2.5 cm (1 in.) above the lowest point previously sampled. The sampler tube is opened, the sampler is lowered, and the sample is collected. Samples are continually collected as above at successively lower depths until a hard surface is encountered. The depth the level resistance was encountered should be recorded.
 - 8.5.6.2 If solids fill less than 2/3 of the sampler from the first sampling (8.5.6.1), a second sample should be taken from a different hole as much as possible to obtain a larger quantity of solids.
 - 8.5.6.3 Samples should be removed and packaged as described in 8.7.2, and sampling equipment should be decontaminated as described in 8.4.10.

8.6 Hard Sludge Sampling

- 8.6.1 If hard sludge is encountered, a commercial hard-sludge sampler (Figure 5) containing an auger type bit should be used. Alternatively, a backup to the commercial sampler can be used (Figure 6 can be used for very thick, sticky sludges—see section 8.6.1.2).

8.6.1.1 Commercial Hard Sludge Sampler

- The sampler sections and handle should be assembled. The PVC container and the can that will be used to package the sample

should be labeled. The PVC container should be placed near the sampling port.

- The sampler is lowered into the tank. When the sampler reaches the hard sludge, the cross handle is turned to cut the sludge. Only manual pressure should be used and not force.
- After the hard sludge has been cut, the sampler is removed from the tank. Gentle water spray is used to rinse the outside, and the handle and the outside of the sampler are wiped down as the assembly is removed from the tank. The cutting blades must not be wiped. The handle is removed, and the sampler is placed into the PVC container. The PVC container is sealed with the cap. The sample is prepared for transport according to instructions in 8.7.3.1.
- The sampling equipment should be decontaminated as described in sections 8.9.3 and 8.9.4.

8.6.1.2 Alternate Hard Sludge Sampler

- The handle sections should be assembled and attached to the sampler. The stainless steel container and a "paint" can with bail handle should be labeled (used for secondary containment inside stainless steel container).
- The sampler is lowered into the tank. The sampler is forced into the sludge by pushing down or twisting the handle. No impact force should be used, and no more than one person at a time should be allowed to push on the sampler.
- The sample container should be positioned near the tank port.
- The sampler assembly should be removed from the tank, wiping down the mast sections and removing all but the last mast section as they clear the tank.
- The final mast section and hard-sludge sampling device should be lifted from the tank, and the sampler should be inserted into the sample container. The mast section should be unscrewed from the sampler. The sample container should be sealed using the cap. Any residues should be wiped from the outside surface

of the container, and the sample should be prepared for transport according to instructions in section 8.7.3.2.

- Sampling equipment should be decontaminated according to instructions in sections 8.9.3 and 8.9.4.

8.7 Sample Packaging

8.7.1 Liquid Samples

8.7.1.1 Liquid sample bottles should be placed in plastic bags that are then sealed with tape. The radiation level of the bagged sample should be measured, and then the sample should be placed in a wire-handled lead pig (wire-handle used in case sample had to be manipulated in hot cell) for transport. The container should be labeled with information on the radiation level. The radiation level at the surface of the pig should be monitored. For a radiation level equal to or less than 1m Sv/h (100 mrem/h), the sample can be transported in the pig.

8.7.1.2 The organic sampler tube should be placed in the prelabeled plastic bag that is then taped shut. The bagged sample should be placed into a paint can for transport. For radiation levels greater than 1m Sv/h (100 mrem/h), the paint can with crumpled plastic for padding should be placed into a shielded transport carrier.

8.7.2 **Soft Sludge Sample:** The sample collection tube should be placed in the prelabeled plastic bag that is then taped shut. The wrapped sample tube is placed in a second bag, the bag is closed, and then the wrapped sample is placed in the pre-labeled can. The packaged sample should be placed into the shielded transport carrier.

8.7.3 Hard Sludge Samples

8.7.3.1 The commercial hard-sludge sampler should be placed into a PVC container, and the container should be placed in a can. The can should be placed into the shielded transport carrier. The wipes should be placed in a plastic bag.

8.7.3.2 For alternate hard-sludge sampler, the sample container should be wrapped in a plastic bag and placed into a "paint" can. The packaged sample should be placed into a stainless steel transport carrier.

8.8 Sample Transport to Laboratory/Storage

Sample transport is done according to the radiation level of the sample, where it is going, and DOE and site regulations.

8.9 Decontamination of Sampling Equipment

8.9.1 Sludge Level Detector

8.9.1.1 The detector head and cable should be wiped down with cleaner and wipes after use in each tank. Visible contamination and oils should be removed.

8.9.1.2 The detector should be checked for radioactivity.

8.9.2 Liquid Sampling Equipment

8.9.2.1 Stainless steel tubing should be rinsed with deionized water and methanol and allowed to dry before use.

8.9.2.2 Teflon tubing used as purchased.

8.9.2.3 Organic layer samplers and bottles should be cleaned with tap water and "Micro" detergent, rinsed with tap water, and then rinsed well with deionized water. After drying, sampler/jars should be placed in plastic bags or wrapped in plastic to keep equipment clean until use.

8.9.3 Soft-Sludge and Hard-Sludge (except for handles) Sampling Equipment

Instructions in step 8.9.2.3 should be followed for cleaning the PVC sludge sample collectors and the plastic containers for the commercial hard-sludge samplers. The soft-sludge sampler should be stored with the bottom open so the probe does not indent the gasket.

8.9.4 Cleaning Sludge Sampler Handles

8.9.4.1 Before each tank sampling, the outside of the sampler handles should be cleaned with cleaner and wipes. The wipes should be placed in a plastic bag. Between each tank sampling, components should be rinsed with water and residues sluiced into the tank. Also, equipment should be cleaned before storage.

- 8.9.4.2 If sludge has entered the handle interior, an attempt should be made to wipe it out, and the radioactivity level should be checked. If the handle cannot be cleaned satisfactorily in the field, the handle should be wrapped in plastic and returned to a laboratory facility for decontamination.

9.0 Quality Control

Insufficient samples should be occasionally collected. Efforts should be made to conduct routine visual inspections of all samples (e.g., liquids in glass jars, soft-sludge sampler-clear PVC, homemade hard-sludge sampler, look-down tube, commercial sludge-sampler radiation survey) to ensure that a sample has been collected. Liquids can be resampled; however, sludge samples are constrained by the tank design.

10.0 Method Performance

Information not available.

11.0 Reference

Sears, M. B., J. L. Botts, R. N. Ceo, J. J. Ferrada, W. H. Greist, J. M. Keller, and R. L. Schenly. 1990. *Sampling and Analysis of Radioactive Liquid Wastes and Sludges in the Melton Valley and Evaporator Facility Storage Tanks at ORNL*. ORNL/TM-11652. Oak Ridge National Laboratory, operated by Martin Marietta Energy Systems, Inc., Oak Ridge, Tennessee.

Chapter 8

Organic Methods

Scope and Application

This chapter summarizes guidance pertinent to U.S. Department of Energy (DOE) sites for successfully characterizing organic constituents in environmental and waste management (EM) samples. It presents information that applies specifically to organic methods and directs the reader to other pertinent information related to safety, quality control (QC), and sampling techniques within the methods compendium document.

The scope of this chapter includes methods available for determining total organic carbon (TOC), total organic halides (TOX), volatile organics, semivolatile organics, thermally labile organics and/or nonvolatile organics in soil, water, air, and tanks, with an emphasis on radioactive samples. Both field and laboratory methods are covered, including screening, cleanup, sample preparation, and analysis. Examples of organic methods include (but are not limited to) gas chromatography (GC), high-performance liquid chromatography (HPLC), mass spectrometry (MS), infrared spectroscopy (IR), purge and trap, and immunoassays.

The mixed-waste samples typically found at DOE sites include those that frequently contain organics that were used in processing radionuclides, but that are not U.S. Environmental Protection Agency (EPA) "targeted compounds." Examples include ethylenediaminetetracetic acid (EDTA), N-(2-hydroxyethyl)ethylene-diaminetriacetic acid (HEDTA), citrate, tributyl phosphate (TBP), lard oil, hexone (methyl isobutyl ketone), methyl ethyl ketone, and formaldehyde. Analyses for these organics are important because they can strongly

influence the transport of the associated radionuclides, as well as the transport of targeted organic compounds, in the environment. Therefore, their presence needs to be considered in remediation technology, and their characterization is included within the scope of organic methods.

Analyses for organic constituents in wastes and environmental samples from DOE sites are typically performed using standard EPA procedures, such as those from SW-846 (EPA 1992) and contract laboratory programs (CLPs) (EPA 1991), or other nationally recognized procedures {e.g., procedures from the American Society for Testing and Materials (ASTM)}. Many of these recognized procedures are generally applicable without modification to the analysis of nonradioactive samples. However, because samples from the DOE sites are often mixed waste (hazardous and radioactive waste), these procedures may need to be modified. This chapter supplements EPA and ASTM procedures by including methods that range from adaptations to these standard procedures (Adapted/Organic) to new methods based on new technologies.

Limitations

It is important to understand the limitations inherent in organic sample preparation and instrumental analysis. Certain general precautions common to most analytical organic laboratories are mentioned in this section as are limitations and matrix effects caused by the association of radioactive materials with organics, a condition that is common at DOE sites. Sampling and safety considerations are also included.

Precautions

Analysis for trace organics requires that certain precautions be observed. Some of these precautions are summarized below as a guideline to general good practices in organic laboratories.

1. Plastics generally cannot be used because of the potential for contaminant absorption into the polymer, or the likelihood of phthalate or other contamination from the polymer. Sample containers should be of glass or Teflon[®] with glass or Teflon[®]-lined enclosures. Teflon[®] should be used with caution because some volatile organics may preferentially absorb into the polymer. Aluminum foil (rinsed with clean solvent) may be used as a liner for samples that are not highly acidic or basic. Tubing that may contact samples or vapors from samples should be made of Teflon[®] or stainless steel (solvent washed), not plastic.
2. Clean glassware/Teflonware is essential to prevent contamination. Considerations of the DOE principle of "as low as reasonably achievable" (ALARA), as well as the relative costs of cleaning versus disposal, should be considered for glassware used with high-level wastes. Glassware cleaning methods are discussed in detail in SW-846 (EPA 1992).
3. Glassware/Teflonware should be covered with aluminum foil to prevent contamination from lab dust. During sample preparation and analysis, samples should be protected from lab dust as much as possible.
4. A clean water source is essential in the lab. An example is the MilliQ water system.

Blanks should be run periodically to ensure that contamination is not a problem.

5. All solvents used in analysis should be GC or HPLC grade or equivalent. Blanks should be run to ensure that contamination is not a problem.

Effects of Radioactivity on Organic Analyses

Radioactivity generally affects organic analyses in a number of ways:

1. Radioactivity presents additional safety constraints for handling materials, constraints that may require adaptations of standard methods. The direct analysis of samples might be limited by radiation exposure levels. Using hot cells or gloveboxes to prepare samples may minimize the exposure of personnel to radioactivity, but it might also restrict the sample preparation or analysis methods available.
2. Without modifying the analytical procedure, radioactivity may lead to the radioisotopic contamination of expensive instrumentation. More calibration checks and more maintenance may be needed as well. Additional sample preparation to isolate the organic fraction of the sample from the radioactive fraction could help to circumvent this problem.
3. The presence of radioactivity may increase the time required for sampling and analysis, thereby exceeding standard QC time limits. Even simple tasks may require significantly greater amounts of time to complete, a factor that could lead to losing volatile organics in

samples. At times of high sampling activity or manipulator maintenance, longer storage times that may exceed SW-846 holding time limits may be required (Winters et al. 1990).

4. The presence of radioactivity may impose a limitation on sample size that could affect quantitation limits. For example, standard EPA volumes of 1 L of sample for liquid-liquid extraction of semivolatile organics may contain dangerous levels of radioactivity. Tomkins et al. (1990) reduced the sample volume to 20 mL to allow handling the sample in a "contamination zone" radiochemical hood, with a consequent reporting limit 50 times greater than the conventional SW-846 method.
5. Glassware that is specified in EPA procedures may not be adequate because of certain characteristics of the samples. For example, aqueous samples from waste storage tanks sometimes foam upon sparging during analysis for volatile organics; with radioactive samples, the vessel used must be large enough to accommodate foaming and minimize contamination (Tomkins et al. 1989).
6. Storage conditions applicable to radioactive samples are not necessarily acceptable for organic samples. Highly radioactive samples are heat-generating, making it difficult to store them at 4°C. Samples in hot cells are stored at room temperature rather than at 4°C. The high airflow rates in the hot cell, high temperature, and prolonged exposure to the environment may lead to loss of volatile organics (Winters et al. 1990).
7. The use of hydraulic fluids and lubrication greases during sampling must be taken into account when reporting analytical results.

Additional sample preparation steps are needed to eliminate interferences introduced by the sample-collection method.

8. Because disposal of mixed wastes (liquid and solid, including containers) is difficult and expensive, methods are needed that result in waste minimization.

A number of methods in this chapter have been developed to accommodate the effects described above.

Matrix Effects

Matrix-specific effects may increase analytical difficulties. In some cases, these effects are related to the radioactivity of the samples or to the codisposal of radioactive salts. Significant concentrations of nitrite may generate nitrous oxides upon sample acidification, which, because of their reactivity, may affect the integrity of the samples (Tomkins et al. 1990). Organic complexing reagents present in some samples may make it more difficult to completely isolate the organic fraction of the sample from the radionuclide fraction, thereby increasing the safety hazard and the potential for instrument contamination. The complexity of the mixed wastes could make it impossible to match the detection limits stated in the standard procedures.

Safety

Safety considerations present in organic-chemistry laboratories are complicated by safety concerns generated by the presence of radioactive samples. Radioactivity in samples might require using additional protection (supplied air, specialized clothing) or modifying facilities (special hoods or hot cells). General safety considerations for organic and mixed waste analysis are discussed in Chapter 4 of this

document. Additional specific safety requirements for a particular method are described in the method.

For analyzing samples that may have low-level or medium-level radioactivity, certain precautions must be taken to prevent any material from escaping into the laboratory. For example, the roughing pumps on the mass spectrometer should have high-efficiency particulate air (HEPA) filters and a venting system above the injection port to collect any vapors; both should be vented through a hood. Other instruments should have venting systems as appropriate. As required by the DOE ALARA principle, to minimize radiation exposure and contamination of personnel and facilities, laboratory staff should follow all radiochemical laboratory procedures for handling radioactive samples and for monitoring associated with health physics issues (see Chapter 4).

Sampling Considerations

Large samples are usually obtained in the field so that many different types of analyses can be conducted on one sample. The samples are generally subsampled in the laboratory for a particular analysis so that representative samples are taken. Standards established for subsampling (e.g., grinding and coning and quartering soils) may not be practical for use with highly radioactive samples. Laboratory protocols should be developed to ensure that representative samples are taken. The protocols should incorporate limitations imposed by the radioactive and/or hazardous nature of the samples as well as specific project needs.

Refer to Chapter 7 for details on sampling methods. Recommended sample containers, sample preservation techniques, and holding times should be addressed in the planning process.

Definitions

The definitions included here are specific to organic methods. Refer to Chapter 3 (Quality Control) and the glossary for additional definitions.

For the purposes of analysis, organic compounds are typically divided into three classes: volatile compounds, semivolatile compounds, and thermally labile or nonvolatile compounds. These classes are defined operationally as follows.

Volatile Compounds - Organic compounds with boiling points below 200°C that range from insoluble to soluble in water.

Semivolatile Compounds - Most acidic, neutral, and basic organic compounds that are soluble in methylene chloride and can be eluted without derivatization as sharp peaks from a capillary GC column. Such compounds include polynuclear aromatic hydrocarbons (PAHs), pesticides, pyridines, and phenols.

Thermally Labile Compounds (i.e., compounds that are thermally degraded under GC conditions) or **Nonvolatile Compounds** - Compounds that are typically analyzed by HPLC. Examples of these compounds include nitroaromatics and high-molecular-weight polynuclear aromatic hydrocarbons.

For other definitions related to QC and safety, see Chapters 3 and 4, respectively, or the glossary.

Quality Control

General QC procedures are discussed in Chapter 3, and data quality objectives (DQOs) are discussed in Chapter 1 of this document. Specific QC procedures are found in each method. This section presents a

few guidelines about QC procedures in organic analyses.

Modifications to standard methods presented in this document or in SW-846 should be supported by appropriate QC procedures (e.g., in Chapter 3 of this document) and should meet the objectives of the project (see Appendix B). For example, GC columns can be substituted and temperature programs varied after QC checks of retention times, interferences, and check sample quantitation; traps can be substituted in purge-and-trap (after QC for retention characteristics, trap contaminants, breakthrough volumes, etc.); GC detectors can be substituted in some cases (with consideration of calibration curves, quantitation ranges, interferences).

General terms describing QC elements, such as method proficiency, control limits, laboratory control procedures, method blanks, matrix-specific bias, and matrix-specific precision, are described in Chapter 3. The following definition of surrogate compounds has specific application for organic analysis.

Surrogate compounds are organic compounds that are similar to analytes of interest in chemical composition, extraction, and chromatography, but that are not normally found in environmental samples. As appropriate for the method, each sample (including QC samples, blanks, and standards) should be spiked with surrogate compounds before purging or extraction. Surrogates should be spiked into samples according to the appropriate analytical methods. Percent recoveries are calculated for each surrogate as a basis for determining accuracy and precision of data generated on environmental samples. It should be noted that matrix effects (described earlier under "Limitations") may affect spike integrity; it is important to choose surrogates that are compatible with the matrix.

Standards

Standards should be traceable to the National Institute of Standards and Technology (NIST) or other certified vendor. Storage conditions need to be considered to maintain standard integrity. Standard soil or sludge matrices of known organic analyte content may not be available. Furthermore, no satisfactory way exists to add inorganic analytes to these matrices to mimic the chemical and physical form of the analytes in the field sample.

Cleanup QC

Quality control procedures should be followed for materials used in cleanup techniques. Adsorbents used for cleanup should be checked for analyte recovery by periodically using standards. The method should be optimized for maximum recovery of analytes and maximum rejection of interfering materials.

Immunoassay QC

Appropriate analyte controls should be included with each assay. Timing and temperature are critical factors to consider in designing immunoassay experiments. False positive and false negative rates are important QC parameters to determine.

Instrumental QC

The following guidelines can be applied to analyzing samples by GC, HPLC, GC-MS, IR, etc.

The calibration of each instrument should be verified at intervals specified in the methods. Standard curves should also be generated as specified in the methods. Instrument performance should be veri-

fied as appropriate—e. g., a GC-MS system should be tuned according to instrument specifications.

When applicable for the method, the identification of all analytes should be verified using an authentic standard of the analyte. When authentic standards are not available, identification is tentative.

For GC or HPLC determinations of specific analytes, the relative retention time of the unknown should be compared with that of an authentic standard. For compound confirmation, a sample and standard should be analyzed on at least two columns of different selectivity. Peaks should elute within daily retention-time windows to be declared a tentative or confirmed identification.

For GC-MS determinations of specific analytes, the spectrum of the analyte should conform to a literature representation of the spectrum or to a spectrum of the authentic standard obtained after satisfactory tuning of the MS. The appropriate analytical methods should be consulted for specific criteria for matching the mass spectra, relative response factors, and relative retention times to those of authentic standards.

Data Reporting

The client should specify what is needed in the data report. As a guideline, the following items should be included:

- sample identification
- identification and quantitation of analytes
- sample volume or weight analyzed
- estimate of uncertainty
- matrix-specific detection limit.

If holding times are of concern, the sample receipt date and the sample preparation or analysis date should be specified, whichever is appropriate.

The following should be available in reference files for client review:

- QC data, demonstrating the quality of the measurement process, including available calibrations, surrogate recoveries, performance evaluation results, and blank results (false positive and false negative rates may be appropriate for field screening)
- identification of measuring and test equipment and associated parameters
- preparation and analysis method and associated parameters
- identification of standards
- date of sample prep and analysis
- chain-of-custody information, if applicable
- run log for the analytical session
- procedural deviations
- primary data
- sampling and field notebook information.

Summary of Methods

Methods incorporated in this chapter address the problem of analyzing organic constituents, especially in radioactive samples. Previously accepted methods, such as those in SW-846, are not included in this document. Modified SW-846 methods are included if the modifications are significant. De-

pending on the types of modifications, adapted methods may simply reference SW-846 or may include large parts of the original method if necessary to ensure that the adaptations made can be understood within the context of the procedural steps. In the latter case, the parts from the original method are italicized for ease of reference. It is assumed that the reader has access to standard methods, including those in SW-846.

Table 8.1 summarizes methods provided in this chapter.

References

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Table 8.1. Methods for Analyzing Organic Constituents in Waste and Environmental Samples

Method Number	Title	Summary
OS010	Total Organic Chlorine in Oil: Field Test Kit Method	Polychlorinated biphenyls in transformer oils are determined semi-quantitatively in this field-screening method by measuring the total chlorine content using an ion-selective electrode.
OS020 Rev. 1	Immunoassay for Polychlorinated Biphenyls in Soils	An immunoassay-based field-screening method is used for the semiquantitative determination of PCBs in soils. The method is suitable for radioactively contaminated soils.
OS030	A Photoacoustic Infrared-Based Screening Method for the Detection of Selected Chlorinated Volatile Organic Chemicals in Water	In this field-screening method, volatile chlorinated hydrocarbons are measured in water by purging and analyzing the resulting air sample using a photoacoustic infrared detection method. Infrared energy absorbed by a molecule produces heat, producing an increase in pressure in a closed cell, which is detected as an acoustic signal. The method is rapid and is useful as a monitoring tool to detect changes in analyte concentrations with time.
OS040	Rapid Determination of Volatile Organic Contaminants in Water and Soils by Direct-Purge Mass Spectrometry	This field screening method rapidly measures selected combinations of volatile organic compounds. Water samples or water-methanol extracts of soils/sediments are purged directly over a permeable membrane into a mass spectrometer for quantitative analysis. Careful selection of mass peaks is required to minimize interferences. The method is suitable for moderately radioactive samples.
OS050	Supercritical Fluid Extraction for the Analysis of Contaminated Soils	Nonpolar semivolatile organic compounds are extracted using supercritical fluid CO ₂ and analyzed by capillary GC in this field-screening method. This technique has been demonstrated for PAHs and PCBs and is applicable to soils, sludges, and ashes.
OC010R	Preparation and Cleanup of Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds	Normal paraffin hydrocarbons are removed from samples in which they interfere with analysis by purge and trap - GC. A methanolic extraction of the sample is followed by cleanup with a C ₁₈ solid-phase sorbent cartridge. Sample radioactivity has been found to decrease significantly. The method is suitable for any sample matrix containing excessive quantities of normal hydrocarbons, such as waters, sorbents, or soils.
OP010R	Remote Purge and Trap-Gas Chromatography of Volatile Organics in High-Level Radioactive Wastes	A remote purge-and-trap procedure followed by thermal desorption - GC is used to analyze volatile organic compounds in highly radioactive liquid wastes. A modified purge-and-trap apparatus is described for use in a hot cell.

Table 8.1. (contd)

Method Number	Title	Summary
OP020R	Ultrasonic Solvent Extraction for Analysis of Volatile Organic Compounds in Solid Radioactive Mixed Wastes	Ultrasonic extraction is used to extract volatile organics from solid radioactive wastes that cannot be directly analyzed by purge-and-trap GC-MS because of their radioactivity. The method is suitable for hot cell, glovebox, or radiochemical hood use. Sample radioactivity has been found to be significantly decreased during extraction.
OP030R	Purge and Trap in a Glovebox	A purge-and-trap procedure is used to analyze volatile organics from radioactive samples. A modified purge-and-trap apparatus is described for use in a glovebox.
OP100R	PCBs in Aqueous Radioactive Mixed Wastes Using Solid Phase Extraction Disks and GC-ECD	Polychlorinated biphenyls as Aroclors are quantitatively determined in extracts from radioactive aqueous matrices. Sample radioactivity is significantly decreased during extraction with solid-phase extraction disks, which also minimize laboratory waste generation. The method is suitable for use in a glovebox or hot cell.
OP120R	Reduced-Scale Liquid-Liquid Extraction of Semivolatile Organic Compounds	A reduced-scale liquid-liquid extraction method is used for semivolatile organic compounds in aqueous samples that are too radioactive to be handled outside a hot cell or glovebox in the 1-L volumes required by SW-846 method 3510. Sample radioactivity has been found to be significantly decreased during extraction.
OP130R	Analysis of TCLP Semivolatiles and Pesticides in Radioactive Mixed Waste Sludges	Semivolatile organic (nonacidic) compounds and pesticides from radioactive mixed waste sludges are extracted by sonication and analyzed by GC-ECD. The method is suitable for glovebox and hot cell operation.
OP150R	Ultrasonic Extraction in a Glovebox or Hot Cell	Nonvolatile and semivolatile organic compounds are ultrasonically extracted from solids such as soils, sludges, and wastes. A glovebox or hot cell may be used.
OG015R Rev. 1	Major Nonhalogenated Volatile Organics in Radioactive Aqueous Liquids Analyzed by Direct Aqueous Injection Gas Chromatography	Sample aliquots are taken in a radiochemical glovebox or hot cell to analyze major nonhalogenated volatile organic compounds in radioactive aqueous liquids that cannot be analyzed in a conventional laboratory. The direct aqueous injection-gas chromatography (DAI-GC) method is used to provide data on highly polar, water-soluble organic compounds that are not readily determined by purge and trap.
OG100R Rev. 1	Analysis of Polychlorinated Biphenyls as Aroclors in Solid Rev. 1 Radioactive Mixed Wastes	Waste samples are weighed and extracted in a radiochemical glovebox or hot cell and then subjected to a modified standard GC-electron capture detector (ECD) method for quantification of PCBs (Aroclors). Sample radioactivity has not been found to be appreciable in extracts, which facilitates analysis.

DRAFT

Table 8.1. (contd)

Method Number	Title	Summary
OH100R	Direct Analysis of TCLP Acidic Semivolatile Compounds in Radioactive Liquid Wastes or Leachates Using HPLC with Ultraviolet Absorbance Detection	Leachates and aqueous liquid wastes are directly injected into a reverse phase HPLC column for analysis of acidic semivolatile compounds. This method minimizes both operator exposure to sample radioactivity and laboratory waste generation.

OS010^(a)

Total Organic Chlorine in Oil: Field Test Kit Method

1.0 Scope and Application

This method may be used as a field screening method to determine the concentration of polychlorinated biphenyls (PCBs) in transformer oils by measuring the total chlorine content using an ion selective electrode.

2.0 Summary of Method

Oil samples (5 mL) are reacted with metallic sodium and catalyzed with naphthalene and diglyme to convert the PCBs to sodium chloride. An aqueous buffer solution is then added to the sample and shaken to extract the sodium chloride into the pH stabilized aqueous phase. The aqueous layer is then drawn off, and the total chloride content is measured using a chloride-ion specific electrode. The cell potential measured by the ion-selective electrode relates directly to chloride concentration. The L2000 converts this signal electronically and presents PCB concentration in µg/g (ppm), Aroclor 1242, Aroclor 1260, or Askarel depending on the setting selected. The Askarel setting is used for mixtures of Aroclor 1260 and trichlorobenzene.

3.0 Interferences

- 3.1 Since this method measures total chloride content, inorganic chlorides as well as chlorinated organics are potential interferants and may cause false positives or a positive bias in the result. Samples that are determined to contain PCBs at concentrations greater than the regulated level when using this methodology can be analyzed using an alternate test method. Gas chromatography (e.g., SW-846 method 8080) can be used to confirm the presence and concentration of PCBs or detect false positives obtained using this field method.
- 3.2 Digestion may be incomplete in samples with greater viscosity than transformer oil (e.g., mineral oil). Since this could result in false negative results, great caution should be used when interpreting the results obtained from samples other than transformer oil.

(a) This method was supplied by C. P. Leibman and W. Braustein (Los Alamos National Laboratory, Environmental Chemistry, EM-9, Los Alamos, New Mexico).

- 3.3 Digestion of PCBs may be incomplete if water soluble cutting fluids are present in the oil sample. The sodium reagent available for digesting the oil sample is reduced from reaction with water present in the cutting fluids. This can result in false negatives or results that are biased low. For the same reason, any free water (as second phase) must not be part of the 5-mL oil sample. Adequate sample must be obtained to draw off 5 mL of oil.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to PCBs.

5.0 Apparatus and Materials

- 5.1 PCB/chloride analyzer: Complete L2000 Electronic PCB/Chloride Analyzer (Dexsil Corporation, Hamden, Connecticut), or equivalent
- 5.1.1 Electrode: Chloride-ion specific (Orion 96-17B or Dexsil Cl-01 or equivalent). Note that one is supplied with the L2000 analyzer system.
- 5.2 Disposable pipettes, 5 mL (available from Dexsil Corporation)
- 5.3 Disposable filters, 5 mL (available from Dexsil Corporation)
- 5.4 Automatic pipettor, 5 mL (One is supplied with the L2000 analyzer.)
- 5.5 Glass vials, 20 mL, with screw-cap closures
- 5.6 Test tube rack: Large enough to support 25-mL test tubes (One is supplied with the L2000.)
- 5.7 Vial rack: Large enough to accommodate 20-mL glass vials (One is supplied with the L2000.)
- 5.8 Membrane polishing strips

6.0 Reagents

All of the reagents listed below are supplied with either the analyzer system or with option packages supplied by Dexsil Corporation, Hamden, Connecticut. Refills may be obtained by contacting the company. No catalog numbers are currently available.

- 6.1 Sodium reaction tubes

- 6.2 Extract solution
- 6.3 Rinse solution
- 6.4 Calibration solution
- 6.5 Electrode filling solution

7.0 Sample Collection, Preservation, and Handling

- 7.1 All samples should be considered hazardous and handled accordingly.
- 7.2 Since this method is intended primarily as an on-site field technique, no special handling procedures are required. Should samples be collected for subsequent laboratory analysis by either this method or GC methods, they should be collected in clean glass jars and tightly capped to avoid spillage and contamination.

8.0 Procedure

8.1 Sample Preparation

- 8.1.1 The cap should be removed from the sodium reaction tube, and oil should be added to the 5-mL mark. The cap should be replaced tightly. The bottom ampule in the tube should be broken and shaken well for 10 sec. The top ampule in the tube should be broken and shaken vigorously for 10 sec and occasionally over the next minute while the reaction proceeds.
- 8.1.2 A 5-mL extract solution is added using the 5-mL automatic pipette. The cap is tightened securely and shaken vigorously until the foam and dark color disappear. The tube is vented carefully by partially unscrewing the black cap. The cap is retightened and shaken again for 10 sec. The tube is stood upside down on the flat top of the cap and allowed to settle for 2 min.
- 8.1.3 One of the filter funnels supplied with the L2000 kit should be placed in a 20-mL glass vial and marked with the sample identification. The sodium reaction tube is positioned directly over the top of the funnel and the dispenser nozzle opened. The solution is dispensed by carefully squeezing the sides of the tube just until the first drop of oil appears. The solution is allowed to pass through the funnel, but the funnel is removed before any oil can pass through.
- 8.1.4 The vial should be securely capped until ready to perform analysis.

- 8.1.5 The temperature of the extract should be allowed to equilibrate for 2 min before analysis. This time period has been demonstrated to be sufficient for equilibration.

8.2 Analysis

- 8.2.1 **Preparation of the Electrode:** The electrode should be filled according to the manufacturer's instructions.

The electrode's sensing membrane should be polished at the beginning of each day's use. To do this, a membrane polishing strip, abrasive side up, is placed on a flat surface. One or two drops of rinse solution or distilled water is placed on the strip. With the electrode perpendicular to the strip, the electrode tip should be polished by moving it in a "figure 8" position for about 30 sec. Constant pressure that is not too strong should be applied on the electrode.

- 8.2.2 **Preparation of the Instrument:** The instrument should be plugged in and turned on. The temperature knob should be set to the ambient temperature.

The electrode should be plugged securely into the back of the instrument and the electrode placed into a vial of clean rinse solution. The analytical knob is switched to "mV," and the reading should stabilize in a few minutes at a level greater than 140 mV. The electrode is swirled intermittently if the reading does not exceed 140 mV in a couple of minutes.

- 8.2.3 **Calibration:** A 20-mL vial should be filled about half full with calibration solution.

The selector knob should be turned to "CAL."

The electrode should be removed from the rinse solution, dried carefully with a tissue, and placed in the calibration solution. The electrode is swirled gently for a few seconds and stopped. The start button on the instrument is pushed.

When the "read" light comes on, the calibration knob is adjusted so that the instrument reads "50." The electrode is removed from the calibration solution, wiped dry, and placed in the rinse solution.

If this is the first calibration since the instrument has been turned on, the steps in the preceding two paragraphs should be repeated. The "recalibrate" light will come on when the instrument requires recalibration.

- 8.2.4 **PCB Determination:** The analytical mode (chloride, 1242, 1260, or Askarel) appropriate for this analysis should be selected. The most conservative setting is 1242, and it should be used when the PCB is unknown or when 1242 is suspected. The other two settings should only be used if the analyst knows beforehand (e.g., from prior gas chromatographic analysis of the sample site) that either of these will be the only PCB present.

The electrode is removed from the rinse solution and wiped carefully with a tissue. The electrode is placed in the vial (that has been prepared for analysis as in section 8.1) and swirled gently for several seconds.

The start button should be pressed on the instrument. When the "read" light goes on and the beeper sounds, the result from the LCD readout should be recorded. If a "1" appears to the far left of the LCD readout, the sample contains more than 200 $\mu\text{g/g}$ PCB. The "high range" button should be pushed and held and the concentration will appear. If a "1" again appears in the same position, the sample contains greater than 2000 $\mu\text{g/g}$ PCB.

If a reading from another analytical mode (e.g., chloride, Aroclor 1242, Aroclor 1260, or Askarel) is desired, the knob is simply turned to that position and the result will appear.

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example as outlined in Chapter 3 of this document) and should meet the objectives of the project.

9.2 Quality Control Check Standard

- 9.2.1 **Quality Control Check Sample Concentrate:** A QC check sample concentrate should be prepared by diluting pure Aroclor 1242 in iso-octane to the desired concentration (1000 to 500 $\mu\text{g/mL}$ for a 50 $\mu\text{g/g}$ check sample; 10,000 to 50,000 $\mu\text{g/mL}$ for a 500 $\mu\text{g/g}$ check sample).

Alternatively, the concentrate may be obtained from commercial sources. It may be difficult, however, to obtain concentrates at levels greater than 5,000 $\mu\text{g/mL}$.

- 9.2.2 **Quality Control Check Sample:** A QC check sample should be prepared at 50 $\mu\text{g/g}$ or at an amount appropriate for the project by adding the appropriate amount of QC check sample concentrate to 50 g of clean transformer oil and sonicating for a minimum of 2 h to ensure proper mixing.

A 500 $\mu\text{g/g}$ QC sample may be prepared in the same manner, but the resulting solution should be sonicated overnight (at least 8 h) to ensure homogeneity.

The resulting sample should be treated in the exact manner as the field samples. A QC check sample should be analyzed before analyzing any field samples, after every 10 samples thereafter, and at the end of any series of analyses. The results obtained should fall within 10% of the calculated value. A blank should be run after each check sample.

9.3 Calibration Check Sample. In addition to the calibration procedure outlined in section 8.2.3 above, the calibration should be verified periodically (at the beginning and end of the day's analyses at a minimum) with an independently prepared inorganic chloride solution. This solution may be a commercially prepared solution—but not the same one used to calibrate the instrument—or it may be prepared by dissolving 41.21 mg NaCl in 500 mL of water to get a solution that is 50 $\mu\text{g/mL}$ chloride.

9.4 For each batch of samples processed, a laboratory reagent blank should be analyzed. The presence of PCBs or interferences should be evaluated for data impact before analyzing the samples.

10.0 Method Performance

10.1 A study was conducted using the L2000 for replicate analysis of solutions of Aroclor 1242 at approximately 5, 50, and 500 $\mu\text{g/g}$. The solutions were prepared by spiking Aroclor 1242 into dielectric oil and placing the solutions into an ultrasonic bath overnight. The results presented in Tables 1 through 3 are from seven replicate analyses of solutions at 5 $\mu\text{g/g}$ (near the method detection limit) at 50 $\mu\text{g/g}$ and at 500 $\mu\text{g/g}$ respectively. The 50 $\mu\text{g/g}$ and 500 $\mu\text{g/g}$ levels are routinely used to determine which method of disposal can be used for the electric equipment.

10.2 Analyses of blanks gave readings that were $<2 \mu\text{g/g}$.

11.0 Further Reading

Lavigne, D. 1991. "Accurate, On-Site Analysis of PCBs in Soil - A Low Cost Approach." Seventh Annual Waste Testing and Quality Assurance Symposium Proceedings, Washington, DC.

Leibman, C. P. and W. Braunstein. Validation of Ion Selective Electrode Test Kit Method for PCB Screening. LAUR Report, in process.

Table 1. Recovery of Aroclor 1242 from Dielectric Oil at 5 µg/g

<u>Replicate</u>	<u>Aroclor</u>	<u>Actual Concentration (µg/g)</u>	<u>L2000 Reading Aroclor 1242 (µg/g)</u>	<u>Recovery (%)</u>
1	1242	5.02	6.6	131.5
2	1242	5.02	6.0	119.5
3	1242	5.02	7.0	139.4
4	1242	5.02	6.0	119.5
5	1242	5.02	6.8	135.5
6	1242	5.02	6.4	127.5
7	1242	5.02	5.5	109.6
Average			6.3	126.1
Standard Deviation			0.53	
% Rel. Std. Dev			8.3	

Table 2. Recovery of Aroclor 1242 from Dielectric Oil at 50 µg/g

<u>Replicate</u>	<u>Aroclor</u>	<u>Actual Concentration (µg/g)</u>	<u>L2000 Reading Aroclor 1242 (µg/g)</u>	<u>Recovery (%)</u>
1	1242	50.36	51.7	102.7
2	1242	50.36	52.3	103.9
3	1242	50.36	54.9	109.0
4	1242	50.36	55.3	109.8
5	1242	50.36	55.0	109.2
6	1242	50.36	53.3	105.8
7	1242	50.36	55.3	109.8
Average			53.97	107.2
Standard deviation			1.52	
% Rel. Std. Dev.			2.82	

Table 3. Recovery of Aroclor 1242 from Dielectric Oil at 444 $\mu\text{g/g}$

<u>Replicate</u>	<u>Aroclor</u>	<u>Actual Concentration ($\mu\text{g/g}$)</u>	<u>L2000 Reading Aroclor 1242 ($\mu\text{g/g}$)</u>	<u>Recovery (%)</u>
1	1242	444.1	459.0	103.4
2	1242	444.1	468.0	105.4
3	1242	444.1	470.0	105.8
4	1242	444.1	459.0	103.4
5	1242	444.1	464.0	104.5
6	1242	444.1	478.0	107.6
7	1242	444.1	469.0	105.6
Average			466.71	105.1
Standard Deviation			6.73	
% Rel. Std. Dev			1.44	

OS020^(a), Rev. 1**Immunoassay for Polychlorinated Biphenyls in Soils****1.0 Scope and Application**

This is a field screening method for the semi-quantitative determination of polychlorinated biphenyls (PCBs) in soil. Protocols and evaluations for field test kits produced by EnSys, Inc. (P.O. Box 14063, Research Triangle Park, North Carolina 27709) and Millipore Corp. (P.O. Box 255, Bedford, Massachusetts 01730) are presented. This immunoassay-based method is suitable for detecting PCBs in soils that are also contaminated with radioactive wastes.

2.0 Summary of Method

Soil samples are extracted with one or two volumes of methanol by vigorous shaking for 1 to 2 min. Aliquots of the extracts, or dilutions of the extracts, are buffered and added to test tubes that are coated with PCB-specific antibodies. The PCBs are bound to the antibody in proportion to their concentration and their affinity to the antibody. Unoccupied antibody sites are filled by adding a peroxidase-PCB conjugate. The amount of bound peroxidase is then determined by adding substrates that yield a colored product. The color produced is measured spectrophotometrically and is proportional to the amount of peroxidase in the tube. The assay is a typical competitive immunoassay wherein the absorbance, or optical density, of the final reaction mixture is *inversely* proportional to the amount of PCBs in the original sample. The PCB content of the soils is estimated by reference to PCB standards included in the assay. For example, if a 5 µg/mL^(b) Aroclor 1248 standard is the reference, those samples with equal or less color than the standard are indicated to contain a PCB concentration equivalent to ≥5 µg/g 1248. Those samples with more color than the standard are indicated to contain <5 µg/g 1248 equivalents. Different detection levels can be chosen by changing the type and concentration of Aroclor used as standards, by changing the number of standard concentrations used in the assay, and by further diluting the sample extracts.

(a) This method was supplied by L. C. Waters, R. A. Jenkins, R. R. Smith, R. W. Counts, and J. H. Stewart (Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee).

(b) Ppm is used by the kit manufacturers to refer to µg/mL in the standards and µg/g in the soil. For these kits, the assumption is that µg/mL (ppm) in the extract is equivalent to µg/g (ppm) in the soil.

3.0 Interferences

- 3.1 Chemically similar compounds and compounds that might be expected to be found in conjunction with PCB contamination, and to interfere in the assay, were tested by the kit manufacturers. {It should be noted that in a competitive immunoassay, interferants are most likely to act 1) by binding at PCB sites on the antibody or 2) by inactivating the enzymatic activity of the conjugate. Either mechanism results in less than expected color production and a false-positive classification. With screening methods, false positive results are preferred over false negatives.}
- 3.2 Results obtained with compounds tested in the EnSys RISC[®] test kit assay are given in Table 1 (Mapes et al. 1993).
- 3.3 Millipore has determined that the following PCB-related compounds have less than 0.5% (on a weight to weight basis) of the immunoreactivity of Aroclor 1248 when tested in their EnviroGard[™] test kit assay: 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,4-dichlorobenzene; 1,2,4-trichlorobenzene; 2,4-dichlorophenol; 2,5-dichlorophenol; 2,4,5-trichlorophenol; 2,4,6-trichlorophenol; biphenyl; and pentachlorophenol (PCP) (Millipore EnviroGard[™] PCB Test Kit).
- 3.4 It is important to consider the applicability of this assay, and bioassays in general, for testing mixed radioactive/hazardous chemical wastes. Would the presence of radioactivity adversely affect the performance of the immunoassay? Several factors, the most important being the radiation dose, can influence the effect of radiation on biomolecules such as enzymes. It is known that thousands of rads are required to significantly reduce the catalytic activity of enzymes. Therefore, considering the small sample volumes assayed and short incubation times involved, bioassays should remain effective even with very highly radioactive samples.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to PCBs and methanol. The handling of radioactive soil samples should follow all applicable radiochemical handling procedures and health physics monitoring practices.

5.0 Apparatus and Materials

Except for common laboratory items such as paper towels, laboratory tissue, permanent-ink marking pens, and waste containers, all required apparatus and materials are provided in the manufacturers' kits or can be purchased as separate items from them or other vendors. These items include a weighing balance capable of weighing to 0.1 g, weighing boats and spatulas,

polypropylene soil extraction bottles, extract filtration units, extract storage vials and dilution tubes, pipettors, a timer, and a differential photometer capable of reading optical density at 450 nm.

Table 1. Possible Soil Interferences	
Compound	Soil Equivalent Concentration ($\mu\text{g/g}$) Required to Yield a Positive Result Equal to 1 $\mu\text{g/g}$ Aroclor 1248
Halogenated Compounds	
1-Chloronaphthalene	>10000
1,2,4-Trichlorobenzene	10000
2,4-D	10000
2,4-Dichlorophenyl benzene sulfonate	500
2,4-Dichloro-1-naphthol	50
Bifenox	1000
2,4,6-Trichloro- <i>p</i> -terphenyl	>10000
Halowax 1013	10000
Halowax 1051	1000
<i>o,p</i> -DDT	>10000
Silvex	1000
Tetradifon	100
Diclofop methyl	1000
Dichlorofenthion	10000
Trichloroethylene	>10000
Pentachlorobenzene	>10000
Hexachlorobenzene	>10000
2,5-Dichloroaniline	>10000
Miscellaneous Compounds and Substances	
DIALA(R) Oil AX	>10000
Envirotemp 200 fluid	>10000
R-Temp fluid	>10000
Diesel fuel	>10000
Naphthalene	>10000
Toluene	>10000
Gasoline	>10000

6.0 Reagents

Reagents specific to this method include standard Aroclor solutions, buffer solutions, PCB-specific antibody-coated tubes and blank tubes as appropriate, peroxidase-PCB conjugate, substrates for the peroxidase (hydrogen peroxide and a chromogen), and a reaction-terminating solution. All these reagents are provided in the kits. Unless otherwise stated by the supplier, it is recommended that these reagents be stored at 4°C when not being used. The methanol used to extract the soil may or may not be provided in the kits.

7.0 Sample Collection, Preservation, and Handling

Soil should be collected in appropriately-sized, labelled, screw-cap glass jars. This method can extract PCBs in soils that contain 30% by weight, or less, of water. Note that for most soils, 30% water is saturating. Samples should be handled in accordance with U.S. Environmental Protection Agency (EPA) SW-846 Method 8080, i.e., extracted within 14 days and analyzed within 40 days. Samples containing PCBs should be treated as hazardous materials. Residues, including containers, extracts, and dilutions of soils found to contain PCBs, should be handled and disposed of as hazardous waste.

8.0 Procedures

8.1 EnSys RISC[®] Immunoassay (PCB RISC[®] Users and Technical guides, EnSys Inc.)

Each EnSys PCB-RISC[®] 1 µg/g (1 ppm) Test Kit contains enough materials to analyze a standard and four samples at two dilution levels.

8.1.1 Sample Weighing and Extraction

8.1.1.1 A 10 ± 0.1-g quantity of soil is weighed into a plastic weighing boat.

8.1.1.2 The soil is quantitatively transferred to an appropriately labeled extraction jar that contains 20 mL methanol.

8.1.1.3 The jar lip should be wiped to remove debris and capped tightly. The jar should be shaken vigorously for 1 min.

8.1.1.4 The extract is allowed to settle for at least 1 min. Longer may be necessary for some soils. Settlement does not, however, need to go to completion.

8.1.2 Sample Preparation

8.1.2.1 The filter plunger is removed from the barrel.

- 8.1.2.2 Using the plastic transfer pipette, about one half of the bulb capacity of the extract should be transferred to the filter barrel. More than one full bulb should not be used.
- 8.1.2.3 The plunger is reassembled to the filter barrel, and firm downward pressure is applied to the plunger top to force the extract through the filter until about 0.5 mL has been filtered. (If desired, a portion of this extract can be transferred to a capped vial and stored at 4°C for future use or reference.)
- 8.1.3 **Sample and Standard Dilution**
 - 8.1.3.1 Three antibody-coated tubes should be labeled as "S1," "S2," and "1." Also, three buffer tubes should be labeled as "S1," "S2," and "1." Both the antibody-coated tubes and the three buffer tubes should be placed in the foam workstation.
 - 8.1.3.2 If a 10- μ g/mL dilution is being tested, then an additional antibody-coated tube should be labeled as "10." Also, an additional buffer tube should be labeled "10." These tubes should be placed in the foam workstation also.
 - 8.1.3.3 A disposable capillary and tip should be affixed to the micropipette.
 - 8.1.3.4 Caps should be removed from all buffer tubes.
 - 8.1.3.5 The tip from one 1- μ g/mL dilution ampule should be snapped and placed in the foam workstation.
 - 8.1.3.6 If a 10- μ g/mL dilution is required, then the tip from a 10- μ g/mL dilution ampule should be removed and placed in the foam workstation also.
 - 8.1.3.7 Two 30- μ L aliquots of filtered extract should be transferred to the 1- μ g/mL dilution vial. The dilution ampule should be mixed by gently swirling.
 - 8.1.3.8 For a 10- μ g/mL dilution, two 30- μ L aliquots should be transferred from the 1- μ g/mL dilution ampule to the 10- μ g/mL dilution ampule. It should be gently swirled to mix.

- 8.1.3.9 One 30- μ L aliquot should be transferred from the 10- μ g/mL dilution ampule, if used, to the respectively labeled buffer tube. Otherwise, one 30- μ L aliquot is transferred from the 1- μ g/mL dilution ampule to its respectively labeled buffer tube. The buffer tube(s) should be gently shaken to mix the contents.
- 8.1.3.10 The pipette capillary and tip should be discarded as hazardous waste.
- 8.1.3.11 A new disposable capillary and tip should be affixed to the micropipette.
- 8.1.3.12 The cap should be removed from the PCB standard vial, and one 30- μ L aliquot should be transferred to the buffer tube labeled "S1." The pipette should be withdrawn from the buffer tube, and while the capillary is still depressed, the tip should be wiped with laboratory tissue.
- 8.1.3.13 Another 30- μ L aliquot is transferred from the PCB standard vial to the buffer tube labeled "S2."
- 8.1.3.14 The pipette capillary and tip should be discarded as hazardous waste.
- 8.1.3.15 The standard buffer tubes should be gently shaken to mix the contents.

8.1.4 Color Development

This kit has been used at full performance at temperatures of 40° to 90°F.

- 8.1.4.1 The buffer tube contents should be quantitatively poured into the respectively labeled antibody-coated tubes.
- 8.1.4.2 All of the antibody-coated tubes should be gently shaken, and a 10-min timer should be started immediately.
- 8.1.4.3 An enzyme conjugate should be prepared by firmly pressing the middle of the tube against a table edge to crush the interior glass ampule. The enzyme conjugate should be mixed by inverting the tube five times. The seal should be removed from the enzyme tube.

Warning: The tube must not be crushed any further as this increases the chance of glass puncturing the housing and causing personal injury.

- 8.1.4.4 At the end of the 10-min time period started in section 8.1.4.2 above, the cap is removed from the enzyme conjugate tube, and the first drop is discarded into the waste container. Three drops are added successively to each of the antibody-coated tubes. Drops should fall to the bottom of the tube with no or minimal wall contact.
- 8.1.4.5 The antibody-coated tubes should be gently shaken to mix the contents.
- 8.1.4.6 A 5-min timer should be started immediately.
- 8.1.4.7 At the end of the 5-min time period started in section 8.1.4.6 above, all antibody-coated tube contents should be concurrently discarded into an appropriate waste container.
- 8.1.4.8 While holding the antibody-coated tubes at approximately 10 degrees from vertical above the waste container, each tube should be filled vigorously with wash solution and inverted to empty into the waste container.
- 8.1.4.9 Section 8.1.4.8 is repeated three more times for a total of four washes.
- 8.1.4.10 Inverted tubes are tapped on a paper towel several times to empty as nearly as possible.
- 8.1.4.11 The yellow cap is removed from the substrate A dropper bottle. Five drops are added successively to each of the antibody-coated tubes. Drops should fall to the bottom of the tube with no or minimal wall contact.
- 8.1.4.12 The green cap is removed from the substrate B dropper bottle. A 2.5-min timer is started, and five drops are added immediately to each of the antibody-coated tubes in succession. Again, drops should have no or minimal wall contact.
- 8.1.4.13 Each tube should be shaken gently to mix the contents.
- 8.1.4.14 When the end of the 2.5-min time period draws close, the red cap should be removed from the stop-solution dropper bottle.

- 8.1.4.15 Beginning at exactly 2.5 min, five drops of stop solution should be added to each of the antibody-coated tubes in succession.

Note: The antibody-coated tube order to which drops are added in sections 8.1.4.4, 8.1.4.11, 8.1.4.12, and 8.1.4.15 should remain the same. Also, the time required to add the drops should be as nearly the same as possible.

8.1.5 Optical Density Measurement

- 8.1.5.1 The lower half of the antibody-coated tubes "S1" and "S2" should be wiped clean with laboratory tissue. These are placed in the photometer and the reading recorded.
- 8.1.5.2 If the absolute value of the photometer reading in section 8.1.5.1 is greater than 0.20, then the test is invalid and should be rerun.
- 8.1.5.3 If the photometer reading is between 0.00 and 0.20, then the antibody-coated tube is removed from the left well. The antibody-coated tube is moved from the right well to the left well.
- 8.1.5.4 If the photometer reading is zero or between 0.00 and -0.20, then the antibody-coated tube is removed from the right well.
- 8.1.5.5 The lower half of the antibody-coated tube labeled "1" should be wiped clean with laboratory tissue and placed in the right well of the photometer.
- 8.1.5.6 The photometer reading (including the sign) should be recorded.
- 8.1.5.7 Sections 8.1.5.1 through 8.1.5.6 should be repeated if a 10- μ g/mL dilution is being run. The antibody-coated tube labeled "10" should be used instead of "1" in section 8.1.5.5.

8.1.6 Calculations

- 8.1.6.1 A negative or zero optical density (OD) reading in section 8.1.5.6 indicates a positive result for the dilution level. The result should be reported as " $\geq$ " 1 μ g/g or " $\geq$ " 10 μ g/g as appropriate.
- 8.1.6.2 A positive OD reading in section 8.1.5.6 indicates a negative result for the dilution level. The result should be reported as "<" 1 μ g/g or "<" 10 μ g/g as appropriate.

8.2 Millipore EnviroGard™ Immunoassay (instructions provided with Millipore EnviroGard™ PCB Test Kit)

Each EnviroGard™ Soil Extraction Kit and Immunoassay Kit contains enough materials to analyze singly 3 controls and 17 samples, or 3 controls and 7 samples assayed in duplicate.

8.2.1 Sample Weighing and Extraction

- 8.2.1.1 A 5 ± 0.1 -g quantity of soil is weighed onto a plastic weighing boat.
- 8.2.1.2 The soil is transferred quantitatively to a 30-mL polypropylene bottle containing the ball bearings.
- 8.2.1.3 A 5-mL quantity of methanol is added to the soil sample.
- 8.2.1.4 The bottle is capped tightly, and the sample is extracted by vigorous shaking for 2 min.
- 8.2.1.5 The contents are allowed to settle briefly, and the liquid contents are poured into the lower (non-filter) part of the UniPrep filtration device. (When extracting clay samples, it is possible that all of the methanol will be soaked up by the soil, leaving little or no liquid to decant. In this event, another 5 mL of methanol are added to the sample, and the extraction procedure is repeated. *In such a sample, the actual PCB concentration will be twice that indicated by the test.*)
- 8.2.1.6 A polyethylene frit is inserted into the outside-capped filter end of each UniPrep filter piece and secured in place by sliding on a plastic collar. The ensemble is inserted into the lower piece (containing the extract). It is filtered by pushing down on the filter unit.
- 8.2.1.7 For spill-safe and long-term storage, the cap is removed from the UniPrep device, and the methanol extract is poured into a 4-mL glass vial. The vial is capped, and the extract is stored at 4°C until ready to analyze.

8.2.2 Immunoassay

- 8.2.2.1 Reagent preparation: All reagents should be allowed to warm to ambient temperature before use. Whenever possible, the assay should be run at 20 to 30°C. Reagents should be stored at 4°C when not in

use. If performing the assay at temperatures below 10°C, all incubation times should be extended to 10 min (see 8.2.2.4, 8.2.2.5 and 8.2.2.6).

- 8.2.2.2 Tube preparation: Enough tubes should be labeled, in duplicate if desired, to accommodate 1) a negative calibrator (methanol), 2) at least two positive calibrators (the concentrations of which will depend on the application and specific screening requirement), and 3) no more than 7 sample extracts (for duplicate analysis) or 17 sample extracts (for single analysis). To maintain precise timing, it is recommended that no more than 20 tubes be run in a single assay.) The tubes should be made secure in the tube racks so they will not fall out during subsequent manipulations.
- 8.2.2.3 Sample pipetting: As quickly as possible, duplicate 5- μ L aliquots of the calibrators and sample extracts should be pipetted into the appropriately-labelled tubes using the positive displacement pipettor with a fresh tip for each sample.
- 8.2.2.4 PCB binding: A 500- μ L quantity of assay diluent should be immediately added to each tube. The contents should be mixed by briefly shaking the racks and then allowed to incubate for 5 min. After the incubation, the unbound PCBs are removed by emptying the tubes, which are then rinsed four times with deionized water (filled and decanted). Excess water is removed by inverting the tubes and tamping them on paper towels.
- 8.2.2.5 Conjugate binding: A 200- μ L quantity of PCB-peroxidase conjugate is added to each tube, mixed, and incubated for 5 min. The unbound conjugate is removed as described in 8.2.2.4.
- 8.2.2.6 Substrate addition: A 200- μ L quantity of peroxide (substrate), and 200 μ L of TMB solution (chromogen) are added to each tube, mixed, and incubated for 5 min for color development. After the incubation, 200 μ L of stop solution are added to stop the reaction. An additional 500 μ L of water are added to ensure an adequate volume for the absorbance measurement.
- 8.2.2.7 Absorbance measurements: The absorbance in each tube is measured spectrophotometrically at 450 nm, relative to a water, or stop solution, blank. The intensity of the yellow color is *inversely* related to the concentration of PCBs in the samples.

- 8.2.2.8 Modified assay: A modified immunoassay, with significantly increased sensitivity (see section 10.2), is also available. The modifications are as follows: 1) the volume of sample pipetted is increased from 5 μL to 25 μL , 2) the time for PCB binding is increased from 5 min to 10 min, 3) the conjugate is prediluted 1:2, and 4) the last incubation is increased from 5 min to 10 min.

8.2.3 Estimation of PCB Concentration in Soil Samples

- 8.2.3.1 Standards (both negative and positive calibrators) are included in each assay. The negative calibrator (methanol) should always produce the highest absorbance values, and the positive calibrators are proportionally lower, depending on their PCB composition and concentration.
- 8.2.3.2 The concentration of PCBs in the soil extracts can be estimated by comparing their absorbance values with those of the positive and negative calibrators. For example, if the absorbance of a sample is equal to or greater than that of the negative calibrator, its PCB content would be estimated to be at or near zero. If the absorbance of a sample is less than that of the negative calibrator, but greater than that of a 10- $\mu\text{g/mL}$ positive calibrator, it would be estimated to contain greater than zero, but less than 10 $\mu\text{g/g}$. Similarly, if a sample had an absorbance less than the 10- $\mu\text{g/mL}$ calibrator, it would be estimated to contain greater than 10 $\mu\text{g/g}$ PCB. In situations where the type and composition of PCBs in the samples to be assayed are known, a more accurate estimation of the PCB concentration in the soil can be made by using various concentrations of a positive calibrator made up of PCBs of the same type and composition.
- 8.2.3.3 The antibody used in this assay is most reactive toward Aroclor 1248, and a 1248 blend is used as the positive calibrator in the test. Other blends, e.g., 1260, are less immunoreactive and require higher concentrations to inhibit the reaction to the same extent as 1248. The manufacturer has determined that the other major Aroclors, 1242, 1254, and 1260, are 20% to 100% as immunoreactive as 1248. Accordingly, their 1248 positive calibrators of 3, 5, and 22 $\mu\text{g/mL}$ are conservatively labeled as 5, 10, and 50 $\mu\text{g/mL}$ PCB so that the concentration of even the least immunoreactive PCB that might be present in an unknown sample will not be underestimated. A problem is associated with this "conservative" approach; e.g., if the mandated action level is 5 $\mu\text{g/g}$, and the soil is contaminated with Aroclor 1248

at 5 $\mu\text{g/g}$, it will be measured as 10 $\mu\text{g/g}$, and unwarranted action (for example, remediation) would be indicated.

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.
- 9.2 Because this is a biological assay, the reactions depend strongly on temperature and the integrity of the reagents; therefore, absolute absorbance values for the control samples may not be reproducible. The effects of these factors should, however, be independent of the PCB concentration if the assay is to be valid. Therefore, appropriate PCB controls must be included with each assay. It should be noted that because PCB controls are included with each assay, some latitude in the absolute timing of the reactions is acceptable so long as the final absorbance values remain in the linear range of the photometer, i.e., 0 to 1.5 OD units. However, it is essential that all tubes, both controls and samples, be incubated for the *same* amount of time at each step of the assay.
- 9.2.1 The EnSys method uses two measurements as indicators of QC. First, duplicate standards are used at each dilution level being tested. The relative absorbance of the two standards must fall between -0.20 and 0.20 for the test to be valid. Second, when testing at both the 1- $\mu\text{g/mL}$ and the 10- $\mu\text{g/mL}$ levels, the OD measurement for the 1- $\mu\text{g/mL}$ level should be less than, or approximately equal to, the sample OD measurement for the 10- $\mu\text{g/mL}$ level.
- 9.2.2 During the evaluation of the Millipore method, two positive calibrators were used containing 2 and 10 $\mu\text{g/mL}$ 1248. Thirteen independent analyses of these PCB controls were made. The absorbance values obtained for 2 $\mu\text{g/mL}$ 1248 and 10 $\mu\text{g/mL}$ 1248, relative to the methanol blank, were $53.3 \pm 8.1\%$ and $32.1 \pm 6.8\%$, respectively. Deviation from these relative standard values could indicate deterioration of the reagents, which might invalidate the assay.

10.0 Method Performance

10.1 Accuracy and Reproducibility

- 10.1.1 Evaluation of the EnSys method was conducted using 14 standard soil samples (0 to 200 $\mu\text{g/g}$) and three field samples whose PCB concentration had been established by EPA SW-846 method 8080. Standard soils were spiked with Aroclors 1254, 1260, or a 50/50 mixture of the two. The three field soil samples contained an approximately 70/30 mixture of 1254/1260. Replicates were

performed on seven of the standard soils and on one of the field samples for a total of 25 separate analyses. Each of two different analysts ran the 25 analyses. At the time of this evaluation, samples were being referenced against a 5- $\mu\text{g/mL}$ Aroclor 1248 standard. Consequently, the results were obtained with reference to 5 $\mu\text{g/mL}$ and 50 $\mu\text{g/mL}$ rather than the 1 $\mu\text{g/mL}$ and 10 $\mu\text{g/mL}$ described in the method (see section 8.1.3). The results are presented in Table 2. Method blanks consistently received "<5 $\mu\text{g/g}$ " assignments. At the 5- $\mu\text{g/g}$ testing level, all 14 analyses of samples containing from 5 to 11.5 $\mu\text{g/g}$ were correctly classified as " ≥ 5 $\mu\text{g/g}$," whereas analyses of samples containing from 2 to 4.7 $\mu\text{g/g}$ were correctly classified only 3 out of 10 times. Similar results were obtained at the 50- $\mu\text{g/g}$ testing level (there were no false negatives, but 11 out of 50 were false positives). Because the probability of misclassification becomes greater as the sample concentration approaches the testing level, the actual photometer readings corresponding to the data in Table 2 were used to estimate the error rates for varying concentrations (see Table 3, footnote a). The test is clearly conservatively biased on the side of false positives. At the 5- $\mu\text{g/g}$ testing level, for example, a sample containing 8 $\mu\text{g/g}$ would be correctly classified as " ≥ 5 $\mu\text{g/g}$ " about 99% of the time (1% false negative error rate). However, a sample containing 2 $\mu\text{g/g}$ would be correctly classified as "<5 $\mu\text{g/g}$ " only about 61% of the time (39% false positive error rate). Two factors undoubtedly contribute to the high rate of false positives in this evaluation. First, the Aroclors used, 1254 and 1260, are about 2.5 times more immunoreactive than the reference Aroclor 1248 (see section 10.2). Thus, the samples would test as being about 2.5 times more concentrated than they actually were. Second, the method is conservative in that it has been deliberately biased toward false positive and away from false negative assignments—a proper direction for a screening method. It should be noted that this method has been independently evaluated by Roy F. Weston, Inc.

- 10.1.2 The Millipore method was evaluated using 21 soil samples to screen for PCB content. Fourteen samples were spiked with Aroclor 1254 (0 to 100 $\mu\text{g/g}$), and seven were field samples contaminated with a mixture of Aroclors 1254 (~70%) and 1260 (~30%) ranging from ~2 to 100 $\mu\text{g/g}$. Five-gram portions of each sample were extracted, and the extracts were assayed in duplicate by two independent analysts. A total of four data points were generated per sample. The samples were extracted and analyzed in groups of seven together with a negative control (methanol) and two positive calibrators (2 and 10 $\mu\text{g/mL}$ Aroclor 1248). This arrangement allowed for the samples to be categorized into groups of <2 $\mu\text{g/g}$, 2 to 10 $\mu\text{g/g}$ (Table 4). Fifteen of the samples were accurately categorized by both analysts, five others by one analyst, and one by neither analyst. The latter sample was categorized as having <2 $\mu\text{g/g}$, but had been determined by gas chromatographic analysis to contain 4.2 $\mu\text{g/g}$.

Extraction of this sample may not have been complete due to the soil type, which absorbed most of the extractant. This might have influenced the results obtained. The five samples on which the analysts did not agree were, however, placed in adjacent categories, e.g., 10 or 2 to 10 µg/g by one analyst and >10 µg/g by the other. Four of these samples contained between 11 and 16 µg/g (or 1254/1260 mixture). We have found that 1254, in this range, is about 1.5 times less immunoreactive than the positive calibrator, 1248, used in the assay, and 1260 is even less (Millipore EnviroGard™ PCB Test Kit). Therefore, the absorbance produced by these samples would nearly equal that produced by 10 µg/g 1248 and would explain their being categorized on both sides of 10 µg/g. No false positive results occurred in this study. The false negative results that were obtained can be explained on the basis of the immunoreactivity of the PCBs in the soil samples relative to that of the PCB standard used.

Sample	PCB Conc. (µg/g)	Analyst 1 Interpretation (µg/g)	Analyst 2 Interpretation (µg/g)
1	0	<50	<50
2	2	<50	<50
3	4	<50	<50
4 ^F	47/2.3	<50	<50
5	5	<50	<50
6	6	<50	<50
7	8	<50	<50
8	10	<50	<50
9 ^F	11.1/11.5	<50	<50
10	20	<50	<50
11	40	<50	<50
12	50	<50	<50
13	60	<50	<50
14	80	<50	<50
15 ^F	83/72.5	<50	<50
16	100	<50	<50
17	200	<50	<50
R- indicates field sample			
FP- indicates false positive result			

Table 3. Estimated Error Rates using Data from Table 2(a)

Estimated Error Rates for 5 µg/g Dilution									
True Value (µg/g)	0	1	2	3	4	5	6	7	8
Estimated Rate of False Positives (%)	1.3	13.2	39.2	65.2	82.3				
Estimated Rate of False Negatives (%)				8.5	4.1	2.0	1.0	0.5	0.3
									<0.1
Estimated Error Rates for 50 µg/g Dilution									
True Value (µg/g)	0	5	10	15	20	30	40	50	60
Estimated Rate of False Positives (%)	1.0	7.9	24.5	46.0	65.0	87.3	95.6		
Estimated Rate of False Negatives (%)								1.7	0.7
								0.3	0.2
									<0.1

(a) Counts, R. W., R. R. Smith, J. H. Stewart, and R. A. Jenkins. 1993. *Evaluation of EnSys PCB Rapid Immunoassay Screen Test System*. Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, unpublished.

10.2 Assay Sensitivity

These immunoassay methods are capable of detecting a variety of Aroclors (Mapes et al. 1993) (Millipore EnviroGard™ PCB Test Kit). Because of their different immunoactivities, the levels required for detection can be different for different Aroclors. The concentrations of some common Aroclors that are required to give a positive test with the EnSys PCB-RISC® Test Kit are 1260 (0.4 µg/mL), 1254 (0.4 µg/mL), 1248 (1 µg/mL), 1242 (2 µg/mL), 1232 (4 µg/mL) and 1016 (4 µg/mL) (Mapes et al. 1993).

The most conservative estimate for the sensitivity of the standard Millipore EnviroGard™ Immunoassay Kit is that soils with ≥ 3 µg/g Aroclor 1248 can be unambiguously differentiated from "zero." The modified assay has increased the sensitivity to 1 µg/g 1248 or less (see 8.2.2.8). Other Aroclors, i.e., 1242, 1254, and 1260, are within a factor of 5 as immunoreactive as 1248 and are, therefore, detectable at ≤ 5 µg/g.

- Mapes, J. P., K. D. McKenzie, T. N. Stewart, L. R. McClelland, W. B. Studabaker, W. B. Manning, and S. B. Friedman. 1993. "PCB-RISC® - An On-Site Immunoassay for Detecting PCB in Soil." *Bull. Environ. Contam. Toxicol.* 50:219-225.
- Taylor, J. M., S. D. Wesson, and N. Monacella. 1991. *Laboratory Evaluation of a Rapid Immunoassay Screen Test for Determination of Polychlorinated Biphenyls in Soil*. Roy F. Weston, Inc., Lionville, Pennsylvania 19341.

11.0 References

A trained analyst should be capable of analyzing 20 to 40 samples per day using these methods.

10.3 Time Considerations

Table 4. Results of Analyses for PCBs in Soil Samples using the Millipore EnviroGard™ Immunoassay

Sample	PCB Conc (µg/g)	Analyst 1 Interpretation (µg/g)	Analyst 2 Interpretation (µg/g)
1	0	<2	<2
2	0	<2	<2
3F	4.2	<2 _{FN}	<2 _{FN}
4F	4.7/2.3	2-10	2-10
5	5	2-10	2-10
6	8	2-10	2-10
7	10	2-10	10
8F	11.1/11.5	10 _{FN}	>10
9	12	2-10 _{FN}	>10
10	15	2-10 _{FN}	>10
11F	16	2-10 _{FN}	>10
12	20	10 _{FN}	>10
13	30	>10	>10
14F	32	>10	>10
15	40	>10	>10
16	50	>10	>10
17	60	>10	>10
18F	72.5/83.0	>10	>10
19	80	>10	>10
20	100	>10	>10
21F	105	>10	>10

F - indicates field sample
 FN - indicates false negative result

OS030(a)

A Photoacoustic Infrared-Based Screening Method for the Detection of Selected Chlorinated Volatile Organic Chemicals in Water

1.0 Scope and Application

- 1.1 Photoacoustic infrared spectroscopy is a stable and sensitive technique for measuring volatile chemicals in air. *This method is an adaptation of this measurement technique to measure volatile organic chemicals (VOCs) in water.* The Bruel & Kjaer (B&K) Multi-gas Monitor (M-gM) - Type 1302 (Bruel & Kjaer Instruments, 185 Forest St., Marlborough, Massachusetts 01752) was used in the development of this method. Other equivalent infrared-based instruments may also be appropriate for use with this method as they become available. Several features of the B&K M-gM make it appropriate for this method. It can measure up to 5 different gases/vapors in a single air sample by using different optical filters (Bruel & Kjaer Instruction Manual Vol. 1, operation and maintenance, May, 1990). The instrument can be calibrated to correct the measurement of each compound for cross-interference from each of the other measured analytes present, and for water vapor, in the sample. Sample components that are not specifically being measured may interfere. Over 20 different filters are available and have been used to measure over 200 different volatile compounds in air (B&K gas detection limits chart). Analytical results are displayed in real time as mg/m³ or as ppm of air sampled. The application of the method to measure the chlorinated hydrocarbons—chloroform, perchloroethene (PCE), trichloroethene (TCE), and carbon tetrachloride—is described.
- 1.2 A two-step procedure is used. First, VOCs are purged from water into Tedlar bags. The bag contents are then sampled and measured using the M-gM.
- 1.3 The power requirements of the M-gM are 110 or 220V AC with a consumption of ~100 watts. This requirement can also be met in the field by using a generator or an inverter attached to a car battery.

2.0 Summary of Method

- 2.1 Gas/vapor measurement with the M-gM is based on the capacity of molecules to absorb infrared light and give off energy in the form of heat. In a closed cell, the heat produced

(a) This method was supplied by L. C. Waters, R. A. Jenkins, R. W. Counts, and L. Hernandez (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

is translated to an increase in pressure, which is detected as an acoustic signal. The magnitude of the signal is proportional to the concentration of the chemical that is absorbing the light. Any volatile compound that absorbs infrared light can, in theory, be measured using this method. The M-gM was designed to use an array of up to five different optical filters, defining different wavelengths of light, to selectively and simultaneously measure up to five volatile compounds, and water vapor, in air.

- 2.2 Because the M-gM uses relatively large volumes of air to purge the sample cell and the sampling tubing between measurements (≥ 200 mL), it is not practical to purge VOCs from water directly to the instrument. Instead, the approach is to purge the VOCs directly from the water sample with air into a Tedlar bag. The M-gM is then used to sample and measure the contents of the bag. Results, in mg/m^3 or as ppm of air sampled, are shown on the M-gM's display screen as soon as they are available (about 2 min/measurement) and are also stored in its "display" memory. An amount of data equivalent to 12 days monitoring of five volatiles and water vapor, every 10 min, can be stored in the instrument's "display" memory.
- 2.3 The M-gM is calibrated by the manufacturer or user for analyte concentration and for cross-interferences. Calibration is a three/four-stage operation performed by consecutively attaching supplies of 1) dry air, 2) wet air, and 3) one or two different known concentrations of the target analyte to the M-gM's air-inlet. Details of the calibration procedure can be found in the instrument manuals. A two-point concentration calibration is recommended when the measurement range is expected to exceed 10^4 times the detection limit of the analyte.
- 2.4 This evaluation showed the method to have a working range of at least up to $10 \mu\text{g}/\text{mL}$ of the analyte in water. Based on the fact that detection of these four VOCs in air is linear to at least $2500 \text{ mg}/\text{m}^3$, it can be calculated that the working range of the method is linear at least up to 82 to $145 \mu\text{g}/\text{mL}$ of water, depending on the VOC. It is likely that this upper limit is even higher and, in fact, may only be limited by the solubilities of the VOCs in water. Method detection limits (MDLs) for the four VOCs measured are in the range of 200 to $400 \text{ ng}/\text{mL}$ water.

3.0 Interferences

Via the use of appropriate optical filters and calibrations, the M-gM can be set up to measure up to five different volatiles and water vapor in air, selectively and simultaneously. It allows the concentration of each measured VOC to be corrected for cross-interference from any of the other *measured* VOCs and water vapor. Other volatile components that are present in the water samples may interfere. Therefore, it is important for the water source to have had some prior characterization so that potential interferants can be identified and 1) the M-gM can be set up to monitor them and thereby compensate for their interference, or 2) their contribution to those

VOCs being measured can be empirically determined. The interferences from four other chlorinated hydrocarbons often found as contaminants or co-contaminants at U.S. Department of Energy (DOE) waste sites and two common solvents were empirically determined. Results were as follows:

<u>Potential Interferant</u>	<u>Observed Response Relative to an Equal Concentration of Measured Analyte</u>
Dichloromethane	19% of CHCl_3 ; negligible effect on PCE, TCE, or CCl_4
1,2-Dichloroethene	negligible effect on CHCl_3 ; 42% of PCE; 73% of TCE; 21% of CCl_4
1,1,1-Trichloroethane	negligible effect on any analyte
1,1-Dichloroethane	97% of CHCl_3 ; negative effects on PCE, TCE, and CCl_4
Acetone	24% of CHCl_3 ; negligible effects on PCE and TCE; effect on CCl_4 not determined
Methanol	negligible effect on any analyte at up to 10 μg methanol/mL water.

4.0 Safety

- 4.1 The chlorinated hydrocarbons used in this method are known health hazards. Consequently, all solutions should be handled with gloves. The air-outlet of the M-gM should be fitted with a charcoal trap to capture exit volatiles (care should be taken to not generate a back pressure as this would interfere with the performance of the M-gM's pump). The trap should be handled as hazardous waste.
- 4.2 The M-gM is not designed for use in potentially explosive environments.
- 4.3 Liquids should be prevented from entering the M-gM's analysis cell. It is therefore important that warm humid gases are not drawn into a cold analysis cell because condensation will take place. If such a situation is likely to occur, the gases should be drawn through a water-trap filter before they enter the air-inlet of the M-gM. This will condense out water vapor in the gases and thus prevent condensation within the analysis cell. The water-trap filter should be used in the immediate environment of the M-gM so that it remains either the same temperature, or a lower temperature, than the M-gM.

5.0 Apparatus and Materials

5.1 Purge System

- Purge module: Adaptable to 40-mL volatile organic analyte (VOA) vials. The exit side of the module is fitted with a 13-mm Swinny stainless filter holder (Millipore catalog No. xx30 01200, or equivalent) and a 10-micron Teflon® filter to prevent water droplets from reaching the collection bag.
- Filters: 10-micron Teflon®, 13-mm size for use on exit side of the purge module and 25-mm size for use in the M-gM's internal and external air-filtration units.
- Compressed air: The cylinder should be equipped with a fine-control flow regulator. Nitrogen is a suitable substitute. Helium is not compatible with the M-gM's pump.
- Air flow calibrator: For adjusting the purge flow rate
- VOA vials, 40 mL: With Teflon®-lined caps or septa, depending on whether the purge module is designed to accept the opened vial or to puncture a septum
- Tedlar-film bags: 1-L capacity, with stainless steel hose/valve fittings. A larger bag (e.g., 12 L) is useful for generating a blank sample.
- Permanent-ink marking pen, labels and tags: For labeling sample vials and Tedlar bags
- Timer: To measure in min

5.2 Analysis System

- 5.2.1 **VOC Analyzer:** The B&K M-gM (Type 1302) was used to develop and validate this method. Although equivalent commercial instruments are not currently available, such instruments would also be appropriate for use with this method as they do become available. The M-gM is a microprocessor-controlled monitor capable of measuring the concentration of up to five volatile compounds and water vapor in a single sample. Selective analysis is achieved by the use of appropriate optical filters—up to five filters plus one for water vapor can be accommodated in the M-gM's filter carousel. The instrument is factory or user calibrated so that the measurement of each component is compensated for cross-interference from the other components being measured and from water vapor. The M-gM is easy to operate via its front-panel push-button controls.

Measurement results are displayed on the screen as they are generated. About 2 min are required to measure five components and water vapor in a single sample. Results, expressed in either ppm or mg/m³, can be taken manually directly off the screen, printed out as they are generated, and/or printed out at a later time. Data can be stored in the monitor's memory and later transferred, using software provided by B&K, to a computer for analysis.

- 5.2.2 **Printer:** Although a printer is not essential, it allows the user to have a running log of the measurements as they are made, as well as a rapid means of acquiring a hardcopy of the day's results without the need for a computer.

6.0 Reagents

Simulated groundwater (SGW) (Rocky Mountain 1989), or another water source that has been shown to be negative for VOCs, is the only reagent required for this method. This SGW is deionized water to which 0.165 g/L of sodium chloride and 0.145 g/L of sodium sulfate have been added (contains 100 µg/mL of chloride and sulfate ions).

7.0 Sample Collection, Preservation, and Handling

The problems associated with the loss of volatile components from water samples during handling and storage are well known. Therefore, because the purge step of this method is totally portable, it seems appropriate that the samples be taken, and purged into the Tedlar bags, at the source. Bags would be tagged and "strung up" through the grommets and taken to the M-gM for analysis. Excessive exposure of the bags to ultraviolet (UV) light should be avoided to protect the samples from losses caused by photolytic degradation.

8.0 Procedure

This method involves a two-step procedure in which the VOCs are first extracted from the water sample by purging into a Tedlar bag. The second step is to sample and analyze the contents of the bag with the M-gM.

8.1 Purge

- 8.1.1 The purge module is coupled to the air supply.
- 8.1.2 A control water sample, e.g., SGW, 30 or 40 mL (the latter if the purge module has its own headspace), in a VOA vial is attached to the purge module.
- 8.1.3 The flow rate is adjusted to about 100 mL/min.

- 8.1.4 The air flow is stopped, and a large Tedlar bag is coupled to the exit side of the purge module. A small section of Tygon tubing {about 4 cm long (1 1/2 in.) by 0.64 cm OD (1/4 in.) by 0.32 cm ID (1/8 in.)} is used to connect the purge module, through the male Luer slip outlet of the Swinny filter holder, to the open/close valve of the bag. (**Note:** Except for these short sections of Tygon connecting tubing, all connecting tubing should be stainless steel or Teflon®.) A large control-water purge sample (5 to 10 L) is collected for use to determine baseline measurement values for the M-gM.
- 8.1.5 A 30- or 40-mL field water sample is collected in a VOA vial. The vial is tightly closed with a Teflon®-lined lid until the sample is ready to be purged.
- 8.1.6 The sample is purged into a 1-L Tedlar bag for 10 min at a flow of 100 mL/min. The bag valve is closed. Under certain conditions, it may be appropriate to collect less than a 1-L sample (see section 11.0). Multiple samples may be collected at the source in this manner and taken elsewhere for analysis (see sections 7.0 and 11.0).
- 8.1.7 **Bag Reuse:** It was determined that, after manually squeezing out the residual air from a used bag, the carryover was about 1.5% (for CCl₄). Therefore, except in cases where the analyte concentration is very high, bags should be reusable after four to five rinses with air. When in doubt, the used bag should be filled with air, and the contents should be analyzed to be sure the amount of carryover is negligible.

8.2 Analysis

Analysis of the purged volatiles involves two procedures, the setup of the instrument and the measurement. The procedure for instrumental setup depends upon the instrument being used, with details being provided in the particular user's manual. The setup and measurement procedures for the instrument used in the development of this method are given below as examples of the parameters involved.

- 8.2.1 **Setup for M-gM:** The working parameters of the M-gM are organized into an inverted "tree" structure, i.e., the "setup" mode. By systematically following the branches of the tree, parameters can be selected, and the M-gM can be set up to perform a variety of functions. The branches and those parameters relevant to the measurement of VOCs in Tedlar bags are as follows:
- 8.2.1.1 **Filters:** When the same filter is used for two different VOCs, e.g., TCE and CCl₄, the calibration factors are different and are stored in different "filter banks": Bank 1 = TCE; 2 = CCl₄. The appropriate filter bank is chosen.

- 8.2.1.2 Units: Units for analyte concentration (mg/m^3), sampling-tube length (m), temperature ($^{\circ}\text{C}$), atmospheric pressure (mm Hg), and humidity (ppm) are chosen.
- 8.2.1.3 Communication: Parameters relevant to interfacing the M-gM with printers, plotters, and computers are chosen in this branch.
- 8.2.1.4 Tests: "Print data log" is chosen (if printer is available) - provides a continuous printout of 1) the time the sample was taken, and 2) the concentration of each analyte and water vapor. By noting the time at which a bag was sampled, accurate records can be kept.
- 8.2.1.5 Clock: Time and date are accurately set so that analysis times can be synchronized with the M-gM data output.
- 8.2.1.6 Format: Print format is chosen. In addition to a continuous printout of the data log, a printout of the setup used and all measurement data can be obtained at the end of a monitoring task. The measurement printout includes the "monitoring task" setup parameters, the "environment" setup parameters, the start and stop dates and times, the sample number and time taken, and the concentrations of all analytes measured in the samples.
- 8.2.1.7 Environment: Sampling-tube length is set to 0 m to minimize the volume of air sample taken for each measurement. Actual temperature and pressure are entered in this branch. This is particularly important if concentration units in ppm, instead of mg/m^3 , are being used (see section 9.1).
- 8.2.1.8 Monitoring task: Continuous sampling is chosen, rather than a defined interval. Under this condition, the bags are sampled at about 2-min intervals. This allows ample time to connect and disconnect the bags without interrupting the measurement cycle. Compensation for all interferences is chosen.
- 8.2.2 **Measurement:** The air-inlet to the M-gM is fitted with a 30- to 40-cm section of Teflon[®] tubing {0.4 cm OD (5/32 in.) and 0.32 cm ID (1/8 in.)} to which an external 10-micron filter is attached. This filter can be made easily detachable with a short, connecting section of 0.32 cm OD (1/8 in.) Teflon[®] tubing. The filter is removed during sample measurement, but should be replaced between sampling periods to prevent dust or other suspended matter from reaching the analysis cell. The short piece of Tygon tubing used to interface the Tedlar bag

with the purge module (see 8.1.4) can also be used to attach the bag to the M-gM air-inlet tubing. Bags must be attached and removed from the M-gM between pumping cycles. The pumping cycle can be heard, and about 2 min are available between cycles for attaching and removing bags.

- 8.2.2.1 The measurement task is started and the 12-L bag containing the purged SGW is sampled to obtain baseline information.
- 8.2.2.2 The control-sample bag is removed, and the first field-sample bag is attached. **It is imperative that the bag's valve be opened** - failure to do so will cause a vacuum to develop in the system and will cause a shutdown with the associated warning of "airway system blocked." If this does happen, the M-gM can be set to "standby"; then the airway can be opened and the "measurement" resumed.
- 8.2.2.3 At least three measurements are made per bag. The number of samples that can be taken depends on the volume of sample taken for each measurement.
- 8.2.2.4 The previous two steps are repeated until the contents of all bags have been measured. The time at which each sample was analyzed is recorded so that the correlation between sample identification and analytical results can be made. (**Note:** It is often useful to take two or three measurements of ambient air between bags. The water vapor content in the bags compared with ambient air are often different, and, using the data log and measurement printouts, the differences in water vapor concentration can be used to precisely determine when each bag was sampled.)
- 8.2.2.5 The measurement task is stopped.
- 8.2.2.6 "Measurement" data, and "setup" parameters, if desired, are printed out. If a printer is not available, the information can be hand copied by scrolling through the display screen or can be saved to "background memory" for later retrieval. (**Note:** when a new measurement task is started, previous data in "display memory" only will be lost unless it is saved in "background memory." A warning to that effect will be given on the display screen.)

9.0 Calculations

- 9.1 Some of the data generated in this method development and validation were in ppm rather than in mg/m^3 . Data were converted using the formula: $\text{mg}/\text{m}^3 = \text{ppm} \times$

molecular weight (in g)/molar volume (MV). Molar volume was determined from the formula: $MV = RT/P$, where T is the temperature of the gas in °K, R is the gas constant $0.082054 \text{ L atm K}^{-1} \text{ mole}^{-1}$, and P is the pressure of the gas in atmospheres.

- 9.2** Evaluation results are expressed as $\mu\text{g analyte/mL}$ of water sample. This value is obtained by dividing the data, i.e., mg/m^3 ($= \mu\text{g/L}$), by 30 (the volume, in mL, of water purged with 1 L of air).
- 9.3** Estimates of analyte detection limits were determined by two methods. Two common estimates of low-concentration measurement capabilities are the MDL specified by the U.S. Environmental Protection Agency (40 CFR Ch. I. 1990) and the certified reporting limit (CRL) specified by the U.S. Army Toxic and Hazardous Material Agency, now the Army Environmental Center (USATHAMA 1990). The EPA defines an MDL as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the analyte. The USATHAMA definition of CRL is equivalent to determining a found concentration so that both the false-positive and the false-negative error rates are 5%. Like the MDL definition, CRL is associated with the entire method and reflects all sample preparation and measurement steps. The CRL has a larger false-positive error rate (5% versus 1%), but a much smaller false-negative error rate (5% versus 50%) than those for MDL. Both MDL and CRL are concerned with measuring detection limits for a total methods procedure, but defining false-positive and false-negative error rates is different.

10.0 Quality Control

- 10.1** Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.
- 10.2** Stock analyte solutions used in the experimental evaluation of the method were independently analyzed by direct sampling ion trap mass spectrometry (DSITMS) (Wise et al. 1993). The M-gM is calibrated to provide the analytical results in either ppm or mg/m^3 ($= \mu\text{g/L}$). Quality control is assessed by comparing the concentration of analyte in the 30-mL water sample with that found by M-gM analysis in 1 L of air. Percentages of expected values obtained for individually analyzed analytes were in the ranges of CHCl_3 - 80%, PCE - 85%, TCE - 70%, and CCl_4 - 80%. Factors to explain the deviation from 100% could include 1) errors in measurements made by DSITMS, 2) errors in M-gM calibration, 3) differences in purge yields, or 4) a combination of these reasons. Purge differences do not appear to be an important factor because under the purge conditions used, i.e., at 19 to 21°C, 95 to 100% of each of the analytes was purged. Furthermore, purges done at 0 to 5°C showed that CHCl_3 , not TCE, was slowest to purge (TCE, PCE, and CCl_4 purged at similar rates).

11.0 Method Performance

- 11.1 Instrument Setup:** The instrument used in this method's development was set up at the factory, i.e., optical filters were installed and calibrations were made to measure CHCl_3 , vinyl chloride (VC), PCE, and TCE or CCl_4 . A VC measurement was not evaluated in this study. (TCE and CCl_4 were measured in different setups because the same optical filter, but different calibration factors, were used for both.) Results obtained for CHCl_3 and for PCE were the same in both filter setups.
- 11.2 Purge Conditions:** The purge conditions used in this performance evaluation were dictated by the volume of sample used by the M-gM per measurement and the decision to obtain at least three measurements per sample. The instrument used required about 280 mL per measurement (instrument specifications indicated a requirement of about 140 mL). A purge volume of 1 L was chosen so that three measurements could be made per sample and because, under the conditions of the evaluation, 19 to 21°C, greater than 95% of each of the analytes was purged. Because temperature significantly affects purge rate, it is important to determine what proportion of the analyte is purged under the conditions of the analyses and to take this into consideration in determining the actual VOC concentration in the water sample being measured.
- 11.3 Limits and Linearity of Detection:** An experiment typical of those used to determine detection limits and linearity of the method is shown for TCE in Figure 1. A total of seven concentrations, increasing by a factor of 2, were tested. Three or four spiked samples, at each concentration in 30 mL of water, were purged with 1 L of air. Three measurements were made on each sample. (When a fourth sample was measured, it was prepared in deionized water instead of SGW. Because no significant differences between deionized water and SGW were observed, all data were used to generate the results shown in Figures 1 and 2.) The results shown in Figure 1 illustrate 1) the reproducibility of replicate samples, 2) the reproducibility of the three measurements made on each sample, and 3) the lack of interference of TCE on chloroform and PCE. Similar observations were made when CHCl_3 , PCE, or CCl_4 were analyzed.
- 11.3.1 Method detection limits and CRLs** were determined as described (40 CFR Ch. I 1990; USATHAMA 1990). Respective MDLs and CRLs in ng/mL water (ppb), and in increasing order, were CHCl_3 = 220 and 310; PCE = 250 and 360; CCl_4 = 340 and 480; and TCE = 370 and 520 (Figure 2).
- 11.3.2 Working Range of the Method:** The linearity of the method to 7 to 11 $\mu\text{g/mL}$ is shown in Figure 2. Independent experiments showed the measurement of these analytes in gas standards to be linear to 2500 mg/m^3 . This concentration is equivalent to 30 mL of water containing approximately 82 $\mu\text{g/mL}$ CHCl_3 , 115 $\mu\text{g/mL}$ PCE, 145 $\mu\text{g/mL}$ TCE, and 110 $\mu\text{g/mL}$ CCl_4 (see sections 9.1 and 9.2).

Figure 1. Analysis of TCE in Water using the M-gM. Water samples were 30 mL and contained TCE at concentrations in 2X increments from 0.18 to 11.32 µg/mL. Three to four samples at each concentration were analyzed. Three measurements were made per sample. Laboratory air was sampled between purge samples. The data for chloroform and PCE, both at zero concentration, show that there is no interference from the TCE.

Figure 2. Linearity and Detection Limits for VOCs in Water by M-gM Analysis.

This observation indicates that the working range is at least 10 times higher than that shown in Figure 2 and, in fact, may only be limited by the solubility of the analytes in water.

- 11.4 Measurement of VOCs in Mixtures:** Data from the experiments illustrated in Figures 1 and 2 indicate that none of the measured analytes interfere significantly with each other. To investigate this further, composite samples of CHCl_3 , PCE, and TCE at concentrations differing by as much as a factor of 10 were made and analyzed with reference to the results to be expected if the analytes were measured separately. The results in Table 1 show that even low concentrations, i.e., 1.7 to 3.4 times the MDLs, are accurately measured in such composites. Concentrations measured in the composites ranged from 95 to 121% for CHCl_3 , 88 to 106% for PCE, and 90 to 112% for TCE of expected values.
- 11.5 Accuracy of the Method:** As an indicator of accuracy, the M-gM results were compared with those obtained for the same samples by DSITMS. The M-gM measurements were typically lower than those obtained by DSITMS. Relative measurements were typically about 80% for CHCl_3 and CCl_4 , 85% for PCE, and 70% for TCE. Reasons for the deviations from 100% could include 1) error in the DSITMS measurements, 2) error in the M-gM calibration, 3) different purge yields, or 4) combinations of these reasons. Purge differences do not appear to be involved because under the conditions of the purges, i.e., at 19 to 21°C, 95 to 100% of each of the analytes was purged. Furthermore, independent purging experiments showed that CHCl_3 , not TCE, purged most slowly.
- 11.6 Advantages of the Method:** Minimal training or knowledge of the operation parameters are required to use the M-gM. The method is rapid. As is indicated in Figure 1, two workers can easily analyze 24 samples in 4 h. Results can be taken directly off the M-gM screen as the measurements are made and in units that can be directly related to concentrations in the samples. Multiple analytes can be measured simultaneously in a single sample. A large variety of analytes can be measured via the use of appropriate optical filters and calibrations. Data storage, management, and analysis are easily and rapidly accomplished. The M-gM is portable, about the size of a small suitcase, and weighs 9 kg, as are the components used to purge the samples. Power requirements in the field can be provided by using a generator or an inverter attached to a car battery. The accuracy, sensitivity, reproducibility, and wide working range are well within the expectations of a useful field screening method. Important uses of the method would be to monitor, over time, changes in analyte concentrations of wastewater sources where the contamination profile is known, as well as during remediation of such sites.
- 11.7 Limitations of the Method:** The primary limitation of the method is that it is susceptible to interference by contaminating compounds that the instrument has not been calibrated to measure. This necessitates that the contaminated water source have some prior

Table 1. Recovery of VOCs in Composite Samples

Comp. No.	No. of Samples Analyzed		Concentration ($\mu\text{g/mL}$)		
			Chloroform	Perchloroethene	Trichloroethene
1	2	Expected (a)	0.754	0.432	6.44
		Found	0.873 (0.020) ^(b)	0.463 (0.023)	5.98 (0.203)
		% of Expected	116	107	93
2	3	Expected	3.77	2.16	3.22
		Found	3.76 (0.097)	2.06 (0.110)	3.03 (0.084)
		% of Expected	100	95	94
3	2	Expected	0.754	4.32	0.64
		Found	0.912 (0.021)	3.99 (0.224)	0.72 (0.027)
		% of Expected	121	92	113
4	2	Expected	7.54	0.432	0.64
		Found	7.47 (0.287)	0.433 (0.039)	0.59 (0.064)
		% of Expected	99	100	92
5	2	Expected	7.54	4.32	0.64
		Found	7.22 (0.199)	3.80 (0.286)	0.66 (0.056)
		% of Expected	96	88	103
6	2	Expected	7.54	4.32	6.44
		Found	7.16 (0.081)	3.65 (0.266)	5.87 (0.105)
		% of Expected	95	84	91
7	2	Expected	0.754	0.432	0.64
		Found	0.877 (0.020)	0.400 (0.017)	0.66 (0.024)
		% of Expected	116	93	103
8	2	Expected	0.754	0.432	6.44
		Found	0.840 (0.032)	4.39 (0.647)	5.79 (0.063)
		% of Expected	111	102	90

(a) Expected values are based on measurements of the analytes singly.

(b) Standard deviation of measurements in parentheses

Composites samples were prepared using combinations of 1:10, 1:20, or 1:100 dilutions of the VOC stocks ($\text{CHCl}_3 = 75.4 \mu\text{g/mL}$; $\text{PCE} = 43.2 \mu\text{g/mL}$; $\text{TCE} = 64.4 \mu\text{g/mL}$).

characterization. If the M-gM pumping rate could be reduced, then smaller purge volumes could be used with a concomitant increase in sensitivity. For example, even for CHCl_3 , 80% of the analyte is purged within 5 min at 19 to 21°C, i.e., in 500 mL.

12.0 References

40 CFR Ch. I. 1990. "Definition and Procedure for the Determination of the Method Detection Limit", *Revision 1.11. Code of Federal Regulations*, Part 136, Appendix B, pp. 537-539.

Rocky Mountain Arsenal. 1989. *Rocky Mountain Arsenal Chemical Quality Assurance Plan*, section 4-7. Commerce City, Colorado 80022-2180.

U.S. Army Environmental Center (USATHAMA). 1990. *U.S. Army Toxic and Hazardous Materials Agency: Quality Assurance Program*, Aberdeen Proving Ground, Maryland.

Wise, M. B., C. V. Thompson, M. V. Buchanan, R. Merriweather, and M. R. Guerin. 1993. "Direct Sampling Ion Trap Mass Spectrometry." *Spectroscopy*. 5:14-22.

OS040^(a)**Rapid Determination of Volatile Organic Contaminants in Water and Soils by Direct-Purge Mass Spectrometry**

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

- 1.1 This method is designed to rapidly measure the concentration of several of the most commonly found volatile organic contaminants in soils, sediments, or water. It is based on direct-purge mass spectrometry (MS). The method has been tested for the following compounds: methylene chloride, chloroform, carbon tetrachloride, trichloroethene, tetrachloroethene, benzene, toluene, and xylenes (ortho-, para-, meta-xylene, and ethyl benzene can not be distinguished from each other by direct MS). Analysis is complete in 4 min per sample. This method can be implemented in the field using a small mobile laboratory for instrument support.
- 1.2 The method can be applied to simple mixtures of the compounds listed under 1.1. The same method can be applied with minor modifications to numerous other similar compounds, but only in relatively simple combinations after potential mass interferences have been carefully assessed. Samples containing moderate amounts of radioactivity may be analyzed with suitable precautions to limit the spread of contamination. The method is well suited to the analysis of mixed waste because of the limited amount of sample handling involved.
- 1.3 The practical quantitation limit (PQL) for this method is approximately 40 µg/kg for soils and sediments and 8 µg/L for water.

(a) This method was supplied by J. C. Evans (Pacific Northwest Laboratory, Richland, Washington).

2.0 Summary of Method

- 2.1 This method provides mass spectrometric conditions for detecting volatile organic contaminants, including chlorinated solvents and aromatic components of fuels. Samples are analyzed by a direct helium purge of water samples or water-methanol extracts of soils. The purge effluent is introduced into the vacuum inlet of a quadrupole MS by permeation through a heated dimethyl silicone membrane. The dimethyl silicone membrane is used to selectively exclude or minimize the simultaneous introduction of air, water, or methanol. Detection is performed by the mass-selective detector. Quantitation is based on measured detector response at appropriately selected mass peaks for each species relative to an internal standard (trifluorotoluene), which is added to each sample as a quantitation reference.
- 2.2 The method is suitable for analyzing waters or soils. Water samples can be analyzed directly with no pretreatment other than adding the internal standard dissolved in a small volume of methanol. Soil or sediment samples are dispersed in high-purity methanol to dissolve and preserve the volatile organic constituents. After the internal standard and a measured volume of high-purity water are added to the methanol-soil mixture, the entire sample is analyzed by direct-purge MS.
- 2.3 Soil core samples are collected in pre-weighted standard 40 mL volatile organic analyte (VOA) vials containing methanol for preservation and extraction. Minimum handling is required to reduce volatile organic compounds (VOC) loss. After the internal standard and water are added to the vials, the vials are immediately capped with special reusable purge adapter caps. The caps are equipped with removable polytetrafluoroethylene (PTFE) ball-valve seals that permit purging of the sample without reopening the vial and risking VOC loss.

3.0 Interferences

- 3.1 Direct MS determination methods provide more limited selectivity than methods like gas chromatography (GC)-MS that separate compounds. Careful selection of mass peaks is thus required to minimize interferences. In some cases, the most abundant mass peak for a given species may be more subject to interference than a less abundant major peak. For example, in this method carbon tetrachloride is determined at mass 121 rather than either 117 or 119 to limit the interference from chloroform. Mass 119 also exhibits major interference from numerous hydrocarbons present in fuels. The mass peaks shown in Table 1 have been selected to minimize interferences while still providing reasonable sensitivity. Some interferences may still be present, as shown in Table 1. Interferences are shown on an equivalent concentration basis. For example, the presence of 1000 ng of carbon tetrachloride in a sample will result in a 38-ng false-positive response for methylene chloride. The trifluorotoluene internal

standard does not interfere with any of the listed species except benzene. If high-sensitivity detection of benzene is required, fluorobenzene quantified at mass 96 is a suitable alternative internal standard.

Table 1. Mass Interferences (%)

Analyte m/z	CH_2Cl_2 86	CHCl_3 83	CCl_4 121	TCE 130	PCE 164	Benzene 78	Toluene 92	Xylenes 106	TFT 146
CH_2Cl_2	100	1.9	0	0	0	0	0	0	0
CHCl_3	2.1	100	1.0	0	0	0	0	0	0
CCl_4	3.8	0.3	100	0	0	0	0	0	0
TCE	0.2	0.9	0	100	0	0	0	0	0
PCE	1.7	2.0	0.8	2.5	100	0	0	0	0
Benzene	0	0	0	0	0	100	0	0	0
Toluene	0	0	0	0	0	0	100	0	0
Xylenes	0	0	0	0	0	0	0	100	0
TFT	0	0	0	0	0	0.6	0	0	100

- 3.2 Complex mixtures, such as gasoline or other similar hydrocarbon mixtures, may involve additional interferences not addressed in this method. The method should be used with caution in that case, and individual mass spectra should be examined carefully to verify that interferences are minimal.
- 3.3 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. If possible, low-level samples, including blanks, should be run before running known or suspected high-level samples. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross-contamination.
- 3.4 Unacceptably large and erratic blanks may be caused in the soils-analysis procedure by contamination present in the methanol extractant or the makeup water. Benzene and methylene chloride have been found to be common reagent contaminants. Methanol should be purge-and-trap grade of verified purity. The purity of methanol and water should be verified by analyzing laboratory and field blanks.

4.0 Safety

- 4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible by whatever means available. Handling of neat materials should be performed in laboratory fume hoods. The laboratory is responsible for maintaining a current file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis.
- 4.2 Refer to Chapter 4 in this document for general safety information.

5.0 Apparatus and Materials

- 5.1 **Gas Chromatograph-Mass Spectrometer:** The method is based on the use of a commercially procurable Hewlett-Packard (Fullerton, California) HP 5971A GC-MS system or equivalent. The GC column has been replaced by a direct inlet to the MS vacuum system from the back side of the membrane. Purge gas is routed to the front side of the membrane system through a six-port valve mounted on the top of the GC cabinet. A diagram of the system layout is shown in Figure 1. The valve is actuated through the GC run table. During operation, the MS is maintained at 250°C. The MS should be operated and maintained according to manufacturer's recommendations.
- 5.2 **Membrane Inlet System:** The MIS-1 membrane inlet system is supplied by Environmental Devices, Inc. (E/D; Sacramento, California). The membrane is made of a thin layer of dimethyl silicone (1 cm diameter). The membrane is housed in a cylindrical enclosure that provides an integral heater for the membrane. The temperature is controlled by an associated digital temperature controller. The membrane is operated at 90°C.
- 5.3 **Purging System:** Helium purge gas is supplied from a high-purity helium cylinder at a supply pressure of 5 to 10 psig. Flow control is maintained by an external digital mass-flow controller. The purge vessel consists of a standard 40-mL VOA vial fitted with a direct purge cap supplied by Associated Manufacturing and Design (AMD; Alexandria, Virginia). The purge cap uses a PTFE ball-closure system. A diagram of the purge vessel is shown in Figure 2. The caps and PTFE balls may be reused, but a large supply of the balls is needed since balls are frequently lost when running soil samples. The purge vessel mates to the helium purge line and MIS-1 through a Tekmar standard soil-purging adapter. The system layout is shown graphically in Figure 2, with the valve in standby mode (Purge Valve 1: off) and purge mode (Purge Valve 1: on).

Figure 1. Direct Purge MS System Layout

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Figure 2. Purge Vessel

- 5.4 **Block Heater:** Sample VOA vials are heated with a controlled-temperature, six-position, aluminum block heater. Commercially available block heaters require minor modification by machining to accommodate standard VOA vials.
- 5.5 **Data Management System:** Mass spectrometer control, data acquisition, and analysis are provided by the standard HP Chemstation consisting of an MS-DOS-compatible 32-bit computer, a high-capacity hard disk, an HP-IB controller card, a high-resolution graphics system, and a laser printer. All operational parameters except valve control are stored on the hard disk and downloaded as each sample is run. Valve operations must be manually entered with the currently available software.
- 5.6 **Analytical Balances:** A balance capable of accurately weighing 0.0001 g should be used for preparing standards. A top-loading balance capable of weighing to the nearest 0.1 g is needed for weighing soil samples.
- 5.7 **Volumetric Flasks:** 10 mL and 50 mL with ground-glass stoppers
- 5.8 **Microsyringes:** 2 μ L, 10 μ L, 50 μ L, and 500 μ L

6.0 Reagents

- 6.1 **Reagent Water:** Organic free water. Volatile-free water can be prepared in large quantity by boiling high-purity water for 1 to 2 h in a laboratory hood. The purified water should be transferred while hot to a clean glass bottle. The bottle should be capped at all times when not in use.
- 6.2 **Methanol:** Purge-and-trap grade or equivalent of verified purity. It should be stored away from other solvents.
- 6.3 Pure reagent materials for the following analytes: Methylene chloride, chloroform, carbon tetrachloride, trichloroethene, tetrachloroethene, benzene, toluene, and meta-xylene. Reagent purity should be at least 97% or better.
- 6.4 Pure reagent materials for internal standards: Trifluorotoluene or fluorobenzene. Internal standards should be prepared from material of at least 99% certified purity.
- 6.5 **Stock Standards:** Stock standards are prepared for the individual analytes of interest in methanol at approximately 20 mg/L.
- 6.5.1 About 8 mL of methanol are placed in a 10-mL, tared, ground-glass-stoppered volumetric flask. The flask should stand unstoppered for about 10 min or until all alcohol-wetted surfaces have dried. The flask is weighed to the nearest 0.0001 g.

- 6.5.2 Using a 500- μ L syringe, 200 to 300 μ L of the individual components are immediately added to the flask. The flask is then reweighed. The liquid must fall directly into the alcohol without contacting the neck of the flask.
- 6.5.3 The solution is diluted to volume, stoppered, and then mixed by inverting the flask three times. The concentration is calculated in μ g/ μ L from the net gain in weight. Commercially prepared stock standards may also be used if they are certified by the manufacturer or a reliable independent source.
- 6.5.4 The stock standard solution is transferred into a PTFE-sealed, screw-cap/crimp-cap bottle and stored, with minimal headspace, at -10°C to -20°C and protected from light.
- 6.5.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.
- 6.6 **Component Standard Mixture:** Using the stock standard solutions, an eight-component mixture is prepared in methanol in a 50-mL ground-glass-stoppered volumetric flask, at a concentration of 1000 μ g/mL per component. A 1:10 dilution of the eight-component mixture is prepared. The standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation. The diluted standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.
- 6.7 **Internal Standard:** Using the stock standard solution of either trifluorotoluene or fluorobenzene, a dilution in methanol is prepared at a final concentration of 100 μ g/mL in a 50-mL, ground-glass-stoppered volumetric flask. The standard should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation. The standard must be replaced after one month, or sooner if comparison with check standards indicates a problem.
- 6.8 **Calibration Standards:** Calibration standards should be prepared for at least three concentration levels in reagent water from the eight-component mixture. Twenty-five milliliters of reagent water are added to each VOA vial. Fifty microliters of internal standard and an appropriate sized aliquot of the eight-component mixture are added. One of the concentration levels should be at the PQL. The remaining concentration levels should correspond to the desired working range for the analysis. The direct-purge cap should be immediately placed on the vial and the standards run as soon as possible. The procedure should be repeated daily. Dilute standards prepared in water in this manner should not be stored for prolonged periods.

7.0 Sample Collection, Preservation, and Handling

- 7.1 Sample collection, preservation, and handling should be addressed in the planning process.
- 7.2 Aqueous samples should be collected in duplicate without agitation and without headspace in contaminant-free glass VOA vials with PTFE-lined septa in the caps. The PTFE liner must contact the sample. Samples must be preserved with 500 μ L of 50% HCl at the time of collection (acid should be added to the vial before adding the sample). Samples should be cooled to 4°C after collection. Water samples must be held at 4°C and analyzed within 14 days from the date of collection.
- 7.3 Soil can be collected using a 5-mL plastic syringe with the end sliced off or with some equivalent coring device. If the soil is exceptionally dry, a spatula may be used, but significant loss of volatiles is likely to occur in that case. A sufficient number of vials (at least three) should be collected to provide for backup analysis in the event of breakage or instrument overload. Additional samples can also provide an estimate of spatial variability and volatility losses encountered during sampling. If required by project data quality objectives, one vial should be collected for dry-weight determination (without methanol). A methanol handling blank should be provided for each batch of 20 samples (daily at a minimum). Samples should be collected in tared 40-mL VOA vials containing 5 mL of purge-and-trap-grade methanol. Extra vials should be available in case of spillage. Vials should not be analyzed if any of the methanol has spilled during sampling or subsequent handling. Using a cutoff syringe or equivalent, a soil volume of 2 to 3 mL (corresponding to about 5 g) should be added to the vial. Care should be taken to prevent contacting the vial threads with any soil. Excessive soil handling should be avoided to minimize volatilization losses during sampling. All sediment should be cleaned from the vial threads. After securing the vial cap, the vial is shaken. If detectable leakage from the vial occurs at this point, then resampling is required. All samples are cooled to 4°C after collection. The sample should be returned to the laboratory for final weight determination as soon as possible. The samples may be stored at 4°C for up to 14 days from the time of collection.

8.0 Procedure

- 8.1 Volatile organic compounds are introduced into the MS by direct purge over a permeable membrane. The purge procedure may be used directly on groundwater samples. Soils and solids should be analyzed by methanol extraction followed by addition of water and direct-purge analysis. Soil concentrations should be reported on a dry-weight basis. The procedure for determining dry weight can be found in U.S. Environmental Protection Agency (EPA) Method 5030, section 7.3.3.1.5. For the purpose of rapid screening, wet weight may be used. In that case, concentrations should be reported as estimates unless the soil is known to be inherently dry.

8.2 Mass Spectrometry

8.2.1 The MS should be autotuned on a daily basis to reset ion optics and verify satisfactory performance.

8.2.2 Critical MS parameters should be set as follows:

Acquisition Mode : Scan
Solvent Delay : 0.00 min
EMV Offset : +200 volts
Low Mass : 45
High Mass : 200
Sampling # : 4
MS Temperature : 250°C
Vacuum : Typically 2×10^{-5} Torr
Time Window : 4.00 min

8.2.3 Other MS parameters may be set at operator discretion.

8.3 Sample Introduction

8.3.1 The membrane temperature should be set to 90°C.

8.3.2 The purge gas is helium. The purge flow should be set to 65 to 75 mL/min. The sensitivity is flow dependent.

8.3.3 The block heater should be set to 75°C. Approximately 20 min should be allowed for each sample to reach the desired temperature.

8.3.4 The GC run table should contain the following entries:

Purge Valve 1 OFF time = 0.00 min
Purge Valve 1 ON time = 0.20 min
Purge Valve 1 OFF time = 4.00 min

8.4 Calibration

8.4.1 The eight-component standard should be run at a minimum of three concentration levels at and above the PQL and covering the linear range of the instrument. The instrument should be calibrated in recovered ng of added analyte rather than in concentration units to provide ease of conversion for soil

samples. Calibrations for waters may be used interchangeably for soils in that case with an appropriate calculation that includes sample weight or water volume. The recommended calibration range is 200 to 50,000 ng.

8.4.2 Final solutions containing required concentrations of calibration standards should be prepared from the eight-component standard or a 1:10 dilution as follows:

8.4.2.1 Twenty-five milliliters of reagent water are added to a clean VOA vial. An aliquot of the standard is added using an appropriate-sized μL syringe. A 50- μL aliquot (5000 ng) of the internal standard is added. The vial should immediately be sealed with the purge adapter cap.

8.4.2.2 Any excess methanol residue should be wiped from the syringe needle before injection. When discharging the contents of the syringe, the end of the syringe needle should be well beneath the surface of the reagent water.

8.4.3 The standards are placed on the block heater, and at least 20 min are allowed for the samples to attain working temperature before purging.

8.4.4 Samples are purged for 4 min each while acquiring MS data. Elution curves are integrated using GC-MS software. Peak-area response is tabulated from the eight components and the internal standard against the mass injected. The results are used to prepare a calibration curve by linear regression. Results are plotted as ratios relative to the internal standard.

8.4.5 The working calibration curve should be verified on each working day by injecting a mid-range standard (5000 ng). If the response for the verification standard varies from the predicted response by more than 20%, a new calibration curve should be prepared.

8.5 Water Sample Analysis

8.5.1 Twenty-five milliliters of clean water are added to each VOA vial to be used, and the position of the meniscus is marked with an indelible marker pen. All vials are dried. The PTFE ball is placed firmly in the purge-adapter cap. Each vial is pretared and capped before using. The weight is measured with a top-loading balance to the nearest 0.1 g.

8.5.2 The sample vial is uncapped, and approximately 25 mL of sample water are poured into the premarked, pretared vial. Fifty microliters of internal standard (5000 ng) are added, and the vials are sealed with a cap. The vial is inverted to

mix the internal standard and check for leaks. The vial is weighed, and the weight of sample water added is recorded.

- 8.5.3 The samples are placed on the block heater, and at least 20 min are allowed for the samples to attain their working temperature before purging.
- 8.5.4 Samples are purged for 4 min each while acquiring MS data. Elution curves are integrated using GC-MS software while the next sample is being run. The sample is removed after purging is complete and replaced with the next sample. Samples can then be run in rotation so that each has adequate time to attain the correct working temperature in the block heater.

8.6 Soil Sample Analysis

- 8.6.1 The VOA vial is uncapped, and 50 μ L of internal standard are added to the soil-methanol mixture. Twenty-five milliliters of reagent water are added, and the vial is sealed with a purge adapter cap. The vial is inverted to mix and check for leaks. The sample is shaken to fully disperse soil in the water/methanol mixture.
- 8.6.2 The samples are placed on the block heater and at least 20 min are allowed for the samples to attain their working temperature before purging.
- 8.6.3 Each sample is manually agitated for at least 15 sec after the working temperature is attained and before purging.
- 8.6.4 Samples are purged for 4 min each while acquiring MS data. Elution curves are integrated using GC-MS software while the next sample is being run. The sample is removed after purging is complete and replaced with the next sample. The samples can then be run in rotation so that each has adequate time to attain the correct working temperature in the block heater.

8.7 Data Reduction

- 8.7.1 Integration is performed with the standard GC-MS chromatography software. Since the direct-purge method produces a much broader peak than is typical for the standard GC-MS application, some modification to the default GC integration parameters is needed. Retention times should be determined for each species by manual integration and entered into the quantitation table. The integration window should be set very wide, ranging from the time of MS turn-on (0.2 min) to at least 0.5 min after the end of the run (4.5 min). The quantitation setup menu should have the reference window and non-reference windows set to at least 0.3 min to account for variation in retention time on purging.

- 8.7.2 Since the automatic integration may occasionally fail or produce an incomplete integration, a manual check on the integration is required for all results, and if necessary, manual reintegration should be implemented.
- 8.7.3 Calibration curves are computed automatically by the GC software using a force-through-zero linear regression fit.
- 8.7.4 Examples of typical purge spectra are shown in Appendix A.

9.0 Calculations

- 9.1 Results are reported by the GC software in ng of recovered analyte.
- 9.2 The concentration of each analyte in water samples is computed as follows:

$$C = m/W/\rho$$

where:

- C = concentration of sample in $\mu\text{g/L}$
m = mass of recovered analyte in ng
W = measured weight of water in the VOA vial
 ρ = density of sample; for pure water at room temperature ρ may be assumed to be 1.0.

- 9.3 The concentration of each analyte in soil samples is computed as follows:

$$C = m/W$$

where:

- C = concentration of analyte in sample in $\mu\text{g/kg}$
m = mass of recovered analyte in ng
W = measured dry weight of soil in the VOA vial.

10.0 Quality Control

- 10.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.

- 10.2 The analyst should make an initial demonstration of the ability to generate acceptable accuracy and precision with this method by successful analysis of the following:
- 10.2.1 **Replicate Eight-Component Analyte Spikes in Water:** The analysis of five replicates at a concentration of 100 µg/L should have the accuracy and precision of all the replicates falling within 20% of the known concentration.
 - 10.2.2 **Replicate Soil Spikes:** The analysis of five spiked soil samples at a concentration of 1000 µg/kg should have all recoveries between 70% and 140% and the precision of all replicates within 20%. Soil spikes should be prepared and analyzed as described in section 10.3.2.
- 10.3 With every batch of 20 samples or less, the lab should analyze the following:
- 10.3.1 **Replicate Eight-Component Analyte Spikes:** The accuracy and precision of the two replicate spikes prepared at a concentration of 100 µg/L should be within 20% of the known concentration.
 - 10.3.2 **Soil Spike:** The soil spike is prepared by spiking the eight-component standard into a sample of clean soil. The spike amount should fall in the mid range of the calibration curve. A 5-mL aliquot of purge-and-trap methanol should be added immediately following spike addition. Soil spikes should be analyzed with the other samples according to the same protocols. The spike recovery should be between 70% and 140%.
 - 10.3.3 When soil samples are analyzed, a reagent methanol blank should be included in each batch.
 - 10.3.4 Reagent water blank
- 10.4 One methanol trip blank should accompany each sampling event (for each site and for each day that samples are collected).
- 11.0 **Method Performance**
- 11.1 The recommended PQL is 8 µg/L for waters and 40 µg/kg for soils.
 - 11.2 A field-method validation experiment was carried out during the period of September 16 through September 23, 1993. The site chosen was in the Hanford 200 West Area near the Plutonium Finishing Plant. The discharge of carbon tetrachloride over a 26-year period to three liquid waste disposal facilities (LWDFs) resulted in a large burden of carbon

tetrachloride in the vadose zone near the LWDFs. Samples were collected from the vadose zone by the recently developed ResonantSonic™ drilling method. The drilling was performed by Water Resources Corporation (Woodland, California), who have pioneered that method. Drilling was done at a 45° angle to a final vertical depth of 117 ft. A 5-in.-diameter split-spoon sampler was used to recover samples from the borehole ahead of the drill string. The geology in the area is dominated by flood-deposited unconsolidated sediments with diverse mineralogy. Contamination was first encountered at significant levels at a depth of about 40 ft, with a gradual increase seen down to 117 ft. Considerable point-to-point variability was evident at some horizons, but others showed little variability.

- 11.3** Samples were collected from the split-spoon samples with either a core-punching tool or spatula. Because of the very dry character of the soil, particularly near the surface, it was not possible in all cases to obtain good core punches; however, most of the deeper samples were collected as core punches. Four to six samples were collected at each horizon. Samples were placed in pretared 40-mL VOA vials containing 10 mL of purge-and-trap-grade methanol. That is double the amount of methanol used in the direct-purge protocol. It was necessary to double the amount of methanol to perform duplicate measurements by both direct-purge MS and purge-and-trap GC. Twenty-seven samples were chosen for comparative analysis, starting at the deeper depths where significant contamination had been observed. A 5-mL aliquot of the methanol was removed from each sample and analyzed by purge-and-trap GC according to EPA Method 502.2 protocols (EPA 1990). The remaining sample was analyzed by the direct-purge MS procedure with a correction made for removing half the sample, assuming that the extraction was 100% efficient. The samples were found to contain predominantly carbon tetrachloride with trace amounts of methylene chloride, chloroform, trichloroethene, and toluene. Only carbon tetrachloride is reported and compared here. A more extensive additional study is needed to validate the other species.
- 11.4** Results of the intercomparison study are presented in Table 2 and displayed graphically in Figures 3 and 4. Agreement was generally quite satisfactory. In most cases, the direct-purge method produced a somewhat higher but similar result. The simple linear regression plotted in Figure 4 shows a positive bias of 22% for the direct-purge method. That small bias may be indicative of a slightly higher extraction efficiency associated with the 75°C extraction temperature used in the direct-purge method as opposed to the less aggressive conditions used in the room-temperature methanol extraction. The combination of methanol and water used in the final step of the direct-purge method may also produce an enhanced extraction. These results suggest that for simple contaminant mixtures, the direct-purge method is capable of producing satisfactory rapid-screening data with good quantitation quality. The MS system at the field site was based in a 30-ft

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Figure 3. Comparison of Carbon Tetrachloride Concentrations in Methanol Extracts of Hanford Soil Core Samples as Measured by Purge-and-Trap GC vs. Direct-Purge MS.

Figure 4. Comparison of Carbon Tetrachloride Concentrations in Methanol Extracts of Hanford Soil Core Samples as Measured by Purge-and-Trap GC vs. Direct-Purge MS.

motor-home-based mobile laboratory. A portable generator supplied power during the drilling and sampling activity. The results were very encouraging for demonstrating the utility of this technique as a field-screening tool.

Table 2. Comparison of Carbon Tetrachloride Concentration in Methanol Extracts of Hanford Soils as Measured by Purge-and-Trap GC vs Direct-Purge MS.

<u>Vertical Sampling Depth</u> (ft)	<u>Purge-and-Trap GC</u> ($\mu\text{g/kg}$)	<u>Direct-Purge MS</u> ($\mu\text{g/kg}$)
68.1	70	102
68.1	149	212
70.4	93	114
71.1	119	99
71.1	107	109
71.1	114	182
77.8	78	87
77.8	66	90
83.7	201	255
83.7	289	315
85.4	836	792
85.4	263	331
88.8	381	529
88.8	327	377
88.8	337	401
88.8	401	381
88.8	282	298
88.8	331	270
92.9	521	790
92.9	580	1062
96.7	295	393
96.7	211	186
96.7	228	148
99.6	1049	1508
99.6	448	484
103.5	248	256
103.5	515	350

12.0 References

U. S. Environmental Protection Agency (EPA). 1990. "Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series," Method 502.2. Environmental Measurements Laboratory, Cincinnati, Ohio.

13.0 Further Information

Wisconsin DNR. 1992. "Modified GRO, Method for Determining Gasoline Range Organics," PUBL-SW-140.

Lewis, T. E., A. B. Crockett, R. L. Segrist, and K. Zarrabi. 1991. *Soil Sampling and Analysis for Volatile Organic Compounds*. U. S. Environmental Protection Agency (EPA), EPA-540/4-91/001.

OS050^(a)

Supercritical Fluid Extraction for the Analysis of Contaminated Soils

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methodst* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

- 1.1 This method describes a supercritical fluid extraction (SFE) technique for nonpolar, semivolatile organic compounds followed by analysis by capillary gas chromatography (GC). GC-mass spectrometry (GC-MS) may also be used for analysis or confirmation of identifications.
- 1.2 The SFE technique is compared with Soxhlet extraction. It is much more rapid and does not require large amounts of solvent or glassware. (See Wright et al. 1989; Wright and Fruchter 1992.)
- 1.3 The method has been demonstrated for extraction of polycyclic aromatic hydrocarbons (PAHs) from soils using supercritical CO₂. It is also applicable to sludges and ashes. Detection limits are in the 10 to 100 ng/g range. The method is also applicable to organic compounds, such as polychlorinated biphenyls (PCBs), with minor modification.

2.0 Summary of Method

- 2.1 Soil (or other solid-phase matrix) samples (1 to 5 g) are sealed inside an extraction cell and extracted with carbon dioxide at temperatures between 50 and 125°C and pressures of 325 to 400 bar for 15 to 60 min. The extraction time depends upon operating parameters such as flow rate, size of restrictor, and cell dead volume. Analytes are collected as the extraction effluent is bubbled through a collection solvent, such as methylene chloride, in a glass collection vessel with a reflux condenser to minimize solvent losses.

(a) This method was supplied by B. W. Wright, C. W. Wright, and J. S. Fruchter (Pacific Northwest Laboratory, Richland, Washington).

- 2.2 Extracts are concentrated (if necessary) and analyzed by capillary column GC with flame ionization (FID) or MS detection. Electron capture detection (ECD) is recommended for analyzing PCBs. Recoveries are highly matrix dependent.

3.0 Interferences

- 3.1 The extraction and analytical systems may be demonstrated to be free from contamination by running a system blank using fired sand or another organic-free material.
- 3.2 Carbon dioxide does not extract polar materials or high molecular weight materials such as fulvic or humic acids from soils, thus avoiding interferences from these compounds.
- 3.3 Other nonpolar semivolatile organic compounds may be extracted from samples and may interfere with the GC identifications. Coextracted interferences will vary considerably from source to source. Cleanup of the extract and/or GC-MS analysis may be necessary to resolve these potential interferences.
- 3.4 Much of the system is either self-cleaning or can be recycled with minimal cleaning. The system should be purged with supercritical CO₂ while the extraction cell is empty. Spent extraction cells are free of extractable organics and can be rinsed with water. The collection vessels should be adequately rinsed with an appropriate organic solvent to prevent cross contamination.

4.0 Safety

- 4.1 Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants.
- 4.2 The extraction is performed at high pressures (e.g., up to 7500 psi), and adequate precautions should be taken to ensure that the system can withstand the pressure without failure. The extraction cell or any fittings should not be disconnected until pressures return to near ambient. The extraction cell is heated, so caution should be used when handling after an extraction is completed.

5.0 Apparatus and Materials

- 5.1 **Supercritical Fluid Extraction Apparatus:** The apparatus described here is an in-house built portable instrument. Other functionally equivalent commercially-available or in-house built units may be substituted. Basic requirements for the apparatus are a high-pressure pumping system, a heated oven, an extraction cell, a pressure restrictor, a

restrictor heater, and a collection vessel. A schematic diagram of the portable SFE apparatus is shown in Figure 1. It was designed specifically for field applications. It measures approximately 14 in. wide by 14 in. high by 13 in. deep and weighs approximately 23 kg. It must be connected to standard 110-V power. The extraction cell heating mantles and restrictor heaters are mounted on top of the apparatus and the collection vessels are mounted vertically on its right side. This configuration maintains the device's compact design and allows easy manipulation of the extraction cells, restrictors, and collection vessels.

Figure 1. Schematic Diagram of the SFE Apparatus.

- 5.1.1 **Reciprocating High-Pressure Pump:** Supplies the pressurized fluid to the extraction cell. Single-stage thermoelectric devices, which are essentially solid state heat pumps that have a cold and a hot side, are used to cool the pump and incoming flow of liquid CO₂ (Figures 2 and 3). To maintain an appropriate operating temperature on the hot side, a liquid-cooled heat exchanger is incorporated on each thermoelectric device. The cooling liquid, a water-ethylene glycol mixture, is circulated through a muffin-fan-cooled radiator attached to the rear of the apparatus.

Figure 2. Pumphead Cooling Assembly Design of the Portable SFE Apparatus

Figure 3. Fluid Supply Cooling Assembly Design of the Portable SFE Apparatus

- 5.1.2 **Oven:** Provides heat to the pressurized extraction fluid and extraction cell. Transfer lines and extraction cells are maintained in a cylindrical heating mantle oven for control of extraction temperature.
- 5.1.3 **Extraction Cells:** Hold samples for extraction. Cells are made from 1- to 4-in. lengths of 1/4-in. stainless steel tubing capped with Swagelok stainless steel zero-volume 1/4-in. to 1/16-in. column end fittings containing 1.0- μ m pore size sintered stainless steel frits. Alternatively, extraction cells of similar size are commercially available (Keystone Scientific). The internal diameter of the extraction cells should be kept relatively narrow ($\leq 5/16$ in.) to minimize flow from channeling through the matrix.
- 5.1.4 **Flow Restrictors:** Used to maintain the pressure of the system as well as reduce the CO₂ pressure to atmospheric pressure. These are made of uncoated fused silica, 50- to 100- μ m ID, approximately 18 in. in length.
- 5.1.5 **Resistor Heater:** Prevents the restrictor from freezing and plugging. It consists of resistively heated stainless steel tubing through which the restrictor passes. Its temperature is controlled by adjusting the input current.
- 5.1.6 **Collection Flask Assembly:** Contains the collection solvent through which the extraction effluent from the restrictor is bubbled for analyte collection. The collection flask assembly is shown in Figure 4. A thermoelectric-cooled copper block with a tortuous flow path is connected to the exit of the glass collection flask to prevent solvent evaporation. A recirculating, radiator-cooled water-ethylene glycol bath, operated at -15° to -20°C, is used to cool the heat exchanger and copper block of the condenser.
- 5.2 **Glass Vials:** For sample extracts, amber or foil wrapped, 7 mL, with Teflon or foil lined caps.
- 5.3 **Gas Chromatograph:** Hewlett-Packard 5880A or equivalent. Suitable for capillary columns with split-splitless injection with all required accessories including syringes, vials, analytical columns, gases, FID, and integrator or data system. It should be equipped with an ECD for PCB analyses.
- 5.3.1 **Capillary Column:** SE-54, crosslinked or uncrosslinked, 15 to 30 m x 0.25 mm ID with a 0.25- μ m film thickness

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Figure 4. Collection Vessel Assembly Design of the Portable SFE Apparatus.

6.0 Reagents

- 6.1 **Carbon Dioxide:** High-purity, SFE grade (Scott Specialty Gases or equivalent). Small aluminum gas cylinders are commercially available that weigh approximately 50 lb and contain 20 lb of CO₂. Such a cylinder would service between 100 and 200 extractions.
- 6.2 **Methylene Chloride:** Distilled-in-glass, high-purity grade. Isooctane may be substituted for PCB collection.
- 6.3 Polyethylene glycol/water mixture
- 6.4 **Nitrogen:** Ultra-high-purity grade
- 6.5 **Calibration Standards:** Calibration standards consisting of selected PAH compounds should be prepared at five dilutions in methylene chloride to span 2 to 3 orders of magnitude. Concentrations should range from approximately 0.100 µg/mL to 100 µg/mL. Supercritical fluid extracts are concentrated or diluted as necessary so responses fit on the calibration curves. (Standards may be substituted as necessary for the desired particular nonpolar, semivolatile compounds)
- 6.6 **Internal Standard:** A 2-chloroanthracene internal standard at 50 µg/mL in methylene chloride is added to all extracts. (The internal standard is used at a concentration of 250 µg/mL for PCB analysis with ECD detection).

7.0 Sample Collection, Preservation, and Handling

- 7.1 Samples should be protected from exposure to light. Samples should be kept refrigerated. Extract samples containing PAH may be stored up to 3 months before analysis.

8.0 Procedure

- 8.1 Samples are homogenized as received by mixing and are not dried or sieved. Up to approximately 1.5 mol % water does not interfere with analyte extraction. For highly contaminated soils or very dense clays it may be necessary to mix small diameter glass beads to allow sufficient porosity for good fluid flow through the matrix.
- 8.2 Selected soil samples may be characterized for particle size, total organic carbon, weight loss on heating, and elemental oxide composition of the ash after heating, based on traditional standard methods.

- 8.3 Soil samples of approximately 1 to 5 g each (weighed to within ± 0.005 g and depending on the size of the extraction tube) are sealed inside the stainless-steel extraction cell. The extraction cell is placed inside the oven and heated to 50 to 125° C. The sample is extracted with CO₂ at pressures of 325 to 400 bar for 15 to 60 min. Gas flow rates range from 400 to 800 mL/min, with flow restrictors of 50- to 100- μ m I.D. Shorter extraction times are possible with faster flow rates, larger diameter flow restrictors, less dead volume, and low levels of contamination. Longer extraction times are required for slower flow rates, smaller diameter flow restrictors, larger dead volumes, and highly contaminated samples. The extraction effluent is bubbled through methylene chloride solvent and the analytes are collected in a glass collection vessel which is filled with 1.0 to 5.0 mL of internal standard solution and an additional approximately 20 mL of methylene chloride (or other appropriate solvent). It is then wrapped in aluminum foil to minimize sample exposure to light.
- 8.4 Extracts and collection vessel washings (at least three at 1 mL each with methylene chloride) are transferred, combined, and concentrated to approximately 2 mL under a stream of nitrogen in foil-wrapped glass vials.

8.5 Gas Chromatographic Analysis

8.5.1 GC Conditions

Column:	See section 5.3.1.
Carrier gas:	Hydrogen @ 100 cm/s linear velocity or helium @ 50 cm/s linear velocity
Temperature program:	
Initial temperature:	40°C, hold for 2 min
Program:	40°C to 280°C at 3°C/min
Final temperature:	280°C, hold for 2 min
Injection temperature:	250 to 275°C
Detector (FID) temperature:	300°C
Splitless injection:	0.5 min purge

- 8.5.2 An example of a GC is shown in Figure 5 with identifications in Table 1.

Figure 5. High-Resolution Gas Chromatogram of the Supercritical Fluid Extract from a Manufactured Gas Waste Site Sample. Peaks numbered are identified in Table 1. The internal standard is identified with an asterisk. See text for conditions.

Table 1. Identification of Components in a Soil Sample Supercritical Fluid Extract

Peak No. ^(a)	Mol wt.	Compound	Peak No. ^(a)	Mol wt.	Compound
1	116	Indene	20	190	4H-Cyclopenta[def]phenanthrene
2	130	Methylindenes	21	192	4- and 9-Methylphenanthrene
3	128	Aaphthalene	22	192	1-Methylphenanthrene
4	134	Benzo[b]thiophene	23	202	Fluoranthene
5	142	2-Methylnaphthalene	24	202	Accephenanthrylene
6	142	1-Methylnaphthalene	25	202	Pyrene
7	154	Biphenyl	26	216	Benzo[a]fluorene
8	156	Dimethylnaphthalenes	27	216	Benzo[b]fluorene, Methylpyrene
9	152	Acenaphthylene	28	216	Methylpyrenes
10	154	Acenaphthene	29	234	Benzo[b]naphthol[1,2-d]thiophene
11	168	Dibenzofuran	30	228	Benzo[a]anthracene
12	168	Fluorene	31	228	Chrysene, Triphenylene
13	182	Methylfluorenes	32	252	Benzo[fluoranthenes
14	184	Dibenzothiophene	33	252	Benzo[e]pyrene
15	178	Phenanthrene	34	252	Benzo[a]pyrene
16	178	Anthracene	35	252	Perylene
17	167	Carbazole	36	276	Indeno[1,2,3-cd]pyrene
18	192	3-Methylphenanthrene	37	276	Benzo[ghi]perylene
19	192	2-Methylphenanthrene	38	302	Naphthofluoranthenes/pyrenes

(a) Numbers refer to peaks labeled in Figure 1.

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.
- 9.2 Response factors (amount/area) are calculated from standard reference PAH compounds chromatographed at five concentration levels ranging over two orders of magnitude. The response factor of a closely eluting or similar compound is used to quantify components for which standard reference compounds are not available. Response factors are calculated relative to the internal standard (area of compound of interest/area of internal standard). Relative response factors are calculated from the average of two or three analyses of each of the standards. A linear calibration curve is constructed for each compound (amount versus relative response factor).
- 9.3 Components in extracts are identified by retention index (Vassilaros et al. 1982), absolute retention times of standard reference compounds, and/or GC-MS operated in the electron-impact mode at 70 eV.
- 9.4 System blanks should be prepared twice daily, both before and after soil extractions. Sample extracts should be analyzed at random, up to eight at a time between internal standard and calibration standard analyses. Surrogate standard spikes are not recommended for recovery information, as spiked compounds may not extract in the same way as native compounds in the matrix.

10.0 Method Performance

- 10.1 **Recovery Study.** A 1-g (weighed to within ± 0.005 g) sample of a soil known to contain less than 25 ng/g of individual PAH was placed in an SFE extraction cell and spiked with 200 μ L of a PAH standard solution in methylene chloride. The solution, which consisted of 14 PAH standard reference compounds ranging from two to six rings in size at levels of approximately 10 μ g/g (see Table 2), was subsequently evaporated. The spiked soil sample was then extracted as in section 8.3 for 40 min at 325 bar and 100°C; 250 μ L of 2-chloroanthracene internal standard was added to the solvent in the collection vessel. The percent recoveries of each of the PAH standard reference compounds were determined by comparison of the extract's individual PAH FID responses relative to the internal standard to those for 200 μ L of the PAH standard solution with the same amount of internal standard as was added to the SFE extract.

Table 2. SFE Recovery Study Results

Compound	Std. Amt. ng/ μ L	Spike Amt. ^(a) μ g/g	% Recovery
Naphthalene	56.3	11.3	40.7
2-Methylnaphthalene	50.0	10.0	52.4
Biphenyl	50.7	10.1	62.5
Fluorene	49.2	9.84	85.5
Dibenzothiophene	49.3	9.86	91.0
Phenanthrene	50.0	10.0	96.6
1-Methylphenanthrene	50.3	10.1	85.6
Fluoranthene	49.7	9.94	85.1
Pyrene	49.0	9.80	89.7
Benzo[b]fluorene	49.8	9.96	99.4
Chrysene	50.1	10.0	96.0
Benzo[e]pyrene	66.0	13.2	120
Indeno[1,2,3-cd]pyrene	19.9	3.98	119
Benzo[ghi]perylene	49.6	9.93	124

(a) Based on a 200- μ L spike of the standard onto 1.00 g of soil.

The results of the recovery study are shown in Table 2. Recoveries ranged from 44% to 124%, with only the most volatile lower molecular weight PAH compounds giving less than quantitative recoveries (<80%). It is likely that the most significant losses of these volatile compounds occurred during spiking rather than extraction and analysis. The average recovery for all the spiked PAH compounds was 90%. Similar results (95% average recovery) were obtained at spiking levels ranging from 0.8 to 5 ppm.

- 10.2 Replicate Studies.** Ten replicate SFE extractions were performed on a soil from a manufactured gas waste site and were analyzed in triplicate for 14 PAH compounds (Table 3). The average percent standard deviation (representing both the replicate and the multiple analysis variability) was 18, with roughly 25% of the variability attributed to the SFE extraction and 75% of the variability attributed to the analysis. Five replicate SFE extractions were performed on a different soil from a manufactured gas waste site and were analyzed in triplicate for 15 PAH compounds. The average percent standard deviation (representing both the replicate and the multiple analysis variability) was 12, with roughly 20% of the variability attributed to the SFE extraction and 80% of the variability attributed to the analysis. The average percent standard deviation for the two SFE replicate studies was 3.4% (Wright and Fruchter, 1992).

Table 3. Concentrations of Selected PAHs in a Manufactured Gas Waste Site Sample as Determined by GC Analysis of SFE Extracts

<u>Compound</u>	<u>Conc. (a) $\mu\text{g/g}$</u>
Fluorene	20.1 $\pm$ 2.2
Dibenzothiophene	13.3 $\pm$ 4.1
Phenanthrene	45.7 $\pm$ 5.4
Carbazole	49.1 $\pm$ 4.6
3-Methylphenanthrene	47.7 $\pm$ 4.8
2-Methylphenanthrene	41.2 $\pm$ 2.7
9- or 4-Methylphenanthrene	57.2 $\pm$ 3.1
1-Methylphenanthrene	42.2 $\pm$ 3.0
Fluoranthene	48.1 $\pm$ 3.0
Pyrene	57.0 $\pm$ 3.7
Benz[a]anthracene	30.5 $\pm$ 2.6
Chrysene	40.7 $\pm$ 3.2
Benzo[e]pyrene	11.9 $\pm$ 1.1
Benzo[a]pyrene	21.1 $\pm$ 4.2

(a) Average $\pm$ standard deviation from 10 samples

- 10.3 Comparison to Soxhlet Extraction.** In two comparisons with Soxhlet extraction, the quantitative results of 14 or 15 individual PAH compounds in five or ten replicate SFE extracts for two different manufactured gas waste site soils averaged a $\pm 5\%$ to a $\pm 10\%$ difference from the results of five Soxhlet extractions of each of the soils. The amounts quantified for the SFE and Soxhlet extracts were statistically the same for 9 of 14 PAH compounds and 13 of 15 PAH compounds for the two studies (Wright and Fruchter, 1992).
- 10.4** To determine whether a 30-min extraction time is sufficient for SFE, the concentrations of selected PAH were determined from three successive SFE extracts for two soils from a manufactured gas waste site sample. The percent extracted in each successive extraction was then calculated from the total (Table 4). In sample 3-2, which had low levels of high molecular weight species, the first 30-min extraction removed 100% of the PAH. In sample 6-1, which had high levels of the high molecular weight PAHs, a little more than an average of 80% were removed in the first 30 min. It took longer extraction times to remove the higher molecular weight PAHs because of their decreasing solubility in supercritical CO_2 . Thus, increased extraction time and/or increased fluid flow rate may be necessary for samples with high levels of high molecular weight species.

11.0 References

Wright, B. W. and J. S. Fruchter. 1992. *Supercritical Fluid Extraction For the Analysis of Contaminated Soils*. EPRI TR-100754, Pacific Northwest Laboratory, Richland, Washington.

Wright, B. W., C. W. Wright, and J. S. Fruchter. 1989. "Supercritical Fluid Extraction of Coal Tar Contaminated Soil Samples." *Energy & Fuels* 3:474-480.

Vassilaros, D. L., R. C. Kong, D. W. Later, and M. L. Lee. 1982. "Linear Retention Index System for Polycyclic Aromatic Compounds." *J. Chromatogr.* 252:1-20.

Table 4. Concentrations of Selected PAHs in Manufactured Gas Waste Site Samples as Determined by GC Analysis of Successive SFE Extracts

Compound	Conc. in Manufactured Gas Waste Site Samples ^(a)							
	µg/g of Combined	Sample 1			µg/g of Combined	Sample 2		
	Sample 1	% SFE I	% SFE II	% SFE III	Sample 2	% SFE I	% SFE II	% SFE III
Naphthalene	8.2	100	0	0	42	87	9	4
1-Methylnaphthalene	14	100	0	0	8.1	100	0	0
2-Methylnaphthalene	11	100	0	0	4.2	100	0	0
Biphenyl	0.86	100	0	0	1.5	100	0	0
Acenaphthylene	7.6	100	0	0	3.0	83	0	17
Acenaphthene	0.37	100	0	0	7.1	61	24	15
Fluorene	2.0	100	0	0	3.6	100	0	0
Dibenzothiophene	1.0	100	0	0	5.4	100	0	0
Phenanthrene	14	100	0	0	51	91	7	2
3-Methylphenanthrene	4.4	100	0	0	17	84	12	5
2-Methylphenanthrene	4.5	100	0	0	18	81	13	6
Fluoranthene	3.5	100	0	0	110	84	14	2
Pyrene	4.0	100	0	0	180	78	19	3
Benzo[b]fluorene	1.1	100	0	0	80	78	19	3
Benz[a]anthracene	1.3	100	0	0	135	80	17	3
Chrysene	1.2	100	0	0	155	76	20	4
Benzo[e]pyrene	0.18	100	0	0	150	62	29	9
Benzo[a]pyrene	0.29	100	0	0	180	66	27	7
Indeno[1,2,3-cd]pyrene	2.4	100	0	0	130	57	30	13
Benzo[ghi]perylene	0.17	100	0	0	140	43	36	21

(a) Samples were each extracted three times in succession.

OC010R^(a)**Preparation and Cleanup of Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds**

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

- 1.1** This method is useful for analyzing volatile organic compounds in samples containing normal hydrocarbons in quantities that interfere with analysis of purge-and-trap samples. This method was developed to remove normal paraffin hydrocarbons (NPH), typically C₁₂ through C₁₄, which are often used as a non-miscible hydrostatic fluid for sampling radioactive tank wastes. The NPH removal for samples and blank spikes is better than 99%. This method can be used for any sample matrix containing excessive quantities of normal hydrocarbons, such as waters, sorbents, or soils.
- 1.2** This method employs a methanolic extraction of a sample followed by cleanup of the residue using C₁₈ solid-phase sorbent cartridges. The cleanup is based on the selective retention of NPH on a C₁₈ column while the more polar volatile analytes are eluted with a methanol/water mixture. A portion of the resultant residue from this preparation is analyzed using gas chromatography-mass spectrometry (GC-MS) procedures such as U.S. Environmental Protection Agency (EPA) SW-846 Methods 8240 or 8260 (EPA 1992). Using this cleanup method increases the detection limits of a typical purge-and-trap GC-MS procedure by approximately 625 times because of the dilution factor; however, without the cleanup step, much greater dilution factors (10 to 1000 times greater) would be needed to prevent contamination of the instrument.
- 1.3** This method may be used to analyze radioactive storage-tank wastes that contain hydrocarbons in excessive quantity. It does not allow for distinguishing between hydrocarbons introduced during the sampling process as contamination and those that

(a) This method was supplied by R. B. Lucke, J. A. Campbell, G. A. Ross, S. C. Goheen, and E. W. Hoppe (Pacific Northwest Laboratory, Richland, Washington).

are native to the tank wastes. However, it does significantly decrease the radioactivity of the original samples, in some cases by a factor of 1000.

2.0 Summary of Method

An aliquot (nominally 1 g) of the sample is extracted by shaking with 5 mL of methanol/water (90/10) to which surrogate compounds have been added. A 2-mL aliquot of the extract is syringe-pumped through a C₁₈ Sep-Pak[®] Cartridge and followed with 0.5 mL rinses with methanol/water (90/10) until a final volume of 5 mL is obtained. A 100-μL quantity of the eluent is transferred to a purge vessel containing 4.9 mL of water. An analysis procedure, such as SW-846 Method 8240 or 8260, is then performed on the clean residue. The remainder of the solutions can be saved for repetitive analyses, if needed. Solutions are disposed of according to hazardous/radioactive waste protocols.

3.0 Interferences

- 3.1 “Purge-and-Trap” grades of methanol are typically of sufficient quality to use in this method. Continued exposure of the methanol to the ambient air is not desirable. An approach to minimize this problem is to purchase several small quantities of methanol or to aliquot larger amounts to several small containers to reduce exposure time.
- 3.2 Several target compounds are subject to substantial degradation under alkaline conditions. For example, 1,1,2,2-tetrachloroethane degrades to trichloroethene under alkaline conditions, resulting in low results for the former and elevated results for the latter. Vinyl acetate, vinyl chloride, 1,1,2-trichloroethane, chloromethane, bromomethane, and carbon disulfide also appear to exhibit alkali sensitivity. In low moisture conditions, such as dry alkaline soils or where the presence of oil precludes water, the degradation may not be complete. Until validation of a suitable pH adjustment procedure is available, residues of low moisture alkaline soils should be analyzed immediately following the extraction procedure.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Materials

- Balance: Analytical, capable of accurately weighing 0.01 g
- Vials: Pre-cleaned volatile organic analyte (VOA) type 1.5 mL, 5 mL, 20 mL screw top with Teflon[®]-lined silicone-backed closures

- Pipets: Pasteur type or equivalent
- Centrifuge: Bench top, capable of achieving 2000 rpm
- Syringes: Gas-tight, 10 μ L, 100 μ L, 5.0 mL and other assorted sizes as required
- Syringe valve: Two-way with Luer ends (three each)
- Sep-Pak[®] cartridges: C₁₈ Environmental (Waters) or equivalent
- Syringe needle: Blunt tip, luer or luer-lok, 19 gauge, 10 cm long, stainless steel

6.0 Reagents

- Methanol: Purge-and-trap grade or equivalent
- Water: Obtained from a Nanopure water purification unit equipped with an organic-free cartridge or equivalent

7.0 Sample Collection, Preservation, and Handling

- 7.1 Regarding sample collection, EPA (1992) should be referenced. Sample collection, preservation, and handling should be addressed in the planning process.
- 7.2 It has been demonstrated that sample-extraction residues may be stored 12 days at -10°C to -20°C with minimal or no headspace and protected from light.

8.0 Procedure

- 8.1 **Extraction of Sample.** These procedures may be performed remotely in “hot cells” or in gloveboxes as appropriate.
- 8.1.1 Approximately 1 g of sample is accurately weighed into a 20-mL VOA vial. The weight should be recorded to the nearest 0.01 g.
- 8.1.2 To all samples is added a 5.0-mL quantity of methanol/water {90/10, volume to volume (v/v)} solution that has been spiked with 12.5 μ L of surrogate mix at a concentration of 2500 μ g/mL in methanol. (The spike concentration may differ depending on the analysis method chosen.)
- 8.1.3 If this is a matrix spike sample, 12.5 μ L of the spike mix at a concentration of 2500 μ g/mL in methanol was added. (The spike concentration may differ depending on the analysis method chosen.)

- 8.1.4 The vial containing the sample and spiked solution is capped and shaken for 1 min. The contents should be allowed to settle for 10 min or until the liquid phase appears transparent.
- 8.1.5 If the liquid phase is noticeably cloudy or is not well separated, it will be necessary to centrifuge the residue. If the centrifuge is unable to accommodate the 20-mL vial, as much of the liquid as possible is transferred to a clean appropriately sized vial. The capped vial is centrifuged for 3 min at 2000 rpm.
- 8.1.6 The extracted liquid residue is transferred to a 5-mL vial. The vial is capped tightly with the Teflon[®] side of the septum cap liner facing the sample. If the contents of the vial are below established limits of radioactivity (refer to Chapter 4 in this document) as determined by established radioactivity survey techniques, the vial can be removed from the hot cell. The date and time of extraction are recorded.
- 8.1.7 If the cleanup is not done immediately (see precautions in the "Interferences" section), the residues can be stored for up to 12 days at -10°C to -20°C in a freezer appropriate for storing flammable solvents. The residues should be stored away from other solvents as required of standards.

8.2 Residue Cleanup

- 8.2.1 Immediately before using, an Environmental C₁₈ Sep-Pak[®] Cartridge is pre-conditioned by passing 5 mL of methanol followed by 5 mL of methanol/water (90/10) through the cartridge from a clean 5-mL luer-lok, gas-tight syringe. The eluant is discarded.
- 8.2.2 Two milliliters of the sample extract solution are slowly taken up in a 5-mL gas-tight syringe equipped with a Teflon[®] luer-lok and a 19-gauge, 10-cm needle. Pulling the sample too quickly into the syringe imparts excessive partial pressure to the residue and may result in lost volatile components.
- 8.2.3 The needle is removed from the syringe. The sample syringe is connected to a pre-conditioned Sep-Pak[®] cartridge. The other side of the cartridge is connected to a three-port, luer-lok, 2-way valve. A clean, 5-mL gas-tight receiving syringe is connected to another port on the valve.
- 8.2.4 The valve is adjusted so that there is flow between the two ports connecting the sample and receiving syringes. The sample extract solution is slowly syringed through the Sep-Pak cartridge and into the receiving gas-tight syringe.

- 8.2.5 The sample syringe is filled repeatedly with 0.5-mL rinses of methanol/water (90/10). The liquid is pumped through the cartridge and into the receiving syringe until a 5.0-mL final volume is obtained in the receiving syringe.
- 8.2.6 The valve is closed. The syringe is inverted several times to insure adequate mixing of the eluent.
- 8.2.7 If the analysis is not done the same day, the receiving syringe may be removed and an aliquot or all of the cleaned residue may be transferred to a 1.5-mL or 5-mL vial. No headspace should remain in the 1.5-mL vial, and little or no headspace should remain in the 5-mL vial. The date of the cleanup is recorded.
- 8.2.8 The residues should be stored at -10°C to -20°C in a freezer appropriate for storing flammable solvents. The residues should be stored away from other solvents as required of standards. The time from extraction and cleanup to analysis should not exceed 12 days.

8.3 Analysis

- 8.3.1 A 100-μL portion of the cleaned residue is transferred to a purge vessel containing internal standards and 4.9 mL of reagent water. The vessel is attached to a purge-and-trap sample concentrator and purged as specified in the analytical method, such as SW-846 Method 8240 or 8260. The attached recovery data were calculated from data obtained using a heated purge at 180°C. The heated purge, however, is regarded as optional for this procedure, provided consistency is observed per the analytical method.

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project
- 9.2 Before processing samples, the analyst should demonstrate by analyzing a method blank that all glassware and reagents are interference free when used in the quantity as specified in this method. With each batch of samples, and whenever reagents change or the location of performing this procedure changes, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried out through all stages of the sample preparation, including matching the handling and storage times and location.

- 9.3 Standard quality assurance practices consistent with the analysis method should be employed while using this method. Fortified samples should be carried through all stages of sample preparation, adhering to those parameters previously specified with the blank preparation.
- 9.4 Limits of uncertainty for all measurements should be ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL.
- 9.5 **Control Limits**
- 9.5.1 Surrogate standard determinations should be performed on all samples and blanks. All samples and blanks should be fortified with surrogate spiking compounds before extraction to monitor the preparation and analysis of samples.
- 9.5.2 Matrix spike and matrix spike duplicate analyses should be performed for each matrix and for every 20 samples.
- 9.5.3 Table 1 provides surrogate recovery control limits calculated in accordance with EPA procedures ($\pm 3 \times$ standard deviation), and Table 2 provides spiking compound recovery limits. Because of the limited quantity of data provided from validation study samples and sample matrices, all control limits for this method should be considered advisory only.

Table 1. Surrogate Recovery Control Limits		
Surrogate Compound	Level ^(a) (µg)	Recovery Limit (%)
1,2-Dichloroethane-d ₄	50	69-120
Toluene-d ₈	50	63-133
4-Bromofluorobenzene	50	69-127
(a) At time of injection		

Table 2. Matrix Spike Recovery Limits

Matrix Spike Compound	Level ^(a) (µg)	Recovery Limit(%)
1,1-Dichloroethene	50	18-136
Trichloroethene	50	1-229
Chlorobenzene	50	71-129
Toluene	50	56-160
Benzene	50	74-110

(a) At time of injection

10.0 Method Performance

- 10.1** Table 3 provides method accuracy and precision based on analysis of 18 surrogate-spiked samples and 11 target compound list (TCL)-spiked samples on three different matrices.
- 10.2** Table 4 shows the analysis of a blank and the recoveries obtained from a water blank spiked with selected compounds and NPH before and after the cleanup procedure. The difference is presented as the effect of the cleanup procedure. The most volatile and polar analytes show the greatest recovery losses, as much as 38%, although most are quite satisfactory. The ketone recoveries show an increase because of their presence in the methanol. This contamination is best identified by inspecting the corresponding blank results.
- 10.3** An application of this procedure was performed using spikes of the volatile organic compounds on a limited number of authentic single-shell tank wastes and blank samples. An example is provided in Table 5. The matrix effect is calculated by subtracting the blank-spike results from the mean of the sample-spike results. Therefore, a negative number represents the loss that can be expected as a result of the matrix effect of this sample relative to analysis of a blank spike. The loss of 1,1,2,2-tetrachloroethane and the increase in trichloroethylene are discussed in section 3.2.

11.0 Reference

U. S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste. Volume IB, Physical/Chemical Methods, SW-846*. 3rd Edition, Final Update I. Office of Solid Waste and Emergency Response, Washington, D.C. Available from National Technical Information Service, Springfield, Virginia.

Table 3. Method Accuracy and Precision

	Compound Name	Percent Recovery	
		Mean	Standard Deviation (n-1)
1.	Bromochloromethane ^(a)	100.0	0.0
2.	Chloromethane	62.5	18.5
3.	Bromomethane	69.5	6.6
4.	Vinyl chloride	57.6	15.4
5.	Chloroethane	69.1	12.8
6.	Methylene chloride	91.1	10.2
7.	Acetone	81.6	45.6
8.	Carbon disulfide	40.4	25.6
9.	1,1-Dichloroethene	77.0	19.8
10.	1,1-Dichloroethane	93.3	7.8
11.	trans-1,2-Dichloroethene	88.7	8.3
12.	cis-1,2-Dichloroethene	97.5	6.6
13.	Chloroform	100.0	6.7
14.	1,2-Dichloroethane-d ₄ ^(b)	94.5	8.5
15.	1,2-Dichloroethane	93.4	8.4
16.	2-Butanone	74.0	39.8
17.	1,1,1-Trichloroethane	93.4	6.5
18.	Carbon tetrachloride	89.6	8.3
19.	Vinyl acetate	37.0	48.3
20.	Bromodichloromethane	96.1	8.0
21.	1,4-Difluorobenzene ^(a)	100.0	0.0
22.	1,2-Dichloropropane	95.3	5.8
23.	cis-1,3-Dichloropropene	100.0	6.0
24.	Trichloroethene	113.5	38.5
25.	Dibromochloromethane	87.1	10.6
26.	1,1,2-Trichloroethane	79.7	23.0
27.	Benzene	91.8	6.0
28.	trans-1,3-Dichloropropene	81.2	8.4
29.	Bromoform	79.6	13.6
30.	Chlorobenzene-d ₅ ^(a)	100.0	0.0
31.	4-Methyl-2-pentanone	70.0	33.6
32.	2-Hexanone	65.0	37.1
33.	Tetrachloroethene	90.9	15.3
34.	1,1,2,2-Tetrachloroethane	62.1	43.5
35.	Toluene	108.1	17.4
36.	Toluene-d ₈ ^(b)	97.6	11.7
37.	Chlorobenzene	99.7	9.6
38.	Ethylbenzene	96.7	11.1
39.	Styrene	96.9	11.7
40.	p-Xylene	93.4	14.0
41.	o-Xylene	99.9	12.6
42.	Bromofluorobenzene ^(b)	98.0	9.7

(a) Compound is an internal standard

(b) Compound is a surrogate spike

Table 4. Percent Recovery Results Obtained from a Blank Spike Extraction, Followed by the Cleanup Procedures (Using 90% Methanol, 200 μ L for Analysis)

No.	Compound Name	High MeOH Blank	Extracted Blank Spike	Cleaned Blank Spike	Procedure Effect
1.	Bromochloromethane ^(a)	100.0	100.0	100.0	0.0
2.	Chloromethane	0.0	91.0	70.3	-20.7
3.	Bromomethane	0.0	98.0	78.7	-19.3
4.	Vinyl chloride	0.0	91.9	59.2	-32.7
5.	Chloroethane	0.0	96.5	73.6	-22.9
6.	Methylene chloride	0.0	90.3	96.6	6.4
7.	Acetone	29.9	72.1	133.0	60.9
8.	Carbon disulfide	0.0	85.6	47.4	-38.2
9.	1,1-Dichloroethene	0.0	96.3	60.5	-35.9
10.	1,1-Dichloroethane	0.0	102.8	99.8	-3.0
11.	trans-1,2-Dichloroethene	0.0	104.7	97.7	-7.0
12.	cis-1,2-Dichloroethene	0.0	105.6	104.6	-1.0
13.	Chloroform	0.0	106.8	108.1	1.3
14.	1,2-Dichloroethane-d ₄ ^(b)	104.5	107.8	108.4	0.6
15.	1,2-Dichloroethane	0.5	106.1	109.0	2.9
16.	2-Butanone	35.8	71.2	107.6	36.4
17.	1,1,1-Trichloroethane	0.0	102.5	99.5	-3.1
18.	Carbon tetrachloride	0.0	101.3	96.4	-4.8
19.	Vinyl acetate	0.0	101.7	105.5	3.8
20.	Bromodichloromethane	0.0	103.4	108.3	4.9
21.	1,4-Difluorobenzene ^(a)	100.0	100.0	100.0	0.0
22.	1,2-Dichloropropane	0.0	101.5	99.3	-2.1
23.	cis-1,3-Dichloropropene	0.0	102.2	104.9	2.7
24.	Trichloroethene	0.0	100.2	96.4	-3.9
25.	Dibromochloromethane	0.0	95.1	94.9	-0.2
26.	1,1,2-Trichloroethane	0.0	103.0	104.2	1.2
27.	Benzene	0.0	99.1	90.8	-8.3
28.	trans-1,3-Dichloropropene	0.0	90.8	92.3	1.5
29.	Bromoform	0.9	85.0	91.9	7.0
30.	Chlorobenzene-d ₅ ^(a)	100.0	100.0	100.0	0.0
31.	4-Methyl-2-pentanone	9.2	93.8	104.5	10.7
32.	2-Hexanone	11.6	92.0	110.1	18.1
33.	Tetrachloroethene	0.0	111.8	113.8	2.0
34.	1,1,2,2-Tetrachloroethane	3.4	102.3	110.1	7.8
35.	Toluene	0.0	110.2	113.7	3.5
36.	Toluene-d ₈ ^(b)	107.0	111.6	114.2	2.5
37.	Chlorobenzene	0.0	110.8	115.5	4.7
38.	Ethylbenzene	0.0	109.1	114.5	5.5
39.	Styrene	0.0	111.5	112.6	1.1
40.	p-Xylene	0.0	109.8	115.0	5.2
41.	o-Xylene	0.0	105.4	108.9	3.6
42.	Bromofluorobenzene ^(b)	103.9	105.4	111.6	6.2

(a) Compound is an internal standard
(b) Compound is a surrogate spike

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Table 5: Percent Recovery Results and Matrix Effect for Single Shell Tank U110 Sample

No.	Compound Name	Sample	Spike	Spike Duplicate	Matrix Effect
1.	Bromochloromethane ^(a)	100.0	100.0	100.0	0.0
2.	Chloromethane	0.0	58.5	57.1	-42.2
3.	Bromomethane	0.0	57.4	67.0	-37.8
4.	Vinyl chloride	0.0	43.5	48.4	-54.0
5.	Chloroethane	0.0	71.8	71.8	-28.2
6.	Methylene chloride	0.0	103.6	105.0	4.4
7.	Acetone	0.0	44.7	52.8	-51.3
8.	Carbon disulfide	0.0	0.0	0.4	-99.8
9.	1,1-Dichloroethene	0.0	118.7	91.6	5.1
10.	1,1-Dichloroethane	0.0	97.9	99.6	-1.3
11.	trans-1,2-Dichloroethene	0.0	89.5	91.5	9.5
12.	cis-1,2-Dichloroethene	0.0	99.8	102.6	1.2
13.	Chloroform	0.0	102.4	105.2	3.8
14.	1,2-Dichloroethane-d ₄ ^(b)	89.0	90.7	95.3	-7.0
15.	1,2-Dichloroethane	0.0	90.3	92.8	-8.4
16.	2-Butanone	3.0	38.3	44.4	-58.7
17.	1,1,1-Trichloroethane	0.0	98.5	98.4	-1.6
18.	Carbon tetrachloride	0.0	97.2	98.0	-2.4
19.	Vinyl acetate	0.0	0.0	0.5	-99.7
20.	Bromodichloromethane	0.0	99.6	101.6	0.6
21.	1,4-Difluorobenzene ^(a)	100.0	100.0	100.0	0.0
22.	1,2-Dichloropropane	0.0	99.9	101.8	0.8
23.	cis-1,3-Dichloropropene	0.0	104.2	106.7	5.4
24.	Trichloroethene	0.0	188.6	183.8	86.2
25.	Dibromochloromethane	0.0	83.1	87.4	-14.8
26.	1,1,2-Trichloroethane	0.0	30.7	60.2	-54.6
27.	Benzene	0.5	97.8	98.2	-2.0
28.	trans-1,3-Dichloropropene	0.0	80.4	83.5	-18.1
29.	Bromoform	0.0	57.4	65.5	-38.6
30.	Chlorobenzene-d ₅ ^(a)	100.0	100.0	100.0	0.0
31.	4-Methyl-2-pentanone	0.0	46.3	50.2	-51.8
32.	2-Hexanone	0.0	37.2	43.0	-60.0
33.	Tetrachloroethene	0.0	95.0	100.3	-2.4
34.	1,1,2,2-Tetrachloroethane	0.0	0.0	0.0	-100.0
35.	Toluene	15.4	99.9	102.5	1.2
36.	Toluene-d ₈ ^(b)	101.2	101.4	105.3	3.4
37.	Chlorobenzene	0.0	103.9	104.7	4.3
38.	Ethylbenzene	0.0	99.6	103.0	1.3
39.	Styrene	0.0	102.1	104.6	3.3
40.	p-Xylene	0.0	100.7	101.1	0.9
41.	o-Xylene	0.8	113.9	117.7	15.8
42.	Bromofluorobenzene ^(b)	103.0	104.9	104.7	4.8

(a) Compound is an internal standard
(b) Compound is a surrogate spike

12.0 Further Reading

Hoppe, E. W., G. A. Ross, R. B. Lucke, and J. A. Campbell. 1992. *Development and Validation of a Preparation and Cleanup Method for Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds*. Pacific Northwest Laboratory Technical Report, Richland, Washington (in press).

Lucke, R. B., J. A. Campbell, G. A. Ross, S. C. Goheen, and E. W. Hoppe. 1993. "Closed-System, Solid-Phase Extraction Cleanup Method for Removal of Normal Paraffin Hydrocarbons from Samples Prior to Purge-and-Trap Volatile Analysis." *Anal. Chem.* 65:2229-2235.

OPO10R(a)

Remote Purge and Trap - Gas Chromatography of Volatile Organics in High-Level Radioactive Wastes

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

- 1.1 This method describes sample preparation and analysis of volatile organic compounds in highly radioactive liquid wastes by a remote purge and trap procedure followed by thermal desorption and gas chromatography (Christensen et al. 1992). Gas chromatography-mass spectrometry (GC-MS) may also be used for analysis.
- 1.2 The method is designed for the determination of chloroform, carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, and perchloroethylene (tetrachloroethylene) by electron capture detector (ECD); and methylene chloride, acetone, benzene, methyl isobutyl ketone (hexone), and toluene by flame ionization detector (FID). This list of calibrated target analytes was limited to those 10 analytes that had any reasonable chance of being found in the high level waste tanks, based on previous knowledge. Additional compounds could be determined, but would require a more complicated GC analysis system than that described. The described system is simple enough to be executed by shift personnel on an around-the-clock basis.
- 1.3 The method is applicable to condensate from the low-level waste evaporator, the feed to the low-level waste evaporator, tank farm, and other aqueous waste streams. In some cases, finely divided solids, such as soils or solidified high-level waste, can be analyzed by this technique. Radiation dose rates for 15 mL samples analyzed by this method range from 0.01 Gy/h (1 R/h) to greater than 0.5 Gy/h (50 R/h). The high-radiation dose rates require performance of the analysis in a shielded hot cell. Commercial purge-and-trap instrumentation cannot be operated by personnel using master slave manipulators. Therefore, modifications are necessary.

(a) This method was supplied by C.G. Christensen, F.W. Dykes, H.C. Johnson, and C.W. Lundholm (Westinghouse Idaho Nuclear Company, Inc., Idaho Falls, Idaho).

- 1.4 This method is a modification of U.S. Environmental Protection Agency (EPA) SW-846 Method 5030 ("Purge-and-Trap") and Methods 8010 and 8015 ("Halogenated Volatile Organics by GC," "Nonhalogenated Volatile Organics by GC") (EPA 1992). Parts that are the same as SW-846 are in italics; however, some wording may have been changed for consistent formatting and grammar. Additional information about operating procedures and quality control (QC) can be found in SW-846.

2.0 Summary of Method

- 2.1 A remotely operable purge-and-trap device is installed in a hot cell and used for the analysis of selected volatile organic compounds in high-level wastes. All preparation is performed using master slave manipulators. The purge process reduces radiation levels of remotely prepared traps to 5×10^{-5} Gy/h (~5 mR/h) or less.
- 2.2 Traps are transported from the hot cell to a separate GC or GC-MS system for desorption and analysis.
- 2.3 The GC effluent is split between an ECD and an FID for analysis.
- 2.4 The method is designed to measure volatile organic analytes from a few to several hundred ng/mL (see Table 1).

3.0 Interferences

- 3.1 Overloading the system with part per million levels of volatile organics can contaminate the system. Contamination by carryover can occur when analyte concentrations are high. Some prescreening may be necessary when high levels of organics are suspected, e.g., by injecting 1 μ L of aqueous sample directly through the injection port onto the GC column, thus by-passing the purge and trap. A blank reagent water sample should be run to check for contamination.
- 3.2 Extreme care must be taken to prevent loss of volatiles during sample handling and analysis. The use of Teflon[®]-lined septa on sampling bottles and calibration standards is required to prevent evaporation of analyte volatiles to the atmosphere.
- 3.3 Cross-contamination from organics in the hot cell is minimized by the use of Teflon[®]-lined septa on sampling bottles.
- 3.4 Matrix interferences are not currently known. Therefore, most plant waste streams will require the addition of known spikes and calculation of spike recoveries to determine whether matrix interferants are present.

Table 1. The Expected Minimum and Maximum Ranges for Each Organic Analyte

<u>Volatile Organic Analyte</u>	<u>Minimum Nanograms Detectable (ng)</u>	<u>Minimum Detectable Conc./5 mL (ng/mL)^(a)</u>	<u>Maximum Linear Range (ng)^(b)</u>
<u>FID Detector</u>			
Methylene chloride	400	80	3500
Acetone	200	40	5000
Benzene	45	9	5000
Toluene	45	9	5000
Methyl isobutyl ketone	45	9	5000
<u>ECD Detector</u>			
1,1,1-Trichloroethane	10	2	250
Trichloroethylene	10	2	250
Chloroform	15	3	500
Carbon tetrachloride	10	2	150
Tetrachloroethylene	5	1	100

(a) 5 mL is the maximum allowable aliquot in this method.

(b) In practice, to reduce carryover, the upper method limits for FID analytes are reduced to approximately one sixth of the maximum.

3.5 Organic solvents are not to be used in the laboratory when purge-and-trap GC is in progress.

4.0 Safety

4.1 The solutions being analyzed and traps that have been loaded in the hot cell may be highly radioactive. As required by the U.S. Department of Energy (DOE) "as low as reasonably achievable" (ALARA) principle, to minimize radiation exposure and contamination of personnel and facilities, it is imperative to follow all radiochemical laboratory procedures for handling radioactive samples and for health physics monitoring (see Chapter 4 and site-specific documents). These procedures should also be followed when removing loaded traps from the hot cell and connecting to the desorption apparatus attached to the GC in a hood.

4.2 The trap and GC oven are heated to over 200°C during a chromatographic run. The trap or any parts of the GC oven should not be handled until they have cooled down between chromatographic runs.

5.0 Apparatus and Materials

5.1 Remote Purge-and-Trap Apparatus. The remote apparatus can be divided into three distinct components: the purge vessel, the remote purge and trap, and the purge gas-flow controller.

5.1.1 Purge Vessel: Volatile organic analysis (VOA) vials are used instead of commercially available purge vessel glassware because 1) they can be discarded after each use, eliminating the need for special cleaning and reducing the possibility of cross-contamination; 2) they can withstand the rigors of manipulator handling and dropping with minimal breakage; and 3) they have a septum seal which helps maintain sample integrity.

5.1.2 Remote Purge and Trap: This apparatus (Figure 1) consists of a purge head mounted on cylindrical rails so the head can be moved horizontally. The head assembly is mounted to an air pneumatic cylinder to allow vertical up-and-down movement. Two needles of different lengths are attached to the purge head assembly. When the head is pneumatically lowered onto a vial placed in the holding fixture, both needles pierce the septum. Strict vertical alignment tolerances prevent the needles from inadvertently striking the vial cap, which results in bent or broken needles. After the needles pierce the vial septum, the whole purge-head assembly, including the sample vial, is pneumatically raised and moved horizontally over the hot-plate assembly. The purge-head assembly is lowered so that the sample vial is inserted into the hot-plate assembly where the purge temperature is maintained. The hot-plate heating surface is covered with a 5.1 cm (2 in.) aluminum plate. The plate is machined to fit the heated surface and drilled to accept 40 mL VOA vials (e.g., S326-0040 from I-Chem).

Needle sparging is used for gas stripping the sparingly soluble organics from the aqueous phase. Needle sparging was chosen to minimize potential foaming and the attendant radiological and organic cross contamination. The longer needle serves as the purge needle. The tip is lowered to within 3.2 mm (1/8 in.) of the vial bottom to assure intimate gas/liquid contact. The shorter needle serves to vent sparge gas, which is carrying the volatile organic compounds into the trap. Traps are attached to the vent needle by means of a 3.2 mm (1/8 in.) Swagelok tubing quick disconnect. An oversize washer is welded to the quick-disconnect snap ring to facilitate master-slave manipulator operation when traps are attached or removed.

5.1.3 Purge Gas Flow Controller: Because traps are used in the hot cell, radiological safety considerations required that trap effluent gas cannot be vented outside the cell wall for flow measurement. Therefore, flow control and measurement on the

Figure 1. Remote Purge-and-Trap Unit

remote system must be upstream of the purge vessel and located outside the hot-cell containment walls. Leak-free connections from the controller outlet through the trap and pressure-regulated flow control are required.

A mass flow controller is interfaced to an electronic timing circuit to control purge time and wired to a digital display for flow readout. A 3.2 mm (1/8 in.) OD Teflon[®] tubing line is plumbed from the purge gas-flow controller through the cell wall to the purge gas inlet on the remote apparatus located in the cell. Purge gas exits the trap into the cell atmosphere where high efficiency particulate air (HEPA) filtered ventilation controls the spread of airborne contamination. The mass-flow controller is necessary to overcome variable flow resistance, provide reliable flow control, and interface with electronic timing circuits and digital display devices that provide semi-automated operation.

5.2 Gas Chromatograph. An analytical system is needed complete with gas chromatograph and suitable for purge-and-trap analysis and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas and for controlling the desorption of the organic compounds is also needed.

5.2.1 The GC is installed in a fume hood. The detector electronic amplifiers and chromatography data station are located adjacent to the hood and cabled to the instrument inside the hood. Because traps average 5×10^{-5} Gy/h (5 mR/h) or less, it is also possible to have the GC on the benchtop. In this case, a commercially available trap-desorption device is placed in a radiologically controlled hood, and the heated transfer line is run through the hood wall to a GC (or GC-MS) located on adjacent bench space. Because the uncontrolled spread of radioactive contamination is primarily caused by physical contact rather than gaseous mobility, locating the trap desorption system in a hood should provide sufficient radiological protection.

5.2.2 GC Column: Stainless steel column, 2.4 m x 2.5 mm ID (8 ft x 0.1 in. ID), packed with 1% SP-1000 on 60/80 mesh Carbopack-B or equivalent

5.2.3 Detectors: FID and ECD. Argon/methane (95%/5%), ultra-high purity, is used for the ECD.

5.2.3.1 Effluent splitter: The effluent is split at the column outlet using a zero dead-volume tubing tee. Approximately 10 m of 0.32 mm OD deactivated fused silica capillary tubing connects the tee to the ECD; 11 to 12 cm connects the tee to the FID. This results in a split of approximately 10% to the ECD; the balance of the effluent goes to the FID.

5.3 Trapping Media:

- Carbo-pack B, 60/80 mesh, Supelco #2-0273 or equivalent
- Carbosieve S-III, 60/80 mesh, Supelco #1-0184 or equivalent

5.4 Blank Traps: Glass-lined stainless steel tubing, 3.2 mm (1/8 in.) OD x 2.7 mm (0.105 in.) ID x 15 cm (6 in.) long

5.5 Deactivated fused-silica capillary tubing, 0.53 mm OD

5.6 Deactivated fused silica capillary tubing, 0.32 mm OD

5.7 *Volumetric Flasks: 10 and 100 mL with ground glass stoppers*

5.8 Tubing tees and unions, 3.2 mm (1/8 in.) and 1.6 mm (1/16 in.)

5.9 Culture Tubes: 16 x 125 mm. Test tubes with a lip at the tube mouth cannot be inserted in purge-chamber teflon ferrule and must not be used.

5.10 VOA vials, 40 mL, cleaned per EPA cleaning protocol B., with Teflon-lined septa

5.11 *Syringe: 5 mL, gas tight*

5.12 *Microsyringes: 10, 25, and 1000 µL*

6.0 Reagents

6.1 High Resistivity Water: ASTM Type II (a resistivity greater than 10 megohms). The water purification system must contain an activated charcoal carbon bed in the final pass to remove trace organics from the system effluent. Alternatively, distilled water may be used that has been heated to 90°C and subjected to a helium sparge for 15 min to remove any traces of dissolved volatile organics.

6.2 *Methanol: Pesticide quality or equivalent.*

6.3 Calibration Standards: Five calibration standards should be prepared in methanol to span the range listed in Table 2. One standard should be as near the minimum and one as near the maximum as possible. EPA SW-846 Methods 8010, 8015, and 8020 sections 5.2, 5.3, and 5.4 may be referred to for the preparation of stock standards, secondary dilution standards, and calibration standards, respectively.

- 6.4 Calibration Check Standard:** A solution that contains all the volatile organic analytes should be prepared in methanol at concentrations at the approximate mid-range sensitivity for each compound listed in Table 2.

Table 2. Remote Volatile Organics Spike Recovery and Range of Precision

Analyte	Spike Recovery (%)	Spike Recovery Relative Standard Deviation (%)	Percent Precision ^(a)		
			at Minimum Quant. Limit (% @ $\mu\text{g/L}$)	at Mid-Range (% @ $\mu\text{g/L}$)	at Max. Range (% @ $\mu\text{g/L}$)
Acetone	84.3	21	21 @ 40	20 @ 200	19 @ 400
Methylene chloride	98.6	7	16 @ 80	14 @ 200	12 @ 400
Methyl isobutyl ketone	80.0	12	50 @ 10	7 @ 100	7 @ 200
Benzene	100.0	15	50 @ 9	7 @ 100	7 @ 200
Toluene	98.4	5	54 @ 9	7 @ 100	7 @ 200
1,1,1-Trichloroethane	116.0	7	18 @ 2	10 @ 25	9 @ 50
Trichloroethene	111.3	18	25 @ 2	11 @ 25	10 @ 50
Tetrachloroethene	120.0	7	18 @ 1	10 @ 10	10 @ 20
Chloroform	93.5	15	20 @ 3	8 @ 35	7 @ 70
Carbon tetrachloride	109.0	28	32 @ 1	10 @ 10	7 @ 20

Concentrations are based on a 5 mL aliquot.

(a) Precision equals one statistical standard deviation expressed as relative percent at that concentration.

- 6.5 Internal/Surrogate Standards:** A solution should be prepared in methanol that contains 1,2-dichloropropane at a concentration of approximately 250 $\mu\text{g/mL}$ and bromoform at a concentration of approximately 65 $\mu\text{g/mL}$. These concentrations were chosen so that 2 μL of this solution contains approximately 500 ng of 1,2-dichloropropane and 130 ng of bromoform.
- 6.6 Controls:** A series of controls that cover the compound method ranges listed in Table 2 should be prepared in methanol. When a standard dilution of 20 μL of the methanolic standard or control is diluted to 100 mL of water, the final 5-mL aliquot of this solution contains the same amount of organic analyte in nanograms that the methanolic standard contains in $\mu\text{g/mL}$. Five milliliters of this control are used for purge-and-trap analysis. Controls should be prepared from reagent grade chemical sources that are different from the sources used to prepare calibration standards.
- 6.7 Spike Solution:** A spike solution in methanol is prepared that contains concentrations of the organics at the minimum concentrations in $\mu\text{g/mL}$ listed in Table 2. Two microliters of this solution are spiked into the sample aliquot or dilution.

7.0 Sample Collection, Preservation, and Handling

- 7.1 Sample collection, preservation, and handling should be addressed in the planning process. Also, see EPA (1992). Samples of high-level radioactive wastes are taken in a sample collection hot cell and transported to an analytical lab hot cell via a pneumatic transfer system.

8.0 Procedure

8.1 Remote Sample Preparation

- 8.1.1 Before adding sample in the hot cell, the VOA vial is prepared outside the hot cell. Analyte-free reagent water plus a surrogate spike containing 1,2-dichloropropane and bromoform is added to the VOA vial so that the total liquid volume (with sample) will equal 10 mL.
- 8.1.2 A clean trap inside a plastic sheath, the sample vial, and a 5-mL plastic syringe equipped with a 21-gauge needle are placed in a glovebox before transport into the hot cell. The trap is attached to the male portion of the quick disconnect fitting, and the plastic sheath is placed over the trap assembly to reduce radiological contamination from contact with hot-cell surfaces, such as manipulator fingers. This material is transported to the hot-cell work station where sample aliquotting is performed.
- 8.1.3 Using master-slave manipulators, the plastic syringe is locked into a vice grip that has jaws modified to hold syringes. *The plunger is removed from the syringe*, the sample vial tare weighed, and the cap unscrewed from the sample bottle. *Sample is immediately poured into the syringe barrel, completely filling the syringe.* The plunger is replaced so that no gaseous headspace is contained with the sample aliquot. *The plunger is depressed to the syringe graduation of the desired aliquot size to expel excess sample through the syringe needle.* The VOA sample vial (containing water and surrogate spike) is placed under the syringe needle and pushed up so the needle penetrates the vial septum.

The aliquot is expelled into the vial, the vial removed from the syringe needle, and the gross sample vial weight obtained to determine aliquot weight. Gravimetric determination of sample size is used because the visibility of the graduations is distorted by the hot-cell windows and precise placement of the syringe plunger to the appropriate barrel calibration mark is extremely difficult when performed in a wholly remote, mechanically operated hot-cell environment.

- 8.1.4 The VOA vial and trap assembly is transported to the remote purge-and-trap apparatus where the trap assembly is attached to the apparatus using the quick-disconnect fitting. The sample vial (now the sparge vessel) is placed in the apparatus and the purge-and-trap process started.

8.1.4.1 Purge and trap conditions:

Purge gas (nitrogen):	25 mL/min
Purge time:	14 min
Trap packing:	11.4 cm (4.5 in.) Carbopack B, in front of 1.3 cm (0.5 in.) Carbosieve S-III
Trap length:	15 cm (6 in.) x 3.2 mm (1/8 in.) OD x 2.7 mm (0.105 in.) ID stainless-steel tubing
Trap desorb:	220°C for 3 min, 40 mL/min carrier gas flow rate
Trap bakeout:	220°C for 20 min, 25 mL/min purge gas flow rate

- 8.1.5 When the purge-and-trap process ends at the preset purge time on the flow controller, the trap is removed from the remote apparatus and transported out of the hot cell to the glovebox. The trap should be measured for dose rate. {Actual measured dose rates of traps used for analyzing highly radioactive samples averaged less than approximately 5×10^{-5} Gy/h (5 mR/h).} The trap is then disconnected from the male part of the quick disconnect fitting and the plastic sheath removed. The trap is moved to a fume hood containing a GC where the organic compounds are thermally desorbed and analyzed by GC.

8.2 Gas Chromatographic Analysis

8.2.1 GC Conditions

8.2.1.1 Column: See section 5.2.2.

Carrier gas (helium) flow rate: 40 mL/min

Temperature program:

Initial temperature: 45°C, hold for 4 min

Program: 45°C to 220°C at 8°C/min

Final temperature: 220°C, hold for 3 min

ECD makeup: 95% argon, 5% methane, 50 mL/min

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate QC methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.

- 9.2 Surrogate standard recovery is calculated on all samples, blanks, unknown controls, and check standards to monitor system performance. Bromoform is monitored on the ECD, and 1,2-dichloropropane is detected on the FID. The increase of physical manipulations in remote purge and trap increases the probability of leaks and errors. If recovery is not within limits, measurements and instrument performance should be verified. Re-extraction and analysis may be required.
- 9.3 A five-point calibration is performed for each analyte. A computer program is used to enter peak areas and amounts of analyte and to calculate a standard linear-regression-curve fit. The slope/intercept is stored for future use in calculating sample results until recalibration is required.
- 9.4 A minimum of three replications of QC standards at four levels within the calibration range should be processed before beginning any sample analysis. Statistical bias and precision parameters are calculated using these data. A control should be run each day. Results of controls are automatically tested at the 99% confidence level or approximately three standard deviations for each analyte. All analytes should pass the control check before computer calculation of sample results. The unknown control also functions as the calibration check standard required in EPA SW-846. Repeated control failures require finding and correcting the problem, recalibration, or both.
- 9.5 An analytical blank should be processed before each day's run to confirm the absence of cross contamination. A field (trip) blank should be contained in each sample set and analyzed to confirm that the samples are not contaminated by transport through the pneumatic transfer system and subsequent storage in the hot cell. If system contamination is detected, the system should be cleaned by processing wet (deionized water) or dry purge vial blanks through the remote device until clean.

10.0 Method Performance

- 10.1 Each tank of high-level waste was sampled on three separate occasions. Duplicate analyses on individual bottles of each sample set were performed. A third bottle of a selected set was spiked to determine spike recoveries. A total of six replicate analyses and a single spike-recovery analysis was determined for each tank of high-level waste.
- 10.2 The spike recoveries obtained from analyzing samples from six high-level radioactive waste tanks are summarized in Table 2. Several spiked sample runs were erroneously low indicating obvious problems with that particular analysis. Those runs were repeated and the defective data not included in the table. Table 2 also defines the precision of the remote purge-and-trap apparatus and the GC system over the full calibration range.

- 10.3 Spike recoveries of acetone and methyl isobutyl ketone were somewhat low compared to the other compounds. Reduced spike recovery of ketones was expected because of their increased solvation induced by the high acidity of the high-level waste samples.
- 10.4 Greater than 100% recoveries for many of the halogenated solvents is typically caused by ECD detector response changing with time. Subsequent recalibration and statistical data-base adjustments corrected this problem.

11.0 References

Christensen, C. G., F. W. Dykes, H. C. Johnson, and C. W. Lundholm. 1992. *Remote Purge and Trap of Volatile Organic Compounds in High Level Radioactive Wastes at the Idaho Chemical Processing Plant*. WINCO-1107, Westinghouse Idaho Nuclear Company, Inc., Idaho Falls, Idaho, 13 pp.

U. S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Methods, SW-846*, 3rd Edition, Final Update I. United State Environmental Protection Agency Office of Solid Waste and Emergency Response. Washington, DC. Available from National Technical Information Service, Springfield, Virginia.

OP020R^(a)**Ultrasonic Solvent Extraction for Analysis of Volatile Organic Compounds in Solid Radioactive Mixed Wastes****1.0 Scope**

- 1.1** This method applies to the extraction of volatile organics from solid radioactive mixed wastes that cannot be directly analyzed using purge-and-trap gas chromatography-mass spectrometry (GC-MS) because of their radioactivity. A preparation method suitable for hot-cell, glovebox, or radiochemical-hood use is described for medium- or high-concentration level (>1 mg/kg) volatile organic compound (VOC) analysis. The method has not been tested on low-level-concentration samples, and a replicate study for compounds of interest should be performed, as shown in section 9 and Table 1.
- 1.2** The preparation method is based upon U.S. Environmental Protection Agency (EPA) SW-846 Methods 5030 and 3550 (EPA 1992). The extract is suitable for final analysis by SW-846 determinative methods, such as 8240 or 8260, or by Compendium methods such as OP010R or OP030R, for VOCs.

2.0 Summary of Method

Solid radioactive waste is weighed out and ultrasonically extracted with methanol. An aliquot is taken for analysis of VOCs if radioactivity screening indicates that coextracted radionuclides are sufficiently low.

Caution: Methanol can extract radioactivity, particularly chelated radionuclides, from samples. Extracts must be screened for radioactivity before transfer from the glovebox, hot cell, or radiochemical hood.

3.0 Interferences

Samples can be contaminated by volatile organic solvents or other samples containing solvents in high concentrations. These materials should not be present in the area of sample preparation or storage.

(a) This method was supplied by R. L. Schenley and W. H. Griest (Oak Ridge National Laboratory, Chemical and Analytical Sciences Division, Oak Ridge, Tennessee).

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed. Refer to Chapter 4 in this document for general safety information.

5.0 Apparatus and Materials

- 5.1 Variable-volume pipettors capable of delivering 1 to 50 μL and 1 to 5 mL
- 5.2 Glass vials: 20- to 40-mL capacity, with Teflon[®]-lined screw cap. Smaller vials may be used, if necessary, to minimize headspace during extraction.
- 5.3 Ultrasonic bath with timer (140W)
- 5.4 Balance capable of weighing up to 5 g to the nearest 0.1 g
- 5.5 Stainless steel spatula
- 5.6 Vials: 1- or 2-mL capacity, with Teflon[®]-lined screw caps
- 5.7 Disposable Pasteur pipets

6.0 Reagents

- 6.1 Purge-and-trap grade methanol
- 6.2 Volatile organic compound surrogate standards and matrix spikes as defined in SW-846 method 5030, made up to a concentration of 1 mg/mL in purge-and-trap methanol. Lower concentrations may be prepared if the low-concentration-level analytical method is to be used.

7.0 Sample Collection, Preservation, and Handling

- 7.1 Sample collection, preservation, and handling should be addressed in the planning process.
- 7.2 If the radiation field of the sampling area and the specific radioactivity of the material sampled permit, the collection bottle should be filled as much as possible with the sample, and as little headspace as is feasible should be left in the bottle.

- 7.3 Preservation methods, such as cooling at 4°C or acidification, should be used with great caution because they may lead to sample phase changes or the evolution of nitrogen oxides.
- 7.4 It is suggested that a holding time of 14 days from sample collection to analysis be observed (subject to the constraints of handling radioactive samples safely), unless the holding times for the analytes have been established for the sample matrices to be analyzed.
- 7.5 After sampling, the sample bottle should not be opened until the aliquot for VOC analysis is removed.
- 7.6 Samples should be screened for radioactivity, and appropriate precautions should be taken when handling the samples and extracts.
- 7.7 This procedure is designed to be performed at room temperature (approximately 20° to 23°C). If possible, this method should not be performed at temperatures exceeding 25°C.

8.0 Procedure

- 8.1 One to five grams of the sample should be weighed into the screw-cap vial, and the weight of the sample should be recorded.
- 8.2 Surrogate standards are added to all samples; the volume of surrogate standard should be 50 µL (of 1 mg/mL stock solution) per g of sample. Less concentrated surrogate standards should be added if a low-concentration-level analytical method is desired.
- 8.3 Two milliliters of methanol are added for each g of sample, and the vial is capped.
- 8.4 The vial is shaken and placed in the ultrasonic water bath for 30 min. The bath temperature should be no more than 20° to 23°C.
- 8.5 After ultrasonic extraction, the vial is allowed to stand for 15 to 30 min. An aliquot of the supernatant is pipetted into a 1- or 2-mL screw-cap vial, leaving minimum headspace.
- 8.6 The level of gross-alpha and gross-beta activity is determined. Only if radioactivity meets facility health physics guidelines should the extract be transferred to a laboratory for purge-and-trap GC-MS.
- 8.7 The extract can be filtered using a 0.2-µm Teflon®-filter cartridge and syringe to remove particulate radionuclides. Handling and manipulations of the extract should be

minimized to decrease potential losses of VOCs and contamination of the extract. The effects of filtering have not been documented.

- 8.8 The volume of extract analyzed (e.g., by SW-846 Method 8240 or 8260 or by Compendium methods OP010R or OP030R) depends upon the desired method detection limit.

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.
- 9.2 A blank sample of similar material (e.g., sea sand) should be included with each sample group. This blank is treated in the same manner as the samples, including the addition of surrogates. Two samples in each sample group should be spiked with matrix spikes at a level of 50 µg/g (50 ppm) (or at lower concentrations, if the low-concentration-level analysis is to be performed).

10.0 Method Performance

- 10.1 The method has been applied to the screening of VOCs in 85 low-level waste samples contaminated with depleted or enriched uranium. Many of the samples were contaminated with oils, and most were damp or wet. At the time of this work, the samples were not shipped with cooling. They were extracted immediately after arrival. The extracts were analyzed using SW-846 Method 8240, where 10-µL volumes of the extracts were purged from 5 mL of reagent water. The recoveries of surrogate standards and matrix spikes for four sample matrices and sand blanks are listed in Table 1. Recoveries are generally very good, demonstrating good extractions and minimal losses even with the extraction-vial headspace. Most of the samples would meet the SW-846 or Contract Laboratory Program QC acceptance limits for soil (also listed in Table I), but the relevance of the QC acceptance limits for soil to the low-level wastes has not been established. The toluene matrix spike was low in all three matrices. Relative standard deviations ranged from 5 to 24%. The estimated quantitation limit (EQL) for the method, conducted as described above, was 10 to 200 mg/kg. Lower EQLs could be achieved by analyzing larger aliquots of the methanol extracts.
- 10.2 The methanol did not extract appreciable radioactivity from these samples. The decontamination factors (radioactivity in extract versus sample) ranged from 10^3 to 10^7 .

11.0 Reference

U. S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste, Volume 1B, Physical/Chemical Methods*, SW-846, 3rd Edition, Final Update I, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Table 1. Summary of Surrogate-Standard and Matrix-Spike Recoveries from (Radioactive Mixed Wastes)^(a)						
Surrogate Std. or Matrix Spike ^(b)	QC Acceptance Limits ^(c) %	Recovery for Sample, Average $\pm$ Std. Dev. (%RSD) ^(d)				
		Enriched Sump Cake	Depleted Sump Cake	Soil or Sludge	"Residues"	Sand Blanks
No. of Samples		34	31	12	8	5
Tol-d ₈	81-117	95 $\pm$ 12 (12)	89 $\pm$ 14 (16)	98 $\pm$ 6 (6)	108 $\pm$ 9 (8)	100 $\pm$ 9 (9)
BFB	74-121	102 $\pm$ 12 (12)	94 $\pm$ 15 (16)	98 $\pm$ 5 (5)	100 $\pm$ 14 (14)	110 $\pm$ 10 (9)
DCE-d ₄	70-121	76 $\pm$ 11 (14)	93 $\pm$ 18 (20)	86 $\pm$ 20 (23)	94 $\pm$ 9 (10)	88 $\pm$ 9 (11)
No. of Samples		6	2	4		
DCE	61-145	94 $\pm$ 23 (24)	67	108 $\pm$ 2 (2)		
TCE	71-120	82 $\pm$ 7 (8)	62	87 $\pm$ 3 (4)		
Bz	76-127	81 $\pm$ 7 (9)	59	87 $\pm$ 8 (9)		
Tol	76-125	73 $\pm$ 10 (14)	66	78 $\pm$ 7 (8)		
ClBz	75-130	86 $\pm$ 8 (10)	63	85 $\pm$ 10 (11)		

(a) Uranium-contaminated wastes spiked at 50 mg/kg, extracted with methanol, and analyzed using SW-846 method 8240.

(b) Tol-d₈ = toluene-d₈; BFB = bromofluorobenzene; DCE-d₄ = 1,2-dichloroethane-d₄; DCE = 1,1-dichloroethene; TCE = trichloroethene; Bz = benzene; Tol = toluene; ClBz = chlorobenzene.

(c) QC acceptance limits for soil from SW-846, or Contract Laboratory Program listed for comparison.

(d) Relative standard deviation.

OP030R^(a)**Purge and Trap in a Glovebox****1.0 Scope and Application**

This method is a modification of U.S. Environmental Protection Agency (EPA) SW-846 Method 5030 ("Purge-and-Trap") (EPA 1992). It describes sample preparation for analyzing volatile organics in radioactive samples by a purge-and-trap procedure (Tomkins et al. 1989).

2.0 Summary of Method

A modified purge-and-trap apparatus is described for use in a glovebox. The device is based on a commonly used 40-mL volatile organic analysis (VOA) bottle for convenient handling of samples in a glovebox and a common purging head.

3.0 Interferences

When working in a glovebox, cross contamination from various sources could occur within the box unless the work area is kept clean and solvents or heavily contaminated samples are not stored in the box.

4.0 Safety

When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed. Refer to Chapter 4 in this document for general safety information.

5.0 Apparatus and Materials

5.1 This method uses a modified purge-and-trap apparatus in a glovebox. Most other apparatus and materials information is provided elsewhere, such as in SW-846 Method 5030.

5.2 Purge-and-Trap Apparatus in a Glovebox.

5.2.1 For purge-and-trap in a glovebox and off-line gas chromatography (GC) or gas chromatography-mass spectrometry (GC-MS), the purge head shown in Figure 1

(a) This method was supplied by B. A. Tomkins, R. L. Schenley, and W. H. Griest (Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee).

Figure 1. Teflon® Sampling Head Used for the Collection of Volatile Organics: (a) capillary Teflon® tubing 1.6 mm (1/16 in.) OD x 0.3 mm ID, (b) fingertight fitting, (c) 3.2-mm (10/32) screw port, (d) Teflon®-faced rubber septum with hole, (e) 40-mL VOA vial, (f) Swagelok 3.2-mm (1/8 in.) to 3.2-mm (1/8 in.) union fitting, (g) 3.2-mm (1/8 in.) Swagelok nut, (h) 3.2-mm (1/8 in.) OD Teflon® tubing. Details are given in text.

may be used. The purging head may be custom machined from Teflon[®]. It is fitted with a Teflon[®]-faced silicone rubber septum, and accepts a screw-in 40-mL VOA vial (Shamrock Glass Co., Seaford, Delaware, part no. 6-06K) as a purging chamber. The head has a 10/32 screw fitting to pass 1.6 mm (1/16 in.) OD x 0.3 mm ID Teflon[®] tubing into the bottom of the VOA vial. This line provides the nitrogen gas for purging. The nitrogen is supplied to the line through a bulkhead union in the glovebox wall as shown in Figure 2. Another fitting and a 3.2 mm (1/8 in.) OD Teflon[®] tube provide an outlet for the purged volatile organics. The outlet tubing is connected to a bulkhead fitting in the glovebox wall, where the sorbent trap is connected to the exterior of the glovebox.

6.0 Reagents

This information is provided elsewhere, as in SW-846 Method 5030.

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

8.0 Procedure

- 8.1 This method uses a standard procedure, such as found in SW-846 Method 5030. Modifications that facilitate glovebox operations of the standard procedure are included here.
- 8.2 The purge-and-trap device may be directly connected to a GC using a MS or other appropriate detector, or the purge-and-trap may be performed off-line in a glovebox or hot cell, as described here. With off-line purge-and-trap, the trap may be removed from the original purge-and-trap unit, sealed, and desorbed onto the chromatographic column at a later time. If the trap is removed, it must be sealed and analyzed as soon as possible. It is recommended that the analysis be performed within 12 h to prevent loss of trapped analytes. Subsequent GC or GC-MS analysis may be accomplished, as for example in SW-846, 8010, 8015, 8020, 8240, and 8260.
- 8.3 Special precautions for purging radioactive aqueous samples requiring containment:
 - 8.3.1 The Teflon[®] purging head and chamber are leak tested by screwing in the VOA vial, passing nitrogen gas through the system, and observing the flow rate on the rotameter (30 mL/min). The VOA vial is then removed from the purging head.
 - 8.3.2 The sample jar is opened in the glovebox, and a 5-mL aliquot of the sample is quickly transferred to the VOA vial using a calibrated variable-volume 5-mL

Figure 2. Layout of Volatile Organics Sampling Equipment in and around the Glovebox: (a) nitrogen cylinder with two-stage regulator, (b) needle valve, (c) 3.2-mm (1/8 in.) OD copper line, (d) and (e) 3.2-mm (1/8 in.) to 1.6-mm (1/16 in.) bulkhead union mounted in the glovebox wall, (f) capillary tubing 1.6-mm (1/16 in.) OD x 0.3-mm ID, (g) Teflon® sampling head and 40-mL VOA, (h) 3.2-mm (1/8 in.) OD Teflon® tubing, (i) 3.2-mm (1/8 in.) to 3.2-mm (1/8 in.) bulkhead union mounted in the glovebox wall, (j) EPA Method 624 three-stage trap for volatiles, (k) flow rotameter. The two glove ports (l) and bag-in/bag-out port (m) are fixed features of the glovebox.

capacity pipettor. Ten microliters of the purgeables surrogate standard are immediately added with a 25- μ L syringe, and 10 μ L of the matrix spike solution (if a matrix spiked sample) are also added; then the VOA vial is screwed into the purging head. These operations should be conducted within 30 sec.

8.3.3 The sample is purged at 30 mL/min for 11 min.

8.3.4 After purging is complete, the trap is removed from the system, and the ends are sealed with the plastic caps provided by the manufacturer. The trap should be checked for radioactivity by standard Health Physics procedures before transferring it to the GC or GC-MS laboratory. The purge vial must be handled and disposed of by standard radiochemical laboratory procedures.

9.0 Quality Control

Modifications to this method should be supported by appropriate quality control (QC) procedures (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.

10.0 Method Performance

10.1 For samples requiring off-line purge-and-trap in a glovebox, the method detection limit (MDL) is expected to be essentially the same as comparable VOA purge-and-trap analytical methods because the same volume of sample is analyzed, and the final determination method is the same. However, for some compounds, the recoveries are lower than expected, and the MDL will be higher. Single-laboratory recoveries of the VOA surrogate standards and matrix spikes for aqueous nuclear waste samples and laboratory method blanks are listed in Table 1. GC-MS by Method 8240 ("GC-MS for Volatile Organics") with thermal desorption of the trap similar to Method 5040 was used to generate these data. Surrogate-standard and matrix-spike recoveries are good compared to the QC acceptance limits for Method 8240. A slight reduction occurs in recoveries for bromofluorobenzene and chlorobenzene versus that normally achieved with Method 8240. This behavior is attributed to the purge-and-trap step in the glovebox because the response factors of the purgeable internal standard mix compounds (added only at the second purge-and-trap step) were always within range. Results from the analysis of reagent water spiked with Target Compound List and additional Appendix VIII compounds (40 CFR Part 136) are shown in Table 2. Compounds that are immiscible with water are recovered at 75% or better at the 50- μ g/L level, while those that are freely miscible with water are recovered less efficiently. Most of the latter require special methods.

11.0 References

40 CFR Part 136. 1984. *Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule.* U.S. Environmental Protection Agency (EPA).

U.S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Methods*, SW-846, 3rd Edition, Final Update I, Office of Solid Waste and Emergency Response, Washington, DC. Available from National Technical Information Service, Springfield, Virginia.

Tomkins, B. A., J. E. Caton, M. D. Edwards, M. E. Garcia, R. L. Schenley, L. J. Wachter, and W. H. Griest. 1989. "Determination of Regulatory Organic Compounds in Radioactive Waste Samples. Volatile Organics in Aqueous Liquids." *Anal. Chem.* 61:2751-2756.

Table 1. Summary of VOA Surrogate Standard and Matrix Spike Recoveries for Radioactive Aqueous Liquids and Laboratory Method Blanks

<u>Waste Samples</u>					
<u>Compound</u>	<u>Conc. ($\mu\text{g/L}$)</u>	<u>No. of Samples</u>	<u>Percent Recoveries</u>		
			<u>Mean</u>	<u>Std. Dev.</u>	<u>Rel. Std. Dev.</u>
Surrogate Standards					
d_8 -Toluene	50	65	89	17	19
Bromofluorobenzene	50	65	59	15	25
1,2-Dichloroethane- d_4	50	65	81	11	14
Matrix Spikes					
1,1-Dichloroethene	51	20	105	48	17
Trichloroethene	72	20	87	14	16
Benzene	43	19	89	15	17
Toluene	43	15	81	20	25
Chlorobenzene	55	19	67	13	19
<u>Blanks</u>					
<u>Compound</u>		<u>No. of Blanks</u>	<u>Percent Recoveries</u>		
			<u>Mean</u>	<u>Std. Dev.</u>	<u>Rel. Std. Dev.</u>
Surrogate Standards					
d_8 -Toluene		7	91	11	12
Bromofluorobenzene		7	61	12	20
1,2-Dichloroethane- d_4		7	86	13	15

Table 2. Analysis of Target Compound List and Additional Appendix VIII Compounds Spiked into Reagent Water

Compound	Conc. (µg/L) Avg ± Std Dev (n=3)	
	Actual	Measured
CLP Purgeable Mixture A, B, and Hazardous Substances List		
Methylene chloride	50	37 ± 15 B
Acetone	50	56 ± 15 B
Carbon disulfide	50	96 ± 3.6
1,1-Dichloroethene	50	70 ± 1.7
1,1-Dichloroethane	50	57 ± 1.5
1,2-Dichloroethene (total)	50	54 ± 2.5
Chloroform	50	56 ± 2.5
1,2-Dichloroethane	50	43 ± 2.5
2-Butanone	50	12 ± 1.7
1,1,1-Trichloroethane	50	49 ± 1.5
Carbon tetrachloride	50	53 ± 1.5
Vinyl acetate	50	20 ± 1.6
Bromodichloromethane	50	43 ± 2.1
1,2-Dichloropropane	50	50 ± 1.5
cis-1,3-Dichloropropene	50	36 ± 4.0
Trichloroethene	50	53 ± 1.5
Dibromochloromethane	50	38 ± 4.5
1,1,2-Trichloroethane	50	37 ± 3.1
Benzene	50	51 ± 1.5
trans-1,3-Dichloropropene	50	41 ± 3.1
Bromoform	50	23 ± 4.6
4-Methyl-2-pentanone	50	13 ± 2.1
2-Hexanone	50	9 ± 1.0
Tetrachloroethene	50	44 ± 3.5
1,1,2,2-Tetrachloroethane	50	19 ± 5.1
Toluene	50	49 ± 1.0
Chlorobenzene	50	43 ± 3.5
Ethylbenzene	50	37 ± 4.6
Styrene	50	33 ± 5.7
Xylenes (total)	50	35 ± 2.5
Appendix VIII Compounds		
1,2,3-Trichloropropane	55	11 ^b
Dibromomethane	50	ND
1,2-Dibromoethane	50	12 ± 0.6
trans-1,3-Dichloro-2-butene	51	6 ^b
Fluorotrichloromethane	60	43 ± 3.6
Methacrylonitrile	50	ND
Methylmethacrylate	50	ND
Acrylonitrile	50	ND
Iodomethane	50	33 ± 4.7
2-Picoline	50	ND
Pyridine	51	ND

ND = not detected. B = also detected in blank.

^b Detected in 2 samples. Avg. listed.

OP100R^(a)**PCBs in Aqueous Radioactive Mixed Wastes Using Solid Phase Extraction Disks and GC-ECD****1.0 Scope and Application**

- 1.1** This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from radioactive aqueous matrices, and is suitable for use in a glovebox or hot cell. Sample radioactivity has not been found to be carried over into the purified extracts, which can be analyzed in non-zoned laboratories.
- 1.2** This method is based upon solid phase extraction (SPE) of PCBs as Aroclors from aqueous matrices and adaptation of U.S. Environmental Protection Agency (EPA) SW-846 method 8081 {gas chromatography (GC) with electron capture detection (ECD)} (EPA 1992). It generates much less additional waste than traditional liquid-liquid extraction procedures for semivolatiles, including PCBs.

2.0 Summary of Method

- 2.1** Waste samples are aliquoted into a 100-mL volumetric flask in a radiochemical hood, glovebox, or hot cell from larger samples collected in the field. Samples are spiked with Aroclor standards dissolved in methanol (matrix-spiked samples only), and surrogate standards 2,4,5,6-tetrachloro-meta-xylene (TCMX) and decachloro-biphenyl (DCBP) (both also dissolved in methanol) are added to all samples and blanks.
- 2.2** The aqueous samples are applied to C-18 Empore™ SPE disks, and retained organics are eluted from the disks with 5 mL of hexane.
- 2.3** The Aroclor content is measured using capillary column GC with ECD (Method 8081 in EPA SW-846). The packed column GC method (Method 8080 in EPA SW-846) is also acceptable.

Caution: As required by the U.S. Department of Energy (DOE) "as low as reasonably achievable" (ALARA) principle, to minimize radiation exposure and contamination of personnel and facilities, it is imperative to follow all radiochemical laboratory procedures for handling radioactive samples and for health physics monitoring. It is important that the purified extracts be analyzed for radioactivity before GC analysis. The disks are disposed of as low-level waste.

(a) This method was supplied by G. A. Sega and W. H. Griest (Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee).

3.0 Interferences

- 3.1 The most common sources of interferences are co-extracted phthalate esters, organosulfur, organophosphorus, or chlorinated hydrocarbon pesticides. The presence of high concentrations of co-eluting hydrocarbons will diminish detector response, while the high sensitivity of the ECD often results in significant masking of analytes of interest when organosulfur, organophosphorus, or chlorinated hydrocarbon pesticides are present.
- 3.2 Interferences by phthalate esters are often introduced during sample preparation because reagents or samples contact plastics. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for contamination. Empore™ disks showed no detectable interferences.
- 3.4 Interferences will vary significantly from waste to waste. See EPA SW-846 Method 8081 for additional guidance on interferences and cleanup procedures.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Materials

- 5.1 Glass volumetric flasks, 100 mL size
- 5.2 C-18 Empore™ disks, 47 mm (or other size as appropriate) (BAKERBOND™ or equivalent)
- 5.3 Glass funnel/support base with clamp, 47 mm (or other size as appropriate), 300-mL capacity; stainless steel support screen; vacuum collection flask, 1-L capacity (Gelman, Kontes, Millipore or equivalent)
- 5.4 **Gas Chromatograph:** Analytical system complete with GC suitable for split-splitless injection and all required accessories including syringes, analytical columns, gases, ECD, and recorder/integrator or data system.

5.4.1 Narrow-Bore Capillary Columns:

- DB-5 capillary column, 30 m x 0.32 mm ID with a 0.25- μ m thick film of 5%-phenyl-methylpolysiloxane (or equivalent). Other film thicknesses could also be used.
- DB-1701 capillary column, 30 m x 0.32 mm ID with a 0.25- μ m thick film of 14%-cyanopropylphenyl-methylpolysiloxane (or equivalent) (may be used for confirmation). Other film thicknesses could also be used.

6.0 Reagents

6.1 Solvents and reagents should all be of pesticide quality or equivalent. Each solvent/reagent lot should be checked for possible interferences.

- Hexane
- Methanol

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

The radioactivity of the samples to be analyzed by this method requires that all applicable radiochemical laboratory procedures and health physics monitoring practices be followed to ensure that the DOE ALARA principle is observed.

8.0 Procedure

8.1 Approximately 98 mL of aqueous sample is aliquoted into a 100-mL volumetric flask in a radiochemical hood, glovebox, or hot cell from larger samples collected in the field. Matrix-spiked samples are spiked with 0.4 mL of Aroclor standards (6.25 μ g/mL each of Aroclor 1221 and Aroclor 1260 in methanol) to give a concentration of 25 ng/mL for each Aroclor analyzed when the final volume is brought to 100 mL. Other Aroclors, at this same concentration, or a single Aroclor can be used if appropriate.

A 0.2-mL methanol solution containing both of the surrogates TCMX (1.5 μ g/mL) and DCBP (5.0 μ g/mL) are added to all samples and blanks to achieve concentrations of 3 ng/mL and 10 ng/mL, respectively in a final volume of 100 mL. These particular surrogates are used because they bracket the retention times of all

PCBs. An additional 0.4 mL of methanol is added to the flask, and enough additional sample is added to bring the total volume to 100 mL and the methanol concentration to 1% (v/v).

- 8.2** A 47-mm (or other size as appropriate) C-18 Empore™ disk is placed on the stainless steel support screen of the glass funnel/support base using forceps. A 10-mL quantity of methanol is put on the Empore™ disk and allowed to sit for 2 min; then 8 to 9 mL of the methanol is drawn through the disk by vacuum. It is important not to let the methanol completely drain through the disk. Ten milliliters of water should be added to the remaining methanol on the disk and allowed to sit for 2 min. Approximately 8 mL of liquid should be drained through the disk. Again, it is important not to totally drain off the liquid covering the disk. After removing the methanol and water rinses from the receiving flask, the 100-mL aqueous sample is poured onto the filter and immediately drawn through by vacuum. While the sample is running through the Empore™ disk, the volumetric flask is rinsed with 10 mL of water. When only a few mL of sample are left on the disk, the 10 additional mL of wash water are added. The disk should be allowed to run dry, and then it should be vacuum suctioned for 15 min.
- 8.3** A small glass collection vessel (e.g., a 20-mL vial) is placed below the Empore™ disk. The volumetric flask should be rinsed with 5 mL of hexane and then poured on to the Empore™ disk. After 3 min of contact with the disk, the hexane is vacuum suctioned through the disk into the glass collection vessel. A glass pipette is used to transfer the hexane to a calibrated glass vessel. If more hexane is needed to bring the final volume back to 5 mL, it should be suctioned through the disk for an additional wash.
- 8.4** The purified extract should be screened for radioactivity before GC analysis, using site-specific methods. This screen may include gross-alpha activity, gross-beta activity, or gamma spectroscopy. If required, cleanup with H₂SO₄ (DOE Compendium Method OG100R, "Determination of PCBs as Aroclors in Solid Radioactive Mixed Wastes") may help to further reduce radioactivity in the extract.
- 8.5 Gas Chromatographic Analysis**

8.5.1 Recommended GC Conditions

- DB-5 column, 30 m x 0.32 mm ID with a 0.25-μm film thickness (or other thickness, as appropriate) in a GC with ECD, automatic sample injection system, and chromatography data system

- If a DB-1701 column is used for confirmation, the same GC conditions apply:

Carrier gas:	He (~1 mL/min)
Makeup gas:	N ₂ (~30 mL/min)
Injector temperature:	250°C
Detector temperature:	330°C
Initial temperature:	80°C
Temperature program:	80°C to 180°C at 30°C/min; then 180°C to 280°C at 5°C/min; hold 10 min at 280°C.
Total time:	33.3 min.
Injection volume:	1 µL

8.5.2. GC Analysis

- At least three concentrations of Aroclor standards spanning the expected range of sample concentrations should be injected.
- The purified sample extracts, matrix-spiked samples, and blanks should be injected.
- Aroclors should be identified and quantitated. The PCB residues should be quantitated by comparing the responses of three to five major peaks in each appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using each of the major peaks, and the results of the three to five determinations are averaged.
- If identification of the sample chromatographic pattern with an Aroclor mixture on the primary column is suspect, the secondary column should be used to aid in pattern recognition, or if concentrations are sufficiently high, GC-MS analysis should be employed.

9.0 Quality Control

9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.

9.2 Each day that analysis is performed, a mid-concentration reference (e.g., 500 ng/mL of Aroclor 1221 and Aroclor 1260 or other Aroclor, as appropriate) should be evaluated to determine if the chromatographic system is operating properly. If the daily check

standard indicates greater than $\pm 15\%$ change from the expected concentration, then a new standard curve must be prepared. This is conducted as in EPA SW-846, Method 8081, and should include matrix-spiked samples and laboratory blanks.

- 9.3 Recovery of surrogate standards in all samples, blanks, and spiked samples should be calculated. Surrogate recoveries should be at least 80%. It should be determined if the recovery is within this limit. If recovery is not within this limit, measurements and instrument performance should be verified. Re-extraction and analysis may be required.
- 9.4 A mid-concentration reference (e.g., 500 ng/mL of Aroclor 1221 and Aroclor 1260) should be included after each group of 20 samples in the analytical sequence as a calibration check. If the results exceed $\pm 30\%$ of the expected concentration, analysis should be halted, the injector cleaned, the septum replaced, and the system re-calibrated before resuming the analysis.
- 9.5 A regular preventive maintenance program is required to maintain instrument performance.
- 9.6 For each batch of samples processed, a laboratory reagent blank is analyzed. The presence of PCBs or interferences should be evaluated for data impact before analyzing the samples.
- 9.7 The laboratory should document the effect of the sample matrix on method performance by analyzing at least one matrix spike and either one matrix duplicate or matrix-spike duplicate per analytical batch.

10.0 Method Performance

- 10.1 The extraction technique was applied using laboratory distilled water as one matrix and 5 M NaNO_3 in distilled water as a second matrix. The latter matrix was chosen because it is typical of liquid nuclear wastes from storage tanks.

A typical GC of PCBs recovered from a 100-mL sample of the 5 M NaNO_3 matrix spiked with 25 ng/mL each of Aroclor 1221 and Aroclor 1260 is shown in Figure 1.

The absolute recoveries of Aroclor 1221 and Aroclor 1260 from the two aqueous matrices are shown in Figures 2 and 3. Each Aroclor was spiked at a concentration of 25 ng/mL. Recoveries from the distilled water matrix ranged from 63 to 116%; with 5 M NaNO_3 , the recoveries ranged from 71 to 111%.

Figure 1. Recovery of PCBs from Surrogate Aqueous Matrix Containing 5 M NaNO_3 . One hundred milliliters of 5 M NaNO_3 containing 1% methanol was spiked with Ar 1221 and Ar 1260 (each at 25 ng/mL in 100 mL of matrix). The standard surrogate TCMX was spiked at 3 ng/mL, and DCBP was spiked at 10 ng/mL. Extracted PCBs were in a total volume of 5 mL of hexane. Expanded regions of chromatograph show peaks used for quantitation. See section 8.5.1 DB-5 column for GC conditions.

Sample	Replicate	TCMX (3 ng/mL) (%)	Ar 1221 (25 ng/mL) (%)	Ar 1260 (25 ng/mL) (%)	DCBP (10 ng/mL) (%)
1	v-1	97.6	99.1	76.7	88.2
	v-2	96.3	99.6	76.9	89.6
	v-3	99.1	105.0	78.5	89.4
2(a)	v-1	98.1	102.6	99.2	98.3
	v-2	100.0	105.3	101.7	99.9
	v-3	100.7	104.0	104.0	101.3
3	v-1	93.3	92.6	62.5	91.1
	v-2	96.3	91.9	65.4	93.6
	v-3	95.3	90.6	65.2	92.9
4	v-1	106.9	105.2	80.4	101.1
	v-2	110.5	107.9	81.7	103.3
	v-3	108.6	107.1	82.0	100.9
5	v-1	101.0	101.1	115.2	112.4
	v-2	98.4	100.2	115.5	112.7
	v-3	97.8	98.6	115.9	118.2

(a) Added double the usual amounts of standard surrogates:
TCMX= 6 ng/mL of water matrix; DCBP= 20 ng/mL of water matrix.

Figure 2. Percent Recoveries of Aroclors and Surrogate Standards from Laboratory Distilled Water using C-18 Empore Disks

Sample	Replicate	TCMX (3 ng/mL) (%)	Ar 1221 (25 ng/mL) (%)	Ar 1260 (25 ng/mL) (%)	DCBP (10 ng/mL) (%)
1	v-1	107.5	92.0	99.1	103.5
	v-2	110.4	93.4	102.8	107.3
	v-3	108.2	91.2	100.3	104.1
2	v-1	93.3	98.8	70.9	73.4
	v-2	93.9	98.4	72.0	74.6
	v-3	96.1	101.4	74.1	76.0
3	v-1	84.9	95.1	110.1	102.2
	v-2	85.1	97.1	108.8	101.3
	v-3	85.6	95.6	110.6	103.8

Figure 3. Percent Recoveries of Aroclors and Surrogate Standards from 5 M NaNO₃ using C-18 Empore Disks

- 10.2** The recoveries of the surrogate standards TCMX and DCBP from the two aqueous matrices are also shown in Figures 2 and 3. Recoveries of TCMX ranged from 96 to 110% in water and from 85 to 110% in 5 M NaNO₃. Recoveries of DCBP ranged from 88 to 118% in water and from 73 to 107% in 5 M NaNO₃.

A variance component analysis for Aroclor 1221, Aroclor 1260, TCMX, and DCBP in the two aqueous matrices estimated the variation between runs (i.e., sample to sample variation) and within runs. Estimated standard deviations for recoveries of each component in the water matrix and in the NaNO₃ are shown in Figures 4 and 5, respectively.

The average recoveries of Aroclor 1221, Aroclor 1260, TCMX, and DCBP in each of the two aqueous matrices and the 95% confidence intervals are shown in Figure 6. In all cases, the confidence interval includes 100% recovery.

- 10.3** The recoveries of Aroclor 1221, Aroclor 1260, TCMX, and DCBP that were spiked into actual aqueous, radioactive, mixed-waste samples taken from underground storage tanks are shown in Table 1. The samples were contaminated mostly with ⁶⁰Co and ¹³⁷Cs at levels up to 1.14×10^4 Bq (6.85×10^5 dpm) alpha and up to 1.38×10^6 Bq (8.30×10^7 dpm) beta per 100 mL of sample. After hexane extraction, the gross alpha and beta activities measured in the extracts were reduced by factors of as much as 10^7 , making all the extracts safe to handle in a non-contamination zoned lab. {If radioactivity remains in the extract, further cleanup with H₂SO₄ (DOE Compendium Method OG100R, "Determination of PCBs as Aroclors in Solid Radioactive Mixed Wastes") may help to remove any remaining radioactivity. Of course, if radioactivity still remains in the extract, the analysis needs to be done in a C-zoned lab.} The recoveries of both the Aroclors and surrogates were comparable to the recoveries achieved with the water and 5 M NaNO₃ matrices. Only the recovery of TCMX in the third radioactive sample could not be determined because of a strong interference in that sample.
- 10.4 Minimum Detection Limits.** The GC was calibrated with standards of Aroclor 1221 and Aroclor 1260 mixed together in hexane and each at 200, 500, and 800 ng/mL concentrations. This range of concentrations was used to bracket the expected concentration of the Aroclors in the hexane extracts for 100% recovery (500 ng/mL). Applying the method of Hubaux and Vos (1970) to the calibration curves, the minimum detection limits (MDLs) for Aroclor 1221 and Aroclor 1260 were 62 ng/mL and 48 ng/mL, respectively. Lower MDLs were obtained when a lower range of concentration standards were used. Thus, with Aroclor 1221 and Aroclor 1260 concentration standards at 50, 100, and 200 ng/mL, the MDLs were lowered to 28 ng/mL and 22 ng/mL, respectively.

Figure 4. Standard Deviations - Water Matrix **Figure 5. Standard Deviations - NaNO₃ Matrix**

Figure 6. Ninety-Five Percent Confidence Intervals

Table 1. Percent Recoveries of Aroclors and Surrogate Standards Spiked in Aqueous Samples Taken from Underground Nuclear Waste Storage Tanks Using C-18 Empore Disks

Sample	Replicate	TCMX (3 ng/mL)	Ar 1221 (25 ng/mL)	Ar 1260 (25 ng/mL)	DCBP (10 ng/mL)	Total Activity Applied to Disk Becquerel (Bq)		Total Activity Recovered from Disk Becquerel (Bq)	
						Alpha	Beta	Alpha	Beta
1 (pH=6.5)	v-1	74.5	56.2	53.3	92.1				
	v-2	75.5	55.8	54.9	93.8		3.4 x 10 ³		0
	v-3	76.4	57.0	56.7	95.2				
2 (pH=10.1)	v-1	61.2	61.2	63.2	72.3				
	v-2	63.4	63.7	66.0	72.8	1.14 x 10 ⁴	1.4 x 10 ⁵	0.73	0
	v-3	61.3	59.0	64.6	74.2				
3 (pH=13.2)	v-1	interference ^(a)	94.5	46.7	65.2				
	v-2	interference	99.4	50.6	70.1	1.97 x 10 ³	2.23 x 10 ⁵	3.1	9.4
	v-3	interference	97.6	46.0	74.2				

(a) A very large peak with the same retention time as TCMX was present in this sample. An interference with Ar 1221 may also have occurred in this sample since its recovery was higher than with other samples.

11.0 References

U.S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Methods*, 3rd Edition, Final Update I. EPA/SW-846. Office of Solid Waste and Emergency Response. Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Hubaux, A., and G. Vos. 1970. "Decision and Detection Limits for Linear Calibration Curves," *Anal. Chem.* 42: 849-855.

OP120R^(a)

Reduced-Scale Liquid-Liquid Extraction of Semivolatile Organic Compounds

1.0 Scope and Application

This method is used to extract semivolatile organic compounds from aqueous samples that are too radioactive to handle outside of a hot cell or glovebox in the 1-L volumes required by U.S. Environmental Protection Agency (EPA) SW-846 Method 3510, but which can be handled outside that containment in volumes of 20 mL.

This method is a scaled-down version of SW-846 Method 3510 (EPA 1992). Parts that are the same as SW-846 are in italics; however, some wording has been changed for consistent formatting and grammar.

This method is intended as sample preparation for SW-846 GC-MS Methods 8270 or 8250.

2.0 Summary

- 2.1 A 20-mL aliquot of a radioactive aqueous sample is transferred to a 40-mL volatile organic analysis (VOA) vial.
- 2.2 To determine the order in which the acid and base-neutral fractions are to be extracted, the initial pH of the sample is measured.
- 2.3 After the pH for each fraction is adjusted, the sample is serially extracted with methylene chloride.
- 2.4 Using sodium sulfate or either a disposable syringe and filter cartridge or a Separator X, water is removed from the combined extract. The extract is then concentrated to 1.0 mL.
- 2.5 Using 20 mL of sample, Method 8270 reporting limits will normally range from 250 to 1250 µg/L.

(a) This method was supplied by B. A. Tomkins, J. E. Caton, Jr., G. S. Fleming, M. E. Garcia, S. H. Harmon, R. L. Schenley, C. A. Treese, W. H. Griest, and P. F. Wolfe (Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee).

Caution: As required by the U.S. Department of Energy (DOE) “as low as reasonably achievable” (ALARA) principle, to minimize radiation exposure and contamination of personnel and facilities, it is imperative to follow all radiochemical laboratory procedures for handling radioactive samples and for health physics monitoring. It is important that the purified extracts be analyzed for radioactivity before gas chromatography (GC) or GC-mass spectrometry (MS) analysis.

3.0 Interferences

- 3.1 Wastes containing nitrite may foam and release oxides of nitrogen when acidified. The analyst should be alert to this reactivity. Artifactual nitration of surrogate standards and matrix spikes has been observed in several laboratories.
- 3.2 *Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.*
- 3.3 *Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.*

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Materials

- Disposable Pyrex 25-mL pipets
- *pH indicator paper: pH range including the desired extraction pH*
- Pipetman (or equivalent): 1.0 mL
- Graduated cylinders
- VOA vials: 40 mL, with Teflon screw caps, or other appropriate vials

- Beakers
- Whatman #1 filter paper (or equivalent)
- Separator X (Model B35, Hamamatsu, Japan)
- Pasteur pipets
- Disposable 10-mL polypropylene syringe barrel fitted with a Teflon-membrane filter {0.45- μ m porosity, Gelman Acrodisc CR (Gelman Sciences, Inc., Ann Arbor, Michigan) or equivalent}
- Concentrator tubes: 10 mL, graduated. Graduations should be verified.

6.0 Reagents

- 6.1 **Reagent Water:** *Reagent water is defined as water in which an interferant is not observed at the method detection limit of the compounds of interest.*
- 6.2 **Sodium Hydroxide Solution, 10 N:** (ACS) 40 g NaOH, is dissolved in reagent water and diluted to 100 mL.
- 6.3 **Sodium Sulfate:** (ACS) granular, anhydrous (purified by heating at 400°C for 4 h in a shallow tray)
- 6.4 **Sulfuric Acid Solution (1:1):** A 50-mL quantity of H_2SO_4 (sp gr 1.84) is added slowly to 50 mL of reagent water.
- 6.5 **Extraction Solvent:** Methylene chloride (pesticide quality or equivalent)
- 6.6 **Surrogate Standard Mixes**
- 6.6.1 Acid surrogate standard mix: 2-fluorophenol, phenol- d_5 , 2,4,6-tribromophenol (200 μ g/mL each, in methylene chloride).
- 6.6.2 Base-neutral surrogate standard mix: nitrobenzene- d_5 , 2-fluorobiphenyl, p-terphenyl- d_{14} (100 μ g/mL each, in methylene chloride).
- 6.6.3 A combined mix of 6.6.1 and 6.6.2 at the same concentrations also may be used.

6.7 Matrix Spike Mixes

6.7.1 Acid matrix spike mix: phenol, 2-chlorophenol, 4-chloro-3-methylphenol, 4-nitrophenol, pentachlorophenol (200 µg/mL each, in methylene chloride).

6.7.2 Base-neutral matrix spike mix: 1,4-dichlorobenzene, N-nitrosodipropylamine, 1,2,4-trichlorobenzene, acenaphthene, 2,4-dinitrotoluene, pyrene (100 µg/mL each, in methylene chloride)

6.7.3 A combined mix of 6.7.1 and 6.7.2 at the same concentrations also may be used.

6.8 **Internal Standard Mix:** Acenaphthene-d₁₀, chrysene-d₁₂, 1,4-dichlorobenzene-d₄, perylene-d₁₂, phenanthrene-d₁₀, and naphthalene-d₈ (4 mg/mL each, in methylene chloride)

7.0 Sample Collection, Preservation, and Handling

7.1 Sample collection, preservation, and handling should be addressed in the planning process.

7.2 For organic analysis, samples should be collected in glass amber containers, with Teflon-lined screw caps, if possible.

Note: Highly radioactive samples may degrade Teflon, and other materials such as polyethylene may be required for cap liners and other non-glass or metal surfaces contacting the wastes.

7.3 Conventional sample preservation methods should be used only with caution. Refrigeration to 4°C has been observed to cause precipitation to occur in aqueous wastes having a high salt content. All applicable radiochemical laboratory procedures and health physics monitoring practices should be followed to ensure that the DOE ALARA principle is observed (see Chapter 4 and site-specific documents). The extraction of the semivolatile organics within 14 days of sample receipt follows from EPA SW-846 requirements.

7.4 Additional information can be found in the introductory material of chapter 4 in SW-846, Organic Analytes, section 4.1.

8.0 Procedure

8.1 Twenty milliliters of sample are measured and transferred to a 40-mL VOA vial, or other appropriate vial, using a graduated cylinder or disposable 25-mL pipet.

- 8.2 *The pH of the sample should be checked with wide-range pH paper, recorded, and, if necessary, the pH should be adjusted using the solutions of sodium hydroxide or sulfuric acid as appropriate. If the sample pH is initially alkaline, then the initial extraction should be conducted at a pH >11. However, if the sample pH is initially acidic, then the initial extraction should be conducted at a pH <2.*

Caution: Acidification of some wastes causes foaming and evolution of oxides of nitrogen. The analyst must be alert to sample reactivity. Precipitation also may occur upon pH adjustment.

- 8.3 One milliliter each of both surrogate standard mixes (or 1 mL of a combined mix) should be added to all samples, spikes, and blanks. For the sample in each analytical batch selected for spiking, 1.0 mL each of both matrix spike mixes should be added. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/ μ L of each base/neutral analyte and 200 ng/ μ L of each acid analyte in the extract to be analyzed (assuming a final-extract volume of 1 mL).

- 8.4 Five milliliters of methylene chloride should be added to the 40-mL VOA vial.

- 8.5 The sample and solvent should be sealed and mixed gently, end over end, at least 30 times. A vortex mixer, wrist-action shaker, or automatic rotary-action shaker also may be used, but excessive emulsion formation or pressure buildup may ensue with some wastes.

Note: *Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately by cracking the seal slightly.*

- 8.6 *The organic layer should be allowed to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods (Separator X is usually used for emulsions). The extract is retrieved from the VOA vial (using a pasteur pipet) and collected in another 40-mL VOA vial (or a larger vial if sodium sulfate drying is to be used).*

- 8.7 *The sample should be extracted two more times, using fresh portions of solvent (steps 8.4 through 8.6). The three solvent extracts should be combined.*

- 8.8 If the initial pH for the first extraction was adjusted to >11, the pH of the aqueous phase should be adjusted to a pH <2. If the initial pH was adjusted to <2, then the pH of the aqueous phase should be adjusted to >11. *Serial extraction should be performed three*

times with 5 mL of methylene chloride, as outlined in steps 8.4 through 8.7. The extracts should be collected and combined and the combined extract labeled appropriately.

- 8.9** If GC-MS analysis (Method 8250 or 8270) is to be performed, *the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g., if for regulatory purposes, the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined).*
- 8.10** Water is removed from the combined extracts by using sodium sulfate, a syringe with a Teflon filter, or a Separator X.
- 8.10.1 If sodium sulfate is used, 15 to 30 mL of sodium sulfate are added to the combined extracts in a vial of sufficient volume. The vial contents are mixed thoroughly by swirling, and the sodium sulfate is removed by filtering the mixture through Whatman No. 1 filter paper into a clean vial. Quantitative recovery is achieved by rinsing the original vial (and sodium sulfate) with 20 to 30 mL of methylene chloride. If a syringe and filter or Separator X is used, they should also be rinsed.
- 8.10.2 If a syringe/filter combination or a Separator X is used, it should be conditioned by rinsing with approximately 10 to 20 mL of methylene chloride, and the methylene chloride should be allowed to filter through. The extract should be transferred to the syringe/filter or the Separator X and collected in another vial. The vial, which contained the solvent extract, should be rinsed with 20 to 30 mL of methylene chloride and filtered through the Separator X to complete the quantitative transfer.
- 8.11** The combined, dried extract is transferred in portions from the vial to a 10-mL concentrator tube and concentrated under a gentle stream of nitrogen. After all the extract is transferred, the vial is rinsed with 2 to 3 mL of methylene chloride, and the solvent rinse is transferred. Periodically, during the nitrogen blow-down, 1 to 2 mL of methylene chloride are used to rinse the side walls of the concentrator tube. With dry, flowing nitrogen, the extract is concentrated to exactly 1.0 mL.
- 8.12** The 1.0-mL extract is transferred to a crimp-top vial, spiked with 10 µL of internal standard mix, and sealed.
- 8.13** After gross-alpha and gross-beta activity screens, the extract is transferred for GC-MS if the sample radioactivity meets the requirements of the GC-MS laboratory. Screening the extracts by GC is recommended to identify those that need to be diluted before GC-MS analysis.

9.0 Quality Control

9.1 Modifications to this method should be supported by appropriate quality control (QC) procedures (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.

9.2 *Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.*

10.0 Method Performance

10.1 Surrogate-standard and matrix-spike recovery data are summarized in Table 1 from the analysis of 67 aqueous samples from nuclear waste tanks that received wastes from research and development labs and from separation process development operations. The particular wastes analyzed here had gross-alpha counts as high as 10^4 Bq/mL and gross beta-gamma counts up to 10^6 Bq/mL; the main radionuclides present were ^{137}Cs , ^{90}Sr , and ^{60}Co ; the dominant anions were $\text{SO}_4^{=}$ and NO_3^- ; the pH range was 0.2 to 12.7; the total solids varied from 0.3 to 170 mg/mL. The recovery data for the acid-surrogate standards for four samples were invalidated by apparent laboratory error and were not included. Overall, the mean recoveries were within the guidelines of EPA SW-846 method 8270, but recoveries for some samples did not meet SW-846 QC acceptance limits for water. However, the applicability of the latter to nuclear wastes has not been established. Method accuracy and surrogate standard recovery QC limits calculated from the data in Table 1 (per SW-846 Method 8270 calculations) are listed in Tables 2 and 3, respectively.

10.2 Seven pairs of matrix-spike and matrix-spike-duplicate recoveries were evaluated, as shown in Table 1. While all of the available base-neutral-matrix spike data were used, two pairs (total four samples) of acid-matrix spike data were invalidated either by errors in the sample preparation laboratory or by matrix effects that the existing extraction procedure could not overcome. An additional pair of recovery values for pentachlorophenol was also deleted because the measured recovery exceeded 150%. The problem was traced to an erratic peak shape produced during the GC/MS analysis. The mean recovery values for both the acid and base-neutral-matrix spikes fell within accepted QC limits defined by the EPA Contract Laboratory Program (CLP). No QC acceptance limits for matrix spikes are listed in EPA SW-846. The standard deviation and relative standard deviation of the base-neutral-matrix spikes were almost identical with those observed for the surrogates. These two parameters tended to be somewhat greater for the acid-matrix spikes. Possible reasons for the poorer precision may include the following: 1) the pH of the final extract was insufficient to permit quantitative removal of the smaller, more acidic phenols, notably 4-nitrophenol, and 2) reliable quantitation of at least one species by GC/MS, viz. pentachlorophenol, is historically

Table 1. Summary of Semivolatile Surrogate Standard and Matrix-Spike Recoveries for Radioactive Aqueous Nuclear-Waste-Tank Samples.

Compound Name	Recovery Data, %, for Real Samples			
	No. of Samples	Mean	Std. Dev.	RSD, %
Surrogate Standards				
Nitrobenzene-d ₅	67	70	15	21
2-Fluorobiphenyl	67	64	14	22
Terphenyl-d ₁₄	67	88	17	19
Phenol-d ₅	63	53	12	23
2-Fluorophenol	63	48	11	24
2,4,6-Tribromophenol	63	71	17	24
Acid Matrix Spikes				
Phenol	10	40	9	22
2-Chlorophenol	10	43	7	17
4-Chloro-3-methylphenol	10	55	19	34
4-Nitrophenol	10	69	31	46
Pentachlorophenol	8	74	32	44
Base-Neutral Matrix Spikes				
1,4-Dichlorobenzene	14	50	10	20
N-Nitroso-di-n-propylamine	14	66	10	15
1,2,4-Trichlorobenzene	14	53	12	22
Acenaphthene	14	64	13	21
2,4-Dinitrotoluene	14	71	18	25
Pyrene	14	78	12	15
Compound Name	Recovery Data, %, for Blanks			
	No. of Samples	Mean	Std. Dev.	RSD, %
Nitrobenzene-d ₅	8	65	18	28
2-Fluorobiphenyl	8	58	13	23
Terphenyl-d ₁₄	8	85	18	21
Phenol-d ₅	8	49	12	24
2-Fluorophenol	8	42	8	19
2,4,6-Tribromophenol	8	69	14	20

difficult. The modified procedure clearly worked as well as that defined by EPA Method 3510 on the basis of surrogates and matrix spikes. The agreement between a matrix spike and its companion matrix-spike duplicate was typically between 10 and 20%.

Table 2. Method Accuracy for Nuclear-Waste-Tank Liquid Samples

Compound	Recovery Interval (a) %
Phenol	22
2-Chlorophenol	29
4-Chloro-3-methylphenol	17
4-Nitrophenol	7
Pentachlorophenol	10
1,4-Dichlorobenzene	30
N-Nitroso-di-n-propylamine	46
1,2,4-Trichlorobenzene	29
Acenaphthene	38
2,4-Dinitrotoluene	35
Pyrene	54
	107
	90
	77
	86
	70
	138
	131
	93
	57
	58

(a) Calculated from Table 1 as average ± 2 standard deviations.

Table 3. Surrogate Standard Recovery QC Acceptance Limits for Nuclear-Waste-Tank Liquid Samples

Compound	QC Limits (a) % Recovery
Nitrobenzene-d ₅	25
2-Fluorobiphenyl	22
Terphenyl-d ₁₄	37
Phenol-d ₅	17
2-Fluorophenol	15
2,4,6-Tribromophenol	20
	122
	81
	89
	139
	106
	115

(a) Calculated from Table 1 as average ± 3 standard deviations.

The method blanks (eight in all) were all free of the target compound list (TCL) compounds except for traces (110 and 170 µg/L, respectively) of di-n-butylphthalate and di-n-octyl phthalate detected in one blank. Low levels of hydrocarbons contributed by the Teflon®-membrane filter were found in all blanks and samples (typically at 100 to 200 µg/L), but they did not interfere with the quantitation of the TCL analytes.

10.3 The procedure generally carries very little of the sample radioactivity into the final extract. Decontamination factors of 10^3 and greater were observed.

Caution: Wastes containing chelators may cause greater carry-over of radioactivity into the extracts.

11.0 Reference

U. S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste. Volume IB, Physical/Chemical Methods, SW-846*, 3rd Edition, Final Update I, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

12.0 Further Reading

Tomkins, B. A., J. E. Caton, Jr., G. S. Fleming, M. E. Garcia, S. H. Harmon, R. L. Schenley, C. A. Treese, and W. H. Griest. 1990. "Determination of Regulatory Organic Compounds in Radioactive Waste Samples. Semivolatile Organics in Aqueous Liquids." *Anal. Chem.*, 62:253-257.

Autrey, J. W., D. A. Costanzo, W. H. Griest, L. L. Kaiser, J. M. Keller, C. E. Nix, and B. A. Tomkins. 1990. *Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL*. ORNL/ER-13, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

OP130R^(a)

Analysis of TCLP Semivolatiles and Pesticides in Radioactive Mixed Waste Sludges

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

- 1.1 This method is for the total analysis of the Toxicity Characteristic Leach Procedure (TCLP) semivolatile organic compounds and pesticides in radioactive mixed waste (RMW) sludges. It does not include acidic semivolatiles. The method is suitable for glovebox and hot cell operations. The compounds determined using this method, and the surrogate standards are listed in Table 1.
- 1.2 This method is based upon adaptation of the U.S. Environmental Protection Agency (EPA) (1992) SW-846 Methods 3550 (ultrasonic extraction), 8081 {gas chromatography (GC) of organochlorine pesticides}, 8090 (nitroaromatics by GC), and 8121 (chlorinated hydrocarbons by GC).

2.0 Summary of Method

- 2.1 Waste samples (1 g) are weighed out, spiked with the surrogate standards tetrachlorometaxylene (TCMX) and decachlorobiphenyl (DCBP) and matrix spikes (matrix-spiked samples only). Blanks are spiked only with surrogate standards.

After evaporation of the spike solvents, the samples are extracted three times with 5 mL of methylene chloride (a modification of EPA SW-846 Method 3550). The solvent extracts are pooled and concentrated to 1.0 mL final volume.

- 2.2 The semivolatile organic compounds and pesticides are determined using capillary column GC with electron capture detection (ECD) (modified from EPA SW-846 Methods 8081, 8090, and 8121). The packed column GC-ECD SW-846 Method 8080 is also acceptable if all compounds can be resolved.

(a) This method was supplied by R. L. Schenley, P. F. Wolfe, and W. H. Griest (Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee).

3.0 Interferences

3.1 The most common sources of interferences are co-extracted polychlorinated biphenyls (PCBs,) phthalate esters, organosulfur compounds, lipids, and waxes. The presence of high concentrations of co-eluting hydrocarbons will diminish the detector response. The high sensitivity of the ECD often allows significant masking of analytes of interest by co-eluting phthalate esters, organosulfur compounds, organophosphorus compounds, and PCBs.

3.2 Interferences by phthalate esters are often introduced due to contact of reagents or samples with flexible plastics during sample preparation. Interferences from phthalate esters can be minimized by avoiding contact with any plastic materials and by checking all solvents and reagents for contamination. Reagents and glassware may be purified by solvent extraction or heating to 400°C for 1 h and subsequent storage in covered containers.

Caution: It is important that the sample extracts be analyzed for radioactivity before transport and GC analysis in non-contamination-zoned areas.

Table 1. TCLP Semivolatiles and Pesticides Determined			
Compound	Abbreviation	GAS No. (a)	
Chlordane (technical)	CHD	57-74-9	
1,4-Dichlorobenzene	DCB	106-46-7	
Toxaphene	TOX	8001-35-2	
Hexachlorocyclopentadiene	HCC	67-72-1	
Nitrobenzene	NBz	98-95-3	
Hexachlorobutadiene	HCB	87-68-3	
2,4-Dinitrotoluene	DNT	121-14-2	
Hexachlorobenzene	HCBz	118-74-1	
Lindane	LIN	58-89-9	
Hepachlor	HC	76-44-8	
Hepachlor epoxide	HCE	1024-57-3	
Endrin	END	72-20-8	
Methoxychlor	MC	72-43-5	
Tetrachloromethylene (b)	TCMX	877-09-8	
Decachlorobiphenyl (b)	DCBP	2051-24-3	
(a) Chemical Abstract Services Registry Number			
(b) Surrogate standard			

- 3.3 The presence of elemental sulfur will result in large peaks that obscure a significant portion of the chromatogram. To remove sulfur, EPA SW-846 Method 3660 is recommended.
- 3.4 Interferences will vary significantly from waste to waste. See EPA SW-846 Method 8081 for additional guidance on interferences and cleanup procedures.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples all applicable radiochemical handling procedures and health physics monitoring practices should be followed. Refer to Chapter 4 in this document for general safety information.

5.0 Apparatus and Materials

- 5.1 Balance: Top-loading, accurate to 0.1 g
- 5.2 Vials/Teflon caps: 16 mL and/or 25 mL
- 5.3 Ultrasonic bath: Branson 5200 or equivalent
- 5.4 Centrifuge: Tabletop model
- 5.5 Pasteur glass pipets: Disposable, 1.0 mL
- 5.6 Heating block
- 5.7 Concentrator tube: 10 mL graduated (Organomation Associates Inc., or equivalent), volumetric calibrations verified
- 5.8 Autosampler vials with screw caps
- 5.9 **Gas Chromatograph:** Analytical system suitable for split-splitless injection and all required accessories, including syringes, analytical columns, gases, ECD, and recorder/integrator or data system.
- 5.9.1 **Columns**
- Primary column: DB-5 capillary column, 30 m x 0.32 mm ID, 0.25- μ m-thick film of 5%-phenyl-methylpolysiloxane (or equivalent)

- Confirmation column: DB-1701 capillary column, 30 m x 0.32 mm ID, 0.25- μ m-thick film of 14%-cyanopropylphenyl-methylpolysiloxane (or equivalent)

6.0 Reagents

- 6.1 TCLP Pesticide Surrogate Mix in acetone, 200 μ g/mL (200 ppm) (from Restek, Bellefonte, Pennsylvania, or equivalent)
- 6.2 Toxaphene in hexane, 250 μ g/mL (250 ppm) (from Environmental Resource Associates, Arvada, Colorado, or equivalent)
- 6.3 Chlordane in hexane, 250 μ g/mL (250 ppm) (from Environmental Resource Associates, Arvada, Colorado, or equivalent)
- 6.4 TCLP Pesticide Mix in methanol, 2 mg/mL (2000 ppm) (from Restek, Bellefonte, Pennsylvania, or equivalent)
- 6.5 Hexachloro-1,3-butadiene, 98% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)
- 6.6 Hexachloroethane, 99% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)
- 6.7 2,4-Dinitrotoluene, 99% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)
- 6.8 Nitrobenzene, 99% pure (from CHEM Service, West Chester, Pennsylvania, or equivalent)
- 6.9 p-Dichlorobenzene, 98% pure (from Supelco, Bellefonte, Pennsylvania, or equivalent)
- 6.10 Hexachlorobenzene, 99% pure (from Supelco, Bellefonte, Pennsylvania, or equivalent)
- 6.11 Solvents: Methylene chloride and hexane (pesticide quality or equivalent)

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

The radioactivity of the samples to be analyzed by this method requires that all applicable radiochemical laboratory procedures and health physics monitoring practices be followed to ensure that the U.S. Department of Energy (DOE) "as low as reasonably achievable" (ALARA) principle is observed.

8.0 Procedure

- 8.1 In a radiochemical hood, glovebox, or hot cell, 1.0 g of sludge sample should be weighed into the vial from larger samples collected from the field. If the sample radioactivity permits, this subsample may be removed from a glovebox or hot cell for the remaining steps. Otherwise, all operations must be carried out in the hot cell or glovebox.
- 8.2 All blanks, samples, and matrix-spiked samples are spiked with surrogate standards (TCMX and DCBP) at a final sample concentration of 1 ppm. Matrix-spiked samples are spiked according to the TCLP toxicity characteristic constituents to be analyzed. For example, if analyzing CHD, the final spike concentration would be 600 ng/mL. The final spike concentration of DCB and TOX would be 10 µg/mL (10 ppm). All other TCLP analytes would be spiked at 40 ng/mL.
- 8.3 After evaporation of the spike solvents (ca. 15 min), the samples are extracted three times in 5 mL of methylene chloride, using an ultrasonicator bath for 10 min. The water level in the ultrasonicator should be below the caps on the vials and above the sludge sample to be sonicated. Each 5-mL extract is collected by letting the sample settle and by pipetting off the organic layer. A centrifuge may be helpful in settling the sludge.
- 8.4 The combined methylene chloride extracts are concentrated to 0.1 mL using a heating block and a stream of dry, clean air or nitrogen. One milliliter of hexane is added to the extract and concentrated to 0.1 mL. The extract is diluted to 1.0 mL and transferred to an autosampler vial.
- 8.5 All extracts are analyzed on a GC equipped with an ECD, an automatic sample injector, and a data system.
- 8.6 Gas Chromatographic Analysis
 - 8.6.1 GC Conditions
 - 8.6.1.1 DB-5 (or equivalent) column, 30 m x 0.32 mm ID with a 0.25-µm film thickness in a GC with ECD, automatic sample injection system, and chromatography data system.

Carrier gas: helium (≈ 2.7 mL/min);
Makeup gas : nitrogen (≈ 35 mL/min)
Injector temperature: 250°C
Detector temperature: 330°C
Initial temperature: 60°C
Temperature program: hold for 1 min at 60°C; then 60°C to 140°C at 10°C/min;
then 140°C to 280°C at 14°C/min; hold 7 min at 280°C.
Total time: 26 min
Injection volume: 1.0 μ L

8.6.2 GC Analysis

- 8.6.2.1 Because of mutual chromatographic interferences, calibration curves are prepared from three mixtures: CHD, TOX and DCB, and TCLP pesticides/semivolatile organic compounds. For each calibration curve, at least three concentrations of standards are injected to span the expected range of sample concentrations.
- 8.6.2.2 The blanks and the sample extracts are injected.
- 8.6.2.3 All compounds are identified and quantitated for that particular calibration. The CHD residues are quantitated by comparing the responses of three to four major peaks in each CHD standard with the peaks obtained from the sample extract. The amount of CHD is calculated using each of the major peaks, and the results of the three to four determinations are averaged. The TOX residues are quantitated by comparing the response of the "hump" of peaks in each standard with the peaks obtained from the sample extract. The amount of TOX is calculated by lumping (combining all the peak areas from all the peaks) as a single result. All other analytes are quantitated separately.

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.
- 9.2 Any reagent blanks or matrix spiked samples should be subjected to the same analytical procedures as those used on actual samples.

- 9.3 A calibration curve is prepared for each set of analytes. Analysis of the extracts is not done unless the calibration curve exhibits less than 20% relative standard deviation (RSD) for each analyte, or the continuing daily midpoint calibration is within 15% of the calculated calibration curve. If the deviation of the midpoint calibration is greater than 15%, the calibration curve is reanalyzed after corrective actions are taken. Corrective actions include such steps as cleaning the injector, replacing the septum, and/or trimming the column at the injector, at the detector, or at both.
- 9.4 The midpoint calibration check is analyzed at the beginning of a sample sequence, after every ten samples, and at the end of a sample sequence. If the midpoint calibration deviates more than 15% from the calibration curve, the samples before the midpoint standard are reanalyzed, and another calibration curve is formulated.

10.0 Method Performance

- 10.1 **Chromatographic Performance.** The performance of the GC method for separating and detecting the analytes is presented in Table 2. Typical retention times for the analytes on the primary and confirmation column are listed. The detection limits are calculated according to Hubaux and Vos (1970), and in units of μg of analyte per g of sludge. Chromatograms of standard compounds on the primary column are shown in Figures 1 through 3.
- 10.2 **Analyte and Surrogate Standard Recoveries.** Three sample matrices were spiked, extracted, and analyzed by the method, with the addition that each extract was analyzed in triplicate. The samples included a surrogate Los Alamos National Laboratory (LANL) wastewater treatment sludge, a surrogate Oak Ridge National Laboratory (ORNL) nuclear-waste-tank sludge, and sea sand. For the 13 analytes, there were three sets of extractions: CHD, DCB and TOX, and the remainder of the TCLP analytes. In all three extraction sets, the surrogates (TCMX and DCBP) were spiked into all matrices and blanks. The three extraction sets were established from the following information. Gas chromatograms of CHD and TOX showed multiple peaks in the same region of the chromatogram. Retention times of CHD and TOX corresponded to several other TCLP constituents. To analyze DCB with the other TCLP pesticides/semivolatiles would have resulted in a peak too small for quantitation; therefore, because of the retention time and high regulatory limit for DCB, this TCLP analyte was analyzed with toxaphene that has a "hump" of peaks between the two surrogates.

Tables 3 through 5 list the recoveries of the TCLP semivolatiles and pesticides analyzed using this method. Recoveries are very good with the exception of NBz in the sand sample. The reason for this is not clear, but evaporative losses can be ruled out because the recovery of DCB, which has a lower boiling point, was good. Table 6 shows the very good recoveries for the surrogate standards.

This method should not be used to analyze for the TCLP acidic semivolatiles. Multiple peaks were obtained for the TCLP cresols and trichlorophenols when extracts were analyzed using high-performance liquid chromatography (Method OH100R). These data indicate that these compounds will not be present in matrices of high pH that contain oxidizing agents. The multiple peaks probably are oxidation and nitration products of the cresols and trichlorophenols (see Stromatt et al. 1993; Chen et al. 1991). For the extraction of these compounds in other complex mixtures, the procedure of Stromatt et al. should be used.

Table 2. Analyte Retention Times and Detection Limits on Primary and Confirmation Columns

Compound	Detection Limit	Retention Time (min)	
	on Primary Column (µg/mL)	Primary Column	Confirmation Column
Chlordane (peak 1)	0.123	16.1	16.2
Chlordane (peak 2)	0.368	17.6	16.4
Chlordane (peak 3)	0.133	17.8	18.4
Chlordane (peak 4)	—	—	18.5
1,4-Dichlorobenzene	1.970	5.4	5.8
Toxaphene ^(a)	1.620	18.95	19.85
Hexachloroethane	0.033	6.3	6.2
Nitrobenzene	0.022	6.5	8.0
Hexachlorobutadiene	0.032	8.6	8.3
2,4-Dinitrotoluene	0.012	12.5	14.5
Hexachlorobenzene	0.028	14.4	14.6
Lindane	0.034	14.8	16.1
Heptachlor	0.030	16.1	16.4
Heptachlor epoxide	0.032	17.2	18.0
Endrin	0.028	18.5	19.3
Methoxychlor	0.018	20.1	21.2
Tetrachloro- <i>m</i> -xylene	—	13.5	13.6
Decachlorobiphenyl	—	24.3	24.8

(a) Retention time of central peak.

Figure 1. Chromatogram of Chlordane on Primary Column

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Figure 2. Chromatogram of Toxaphene and DCBP on Primary Column

Figure 3. Chromatogram of Other Pesticides and Semivolatile Organic Compounds on Primary Column

10.3 Sources of Variation. The total variation of percent-recovery measurements are due to three experimental sources: 1) different matrix types, 2) different replicates, and 3) different injections in the GC instrument. The statistical method of variance component analysis (Searle 1971) was used to estimate the contribution to the total variation of each experimental source. Table 7 reports the standard deviations for each experimental source derived from the estimated variance components calculated by the method of maximum likelihood.

Table 3. Analyte Recoveries from LANL Surrogate Sludge

<u>Analyte</u>	<u>Concentration ($\mu\text{g/g}$)</u>	<u>Average Recovery % (STD)(a)</u>	<u>Number of Replicates</u>
Chlordane	0.6	98.2 (0.98)	6
1,4-Dichlorobenzene	10.0	89.7 (7.50)	6
Toxaphene	10.0	81.8 (1.61)	6
Hexachloroethane	0.04	68.8 (10.54)	4
Nitrobenzene	0.04	70.9 (7.12)	4
Hexachlorobutadiene	0.04	89.3 (3.43)	4
2,4-Dinitrotoluene	0.04	106 (5.02)	4
Hexachlorobenzene	0.04	117 (7.63)	4
Lindane	0.04	100 (0.82)	4
Heptachlor	0.04	123 (1.75)	4
Heptachlor epoxide	0.04	119 (2.18)	4
Endrin	0.04	131 (3.71)	4
Methoxychlor	0.04	109 (1.03)	4

(a) STD = standard deviation

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Table 4. Analyte Recoveries from Sand

<u>Analyte</u>	<u>Concentration ($\mu\text{g/g}$)</u>	<u>Average Recovery % (STD)</u>	<u>Number of Replicates</u>
Chlordane	0.6	93.1 (3.78)	5
1,4-Dichlorobenzene	10.0	88.7 (7.68)	5
Toxaphene	10.0	81.5 (1.80)	5
Hexachloroethane	0.04	83.3 (6.66)	3
Nitrobenzene	0.04	39.7 (17.5)	3
Hexachlorobutadiene	0.04	84.8 (5.80)	3
2,4-Dinitrotoluene	0.04	108 (1.76)	3
Hexachlorobenzene	0.04	101 (1.15)	3
Lindane	0.04	78.8 (15.8)	3
Heptachlor	0.04	105 (5.00)	3
Heptachlor epoxide	0.04	85.0 (11.1)	3
Endrin	0.04	109 (7.21)	3
Methoxychlor	0.04	109 (7.00)	3

Table 5. Analyte Recoveries from ORNL Surrogate Sludge

<u>Analyte</u>	<u>Concentration ($\mu\text{g/g}$)</u>	<u>Average Recovery % (STD)</u>	<u>Number of Replicates</u>
Chlordane	0.6	101 (0.82)	4
1,4-Dichlorobenzene	10.0	89.0 (12.1)	4
Toxaphene	10.0	92.5 (10.4)	4
Hexachloroethane	0.04	66.8 (6.85)	4
Nitrobenzene	0.04	86.3 (1.44)	4
Hexachlorobutadiene	0.04	82.4 (2.36)	4
2,4-Dinitrotoluene	0.04	100 (3.82)	4
Hexachlorobenzene	0.04	114 (3.12)	4
Lindane	0.04	103 (0.82)	4
Heptachlor	0.04	132 (1.91)	4
Heptachlor epoxide	0.04	120 (2.19)	4
Endrin	0.04	141 (5.36)	4
Methoxychlor	0.04	117 (3.01)	4

Table 6. Surrogate Standard Recoveries				
Number of Replicates	Average Recovery % (STD)			
	Matrix	TCMX	DCBP	
LANL Sludge	98.7	(8.9)	82.6	(19.3)
Sand	107.0	(13.1)	91.4	(26.2)
ORNL Sludge	108.7	(14.4)	89.3	(17.8)
Total	104.3	(12.6)	87.9	(22.6)
51				

Table 7. Standard Deviations (% Recovery) for Different Sources of Experimental Variation				
Source of Experimental Variation				
Compound	Matrix	Replicate	Injection	
Chlordane	3.1	2.3	0.1	
1,4-Dichlorobenzene	0.0	8.0	0.1	
Toxaphene	4.3	5.4	0.4	
Hexachlorocyclopentadiene	4.4	4.4	9.0	
Nitrobenzene	18.6	9.7	2.0	
Hexachlorobenzene	2.6	2.8	3.4	
2,4-Dinitrotoluene	2.3	3.5	1.9	
Hexachlorobenzene	6.0	4.7	2.0	
Lindane	9.7	7.9	0.3	
Heptachlor	10.7	2.5	1.8	
Heptachlor epoxide	16.2	5.4	2.8	
Endrin	12.8	4.4	3.6	
Methoxychlor	3.2	3.8	1.6	
Tetrachlorometaxylene	0.0	12.3	1.8	
Decachlorobiphenyl	0.0	22.1	3.6	

11.0 References

- Chen, P. H., W. A. VanAusdale, and D. F. Roberts. 1991. "Oxidation of Phenolic Acid Surrogates and Target Analytes during Acid Extraction of Natural Water Samples for Analysis by GC-MS Using EPA Method 625." *Environ. Sci. and Tech.* 25:540-546.
- Hubaux, A. and G. Vos. 1970. "Decision and Detection Limits for Linear Calibration Curves." *Anal. Chem.* 42:849-855.

Searle, S. R.. 1971. *Linear Models*, Wiley & Sons Inc., New York.

Stromatt, R. W., E. W. Hoppe, and M. J. Steele. 1993. *Sample Preparation for Semivolatile Organics Analysis of Hanford Single-Shell Tank Waste with High Nitrate/Nitrite and Water Content*, PNL-8927, Pacific Northwest Laboratory, Richland, Washington.

U.S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste. Volume IB, Physical/Chemical Methods*, SW-846, 3rd Edition, Final Update I, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia. Also Proposed Update II, November, 1992.

12.0 Further Reading

SAS Institute Inc. 1988. PROC VARCOMP, User's Guide, Release 6.03 Edition. Cary, North Carolina.

OP150R*(a)

Ultrasonic Extraction in a Glovebox or Hot Cell

1.0 Scope and Application

Method OP150R is a modification of U.S. Environmental Protection Agency (EPA) SW-846 Method 3550 ("Ultrasonic Extraction") (EPA 1986). It describes a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes, as well as mixed waste samples that must be extracted in a glovebox or hot cell.

The approach, using remote controls for an established apparatus, can be applied to a variety of equipment. This method is provided as an example. Similar modifications to other established methods should not influence data quality.

2.0 Summary of Method

A modified remote ultrasonic disruptor that can be used for extraction in a glove box or hot cell is described.

3.0 Interferences

When working in a glove box or hot cell, cross contamination from various sources could occur unless the work area is kept clean.

4.0 Safety

When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed. Refer to Chapter 4 in this document for general safety information.

5.0 Apparatus and Materials

5.1 Most apparatus and materials information is provided elsewhere, such as in SW-846, Method 3550.

* This method was originally issued as OP550R. It has been renumbered to OP150R.

(a) This method was supplied by John McCown (Westinghouse Hanford Company, Richland, Washington).

- 5.2 Remote Ultrasonic Disruptor:** For samples containing high α and/or β - γ emitting nuclides, the ultrasonic extractor device can be operated in a remote manner for glovebox or hot cell application. A special extra-length (approx. 3 m) cable is required for connecting the electronics to the ultrasonic generator. The extractor head is placed inside the glovebox or hot cell while the electronics are kept outside, protected from high radiation exposure. The cable is inserted through the wall plug or the box-penetrator connectors provided.

6.0 Reagents

This information is provided elsewhere, as in SW-846 Method 3550.

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

8.0 Procedure

This method uses a standard procedure, such as found in SW-846 Method 3550.

9.0 Quality Control

Modifications to this method should be supported by standard quality control (QC) procedures (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.

10.0 Method Performance

Method performance is similar to that found in SW-846 Method 3550.

11.0 Reference

U. S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste: Volume 1B, Laboratory Manual Physical/Chemical Methods*, 3rd Edition. EPA/SW-846, Office of Solid Waste and Emergency Response, Washington, DC. Available from National Technical Information Service, Springfield, Virginia.

OG015R^(a), Rev. 1

Major Nonhalogenated Volatile Organics in Radioactive Aqueous Liquids Analyzed by Direct Aqueous Injection Gas Chromatography

1.0 Scope and Application

- 1.1 This method is similar to U.S. Environmental Protection Agency (EPA) Methods 8015A and 8000 (EPA 1992). Parts that are the same as SW-846 are in italics; however, some wording may have been changed for consistent formatting and grammar. The method uses direct aqueous injection gas chromatography (DAI-GC) to determine major nonhalogenated volatile organic compounds in radioactive aqueous liquids that cannot be analyzed in a conventional laboratory. The following compounds can be determined by this method:

<u>Compound Name</u>	<u>CAS No.^(a)</u>	<u>Appropriate Technique</u>	
		<u>Purge-and-Trap</u>	<u>Direct Injection</u>
Acetone	67-64-1	pp	b
Allyl alcohol	107-18-6	pp	b
i-Butyl alcohol	78-83-1	pp	b
n-Butyl alcohol	71-36-3	pp	b
Diethyl ether	60-29-7	b	b
Ethanol	64-17-5	i	b
Methanol	67-56-1	i	b
Methyl ethyl ketone (MEK)	78-93-3	pp	b
Methyl isobutyl ketone (MIBK)	108-10-1	pp	b
i-Propyl alcohol	67-63-0	i	b
n-Propyl alcohol	71-23-8	i	b

(a) Chemical Abstract Services Registry Number

b Adequate response using this technique

i Inappropriate technique for this analyte

pp Poor purging efficiency, resulting in high quantitation limits (QLs)

2.0 Summary of Method

- 2.1 Sample aliquots (1.5 mL) are taken in a radiochemical glovebox or hot cell from larger volumes collected in the field and are transferred to small vials for analyzing major

(a) This method was supplied by R. L. Schenley, M. E. Garcia, and W. H. Griest (Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee).

volatile organic compounds. The DAI-GC method is used to supplement purge-and-trap analyses by providing data on highly polar, water-soluble organic compounds that are not determined very well by purge-and-trap methods.

- 2.2 Sample vials of 1.5-mL capacity are taken into an appropriate radioactive contamination zone laboratory and 3- μ L are injected, using the solvent flush technique, into a GC equipped as described in section 5.1.

3.0 Interferences

- 3.1 The analytical system should be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks.
- 3.2 *Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A field reagent blank prepared from reagent water and carried through sampling and subsequent storage and handling serve as a check on such contamination.*
- 3.3 *Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe should be rinsed out between samples with reagent water or solvent. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of reagent water to check for cross-contamination.*
- 3.4 Compounds that coelute, such as n-propyl alcohol and allyl alcohol, may interfere.
- 3.5 *The laboratory where volatile analysis is performed should be free of solvents that could potentially contaminate samples.*

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. As required by the U.S. Department of Energy (DOE) "as low as reasonably achievable" (ALARA) principle, to minimize radiation exposure and contamination of personnel and facilities, all radiochemical laboratory procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Materials

- 5.1 This method uses the following equipment that is located in a radioactive contamination zone laboratory.

5.1.1 **Gas Chromatograph:** Analytical system complete with GC suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

5.1.2 **Columns**

Column 1: 2.4-m (8 ft) x 2.5-mm (0.1 in.) ID stainless-steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent

Column 2: 2.4-m (8 ft) x 2.5-mm (0.1 in.) ID glass column packed with a mixture of 60/80 and 35/60 mesh Tenax. This column may be used for confirmation. Capillary columns or other packed columns that achieve comparable results can also be used.

5.1.3 **Detector:** Flame ionization

5.1.4 The glass injector liners used with flash vaporization should be cleaned periodically with concentrated nitric acid and rinsed with distilled water to remove salt deposits that degrade chromatographic performance. The used liners and cleaning solutions may be radioactive and should be handled accordingly.

5.2 The following materials should be used when using this method:

5.2.1 **Syringes:** A 5-mL Luerlok glass hypodermic and a 5-mL gas-tight with shutoff valve

5.2.2 **Volumetric Flasks:** Sizes 10, 50, 100, 500, and 1,000 mL with ground-glass stoppers

5.2.3 **Microsyringes:** Sizes 10 and 25 μL with 0.006-in ID needles (Hamilton 702N or equivalent) and a 100- μL size

6.0 Reagents

6.1 **Reagent Water:** Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the analytes of interest.

6.2 **Stock Standards:** Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Stock standards should be prepared in reagent water using assayed liquids.

6.2.1 About 9.8 mL of reagent water should be placed into a tared ground-glass-stoppered volumetric flask, in such a way as to not wet the ground glass. The flask is weighed to the nearest 0.1 mg.

- 6.2.2 *Two or more drops (approximately 100 mg) of assayed reference material are immediately added to the flask using a 100- μ L syringe; the flask is then reweighed. The liquid must fall directly into the reagent water without contacting the neck of the flask.*
- 6.2.3 *The flask should be reweighed, diluted to volume, stoppered, and then mixed by inverting the flask several times. The concentration is calculated in micrograms per microliter (μ g/ μ L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.*
- 6.2.4 *The stock solution is transferred into a Teflon-sealed screw-cap bottle. It is stored, with zero headspace, at 4°C to 5°C and protected from light.*
- 6.2.5 *Standards should be replaced after 7 months, or sooner if comparison with a reference standard indicates a problem.*
- 6.3 **Calibration Standards.** Calibration standards at a minimum of four concentration levels are prepared from the stock standards. Concentration levels should be prepared to correspond to the working range of the detector. Typical concentration levels for calibration standards might be 5 μ g/mL, 10 μ g/mL, 20 μ g/mL, and 50 μ g/mL. These working calibration solutions are prepared by taking 5, 10, 20, and 50 μ L respectively of each of the stock solutions that contain the compounds of interest and diluting to 10 mL with reagent water. All solutions and reagent water should be at room temperature before preparing calibration solutions. *Each working standard solution should contain each analyte for detection by this method (e.g., some or all of the compounds listed in section 1.1). To prepare accurate aqueous working standard solutions, the following precautions should be observed.*
- 6.3.1 *The stock standard should be rapidly injected into the filled volumetric flask. The needle should be removed as fast as possible after injection.*
- 6.3.2 *Aqueous standards are mixed by inverting the flask three times only.*
- 6.3.3 *The sample syringe is filled from the standard solution contained in the expanded area of the flask (any solution contained in the neck of the flask should not be used).*
- 6.3.4 *Pipets should never be used to dilute or transfer samples or aqueous standards. The use of open pipets may cause loss of sample components.*
- 6.3.5 *Dilute aqueous standards are not stable and should be discarded after 1 h, unless properly sealed and stored. The aqueous standards can be stored up to 24 h if held in sealed vials with zero headspace.*

6.4 External Standard Calibration Procedure

- 6.4.1 *Each calibration standard should be injected using the technique that will be used to introduce the actual samples into the GC (e.g., 2 to 5 μL injections). The solvent flush technique is recommended. Peak height or area responses are tabulated against the mass injected.*

The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the GC using a syringe, the ratio of the response to the concentration injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (% RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Response of Peak}}{\text{Concentration of Standard Injected } (\mu\text{g/mL})}$$

- 6.4.2 *The working calibration curve or calibration factor should be verified on each working day by the injection of one or more calibration standards. The frequency of verification depends on the detector. If the response for any analyte varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that analyte.*

$$\text{Percent difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where

R_1 = Calibration factor from first analysis

R_2 = Calibration factor from succeeding analyses.

7.0 Sample Collection, Preservation, and Handling

- 7.1 *Sample collection, preservation, and handling should be addressed in the planning process. Also, see SW-846 (EPA 1992).*

- 7.2 *The radioactivity of the samples to be analyzed by this method requires that all applicable radiochemical laboratory procedures and health physics monitoring practices be followed to ensure that the DOE ALARA principle is observed (see Chapter 4 and site-specific documents).*

8.0 Procedure

8.1 Chromatographic Conditions

8.1.1 **Column 1.** See section 5.1.2 (primary column).

Carrier gas (helium) flow rate:	30 mL/min
Temperature program:	
Initial temperature:	70°C, hold for 2 min
Program:	70°C to 220°C at 16°C/min
Final Temperature:	220°C, hold for 16 min
Inlet Temperature:	150°C
Detector Temperature:	250°C

8.1.2 **Column 2.** See section 5.1.2 (confirmation column). All chromatographic conditions are the same for the confirmation column as for column 1. Other confirmatory columns may require different conditions for optimum resolution.

8.2 Calibration

The instrument is fully calibrated each day of use with four concentration levels of standards, instead of a once weekly, five-level calibration and daily single-level calibration checks. The sample is analyzed using the method of external standards with peak areas and concentrations of standards ranging from about 5 to 50 µg/mL.

8.3 Blanks and matrix spikes should be analyzed with each group of samples. The latter are prepared as in section 6.2. Blanks consist either of laboratory-distilled water taken from the tap in the contamination-zone laboratory or distilled-in-glass grade water taken into the glovebox or hot cell (see section 2.1) and removed in the same type of vial as the field samples.

8.4 Retention Time Windows

8.4.1 *Before establishing windows, the GC system should be within optimum operation conditions. Three injections of all standard mixtures should be made throughout the course of a 72-h period. Serial injections over less than a 72-h period may result in retention-time windows that are too tight.*

8.4.2 *The standard deviation of the three absolute retention times for each standard should be calculated.*

- 8.4.2.1 *Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention-time window, but the experience of the analyst should weigh heavily in the interpretation of chromatograms.*
- 8.4.2.2 *In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close-eluting, similar compound to develop a valid retention-time window.*
- 8.4.3 *The laboratory should calculate retention-time windows for each standard on each GC column and whenever a new GC column is installed. All data should be retained by the laboratory.*

8.5 Gas Chromatographic Analysis

- 8.5.1 *Direct Injection.* Two to five microliters of the sample should be injected using the solvent flush technique. Smaller (1.0- μ L) volumes can be injected if automatic devices are employed. The volume injected should be recorded to the nearest 0.1 μ L and the resulting peak size in area units or peak height.
- 8.5.2 *If the responses exceed the linear range of the system, the extract should be diluted and reanalyzed. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure that all peaks are on scale over a 100-fold range, is acceptable if linearity is demonstrated. Peak-height measurements are recommended over peak-area integration when overlapping peaks cause errors in area integration.*
- 8.5.3 *If peak detection is prevented by the presence of interferences, a sample detection limit should be evaluated based on dilution of the sample and/or spike recovery.*
- 8.5.4 *The system should be calibrated immediately before conducting any analyses (see section 8.2). A midlevel standard should also be injected periodically, including at the end of the analysis sequence. The calibration factor for each analyte to be quantitated should not exceed a 15% difference when compared to the initial standard of the analysis sequence. When this criterion is exceeded, the GC system should be inspected to determine the causes, and whatever maintenance is necessary should be performed (see section 8.6) before recalibrating and proceeding with sample analysis. All samples injected after the last successful calibration check should be reinjected.*

8.5.5 *Daily retention-time windows should be established for each analyte. The absolute retention time for each analyte from section 8.4 is used as the midpoint of the window for that day. The daily retention-time window equals the midpoint $\pm$ three times the standard deviation determined in section 8.4.*

8.5.5.1 *Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention-time window. Normally, confirmation is recommended on a second GC column, by GC-MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.*

8.5.5.2 *Validation of GC system qualitative performance: The midlevel standards interspersed throughout the analysis sequence (section 8.5.4) are used to evaluate this criterion. If any of the standards fall outside their daily retention-time window, the system is out of control. The cause of the problem should be determined and corrected.*

8.6 ***Suggested Chromatography System Maintenance.*** *Degraded chromatograms may require any one or more of the following remedial actions.*

8.6.1 ***Packed Columns.*** *For instruments with injection-port traps, the demister trap should be replaced. The glass injector-port insert should be cleaned and deactivated or replaced with a cleaned and deactivated insert. The injection end of the column should be inspected and any foreign material (broken glass from the rim of the column or pieces of septa) removed. The glass wool is replaced with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of the packing material if any discoloration is noted; also, the inside walls of the column should be swabbed out if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described in section 8.6.3) and/or repack/replace the column.*

8.6.2 ***Capillary Columns.*** *The glass injection-port insert is cleaned and deactivated or replaced with a cleaned and deactivated insert. The first few inches, up to one foot, of the injection-port side of the column may be broken off. The column is removed, and the solvent is backflushed according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.*

8.6.3 ***Metal Injector Body.*** *The oven is turned off and the analytical column is removed when the oven has cooled. The glass injection-port insert is removed.*

The injection-port temperature is lowered to room temperature. The injection port is inspected, and any noticeable foreign material is removed.

- 8.6.3.1 *A beaker is placed beneath the injector port inside the GC oven. Using a wash bottle, the entire inside of the injector port is serially rinsed with acetone and then toluene, catching the rinsate in the beaker.*
- 8.6.3.2 *A solution of deactivating agent (Sylon-CT[®] or equivalent) is prepared following the manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, the injector body is serially rinsed with toluene, methanol, acetone, and hexane. The injector is reassembled, and the GC column is replaced.*

9.0 Calculations

- 9.1 **External Standard Calibration.** *The concentration of each analyte in the sample may be determined by calculating the amount of standard injected, from the peak response, using the calibration curve or the calibration factor determined in section 6.4. The concentration of a specific analyte is calculated as follows:*

Aqueous Samples:

$$\text{Concentration } (\mu\text{g/mL}) = [(A_X)(D)]/[CF_X]$$

where

- A_X = response for the analyte in the sample; units may be in area counts or peak height
- D = dilution factor, if dilution was made on the sample before analysis. If no dilution was made, $D = 1$, dimensionless
- CF_X = calibration factor for analyte in standard or average calibration factor from calibration curve, units same as A_X .

10.0 Quality Control

- 10.1 Modifications to this method should be supported by standard quality control (QC) procedures (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.

10.2 Instrument QC

- 10.2.1 *The % RSD should be <20% when comparing calibration factors to determine if a five-point calibration curve is linear.*
- 10.2.2 *Typically, less than a $\pm 15\%$ difference should be found when comparing the daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve should be prepared.*
- 10.2.3 *Retention-time windows should be established (see section 8.4).*
- 10.2.4 *Typically less than a $\pm 15\%$ difference should be found when comparing the initial response of a given analyte to any succeeding standards analyzed during an analysis sequence.*
- 10.2.5 *All succeeding standards in an analysis sequence should fall within the daily retention-time window established by the first standard of the sequence.*

10.3 *To establish the ability to generate acceptable accuracy and precision, the analyst should perform the following operations.*

- 10.3.1 *A QC check-sample concentrate is recommended containing each analyte of interest. The QC check sample may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate should be made using stock standards prepared independently from those used for calibration.*
- 10.3.2 *Four aliquots of a well-mixed QC check sample are analyzed by the same procedures used to analyze actual samples (see section 8.5).*
- 10.3.3 *The average recovery $\bar{X}$ in $\mu\text{g/mL}$, and the standard deviation of the recovery(s), in $\mu\text{g/mL}$, are calculated for each analyte of interest using the four results.*
- 10.3.4 *For each analyte, s and $\bar{X}$ are compared with the corresponding acceptance criteria for precision and accuracy, respectively, given the QC acceptance criteria table at the end of each of the determinative methods. If s and $\bar{X}$ for all analytes of interest meet the acceptance criteria, the system performance is acceptable, and the analysis of actual samples can begin. If any individual(s) exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that analyte.*

10.3.5 *When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst should proceed according to section 10.3.5.1 or 10.3.5.2.*

10.3.5.1 *The source of the problem should be located and corrected and the test repeated for all analytes of interest beginning with section 10.3.2.*

10.3.5.2 *Beginning with section 10.3.2, the test should be repeated only for those analytes that failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, the source of the problem should be located and corrected, and the test should be repeated for all compounds of interest beginning with section 10.3.2.*

10.4 *The laboratory should, on an ongoing basis, spike at least one sample per analytical batch (maximum of 20 samples per batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is recommended.*

10.4.1 *The concentration of the spike in the sample should be determined as follows:*

10.4.1.1 *If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in section 10.4.2, whichever concentration would be larger.*

10.4.1.2 *If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC checksample (section 10.3.2) or 1 to 5 times higher than the background concentration determined in section 10.4.2, whichever concentration would be larger.*

10.4.2 *One unspiked and one spiked sample aliquot should be analyzed to determine percent recovery of each of the spiked compounds.*

10.4.3 *The percent recovery (p) for each analyte is compared with the corresponding data presented in Table 1. These data were calculated by one analyst. Additional data should include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error should account for the analyst's spike to background ratio, which should approach 5:1. If spiking is performed at a concentration lower than the QC check-sample concentration (section 10.3.2), the analyst must use either the QC data presented in Table 1, or optional QC acceptance criteria calculated for the specific spike concentration and specific waste.*

10.4.4 *If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria should be analyzed as described in section 10.5.*

10.5 *If any analyte fails the acceptance criteria for recovery in section 10.4, a QC check standard containing each analyte that failed should be prepared and analyzed.*

Note: *The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method must be measured in the sample in section 10.4, the probability that the analysis of a QC check standard will be required is high. In this case, the QC check standard should be routinely analyzed with the spiked sample.*

10.5.1 *The QC check standard should be analyzed to determine the concentration measured (A) of each analyte. Each percent recovery (p_s) should be calculated as $100 (A/T)\%$, where T is the true value of the standard concentration.*

10.5.2 *The percent recovery (p_s) for each analyte should be compared with the corresponding QC acceptance criteria. Only analytes that failed the test in section 10.4 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem should be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and should not be reported.*

10.6 *As part of the QC program for the laboratory, method accuracy for each matrix studied should be assessed, and records should be maintained. After the analysis of five spike samples (of the same matrix type) as in section 10.5, the average percent recovery ($\bar{p}$) and the standard deviation of the percent recovery (s_p) are calculated. The accuracy assessment is expressed as a percent-recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70 to 110%. The accuracy assessment for each analyte should be updated on a regular basis (e.g., after each five to ten new accuracy measurements).*

10.7 *To determine acceptable accuracy and precision limits for surrogate standards (when suitable compounds have been identified and used as surrogate standards), the following procedure should be performed.*

10.7.1 *For each sample analyzed, the percent recovery of each surrogate in the sample is calculated.*

10.7.2 *Once a minimum of thirty samples of the same matrix has been analyzed, the average percent recovery (p) and the standard deviation of the percent recovery (s) are calculated for each of the surrogates.*

10.7.3 *For a given matrix, the upper and lower control limits for method performance are calculated for each surrogate standard. This should be done as follows:*

$$\text{Upper Control Limit (UCL)} = p + 3s$$

$$\text{Lower Control Limit (LCL)} = p - 3s$$

10.7.4 *If recovery is not within limits, the following is recommended.*

- *Checks should be done to be sure that calculations, surrogate solutions, and internal standards have no errors. Also, instrument performance should be checked.*
- *The data should be recalculated and/or the sample reanalyzed if any of the above checks reveal a problem.*
- *The sample should be reanalyzed if none of the above are a problem, or the data should be flagged as "estimated concentrations."*

10.7.5 *At a minimum, each laboratory should update surrogate recovery limits annually.*

10.8 *It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as GC with a dissimilar column, specific element detector, or mass spectrometer should be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.*

11.0 Method Performance

The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in an analysis will vary depending on instrument sensitivity or matrix effects.

11.1 *Although the MDL has not been rigorously evaluated, experience shows linear calibration down to at least 3-µg/mL concentrations for water samples. The results will depend upon the sample matrix.*

11.2 Results from the analysis of radioactive aqueous-liquid waste samples spiked with nonhalogenated, volatile organic compounds are shown in Table 1. The concentration of each spiked compound was ~20 µg/mL. Matrix spike recoveries are typically better than 90% for the sample analyzed, except for isopropyl and allyl alcohols. The latter produces a tailing peak that is difficult to integrate. Table 2 lists the method accuracy interval calculated from the matrix spike data in Table 1, and also the retention time windows for the packed-column primary and secondary columns.

12.0 Reference

U. S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Methods, 3rd Edition*. Final Update I. SW-846, Office of Solid Waste and Emergency Response. Washington, DC. Available from National Technical Information Service, Springfield, Virginia.

13.0 Further Reading

Autrey, J. W., D. A. Costanzo, W. H. Griest, L. L. Kaiser, J. M. Keller, C. E. Nix, and B. A. Tomkins. 1989. *Sampling and Analysis of the Inactive Waste Storage Tank Contents at ORNL*. ORNL/RAP-53, Oak Ridge National Laboratory, Oak Ridge, Tennessee pp 2-8, 2-9, 3-38. Also published as ORNL/ER-13 (September 1990).

Table 1. Summary of Matrix-Spike Recoveries for Direct Aqueous Injection Gas Chromatography (DAI-GC) of Radioactive Aqueous Liquids

<u>Compound</u>	<u>CAS#^(a)</u>	<u>Percent Recoveries</u>		<u>No. of Samples</u>
		<u>Mean</u>	<u>Standard Deviation</u>	
Methyl alcohol	67-56-1	97.8	16.6	15
Ethyl alcohol	64-17-5	94.1	10.7	16
Acetone	67-64-1	94.8	10.6	16
i-Propyl alcohol	67-63-0	89.9	11.4	16
Allyl alcohol/n-Propyl alcohol ^(b)	107-18-6 71-23-8	85.5	8.3	16
2-Butanone (methyl ethyl ketone)	78-93-3	93.6	9.1	16
i-Butyl alcohol	78-83-1	97.3	10.6	16
n-Butyl alcohol	71-36-3	102.4	13.3	16
4-Methyl-2-pentanone (Methyl isobutyl ketone)	108-10-1	94.2	20.4	16

(a) Chemical Abstract Services Registry Number.

(b) Allyl alcohol was used for the analysis. n-Propyl alcohol coelutes with allyl alcohol in this chromatographic system.

Table 2. Matrix Spike Recovery Limits and Retention Time Windows for Packed-Column GC of Nuclear Waste Tank Aqueous Liquid

Compound	Recovery Range ^(a) (%)	Retention Time Window Range ^(b) (min.)	Retention Time Window Range ^(c) (min.)
Methyl alcohol	64.6 to 131	2.02 to 0.88	5.14 to 2.90
Ethyl alcohol	72.7 to 115.5	4.46 to 2.00	8.26 to 6.90
Acetone	73.6 to 116	5.82 to 3.72	10.69 to 9.88
i-Propyl alcohol	67.1 to 112.7	6.69 to 4.72	10.69 to 9.88
Allyl alcohol/n-Propyl alcohol	48.9 to 122.1	7.87 to 6.25	11.98 to 11.38
2-Butanone (methyl ethyl ketone)	75.4 to 111.8	9.79 to 8.82	14.01 to 13.73
i-Butyl alcohol	76.1 to 118.5	10.94 to 10.24	14.31 to 14.04
n-Butyl alcohol	75.8 to 129	12.18 to 11.64	15.28 to 15.08
4-Methyl-2-pentanone (Methyl isobutyl ketone)	53.4 to 135	17.51 to 17.33	17.89 to 17.81

(a) The range was calculated as follows $[P - 2(s_p) \text{ to } P + 2(s_p)]$ where P is the mean of the % Recovery from Table 1 and (s_p) is the standard deviation of the % Recovery from Table 1.

(b) Retention-time window range for the primary column was determined by the injection of a 3-ppm and 20-ppm standard within a 3-day period, and was calculated as the average retention time plus and minus three standard deviations.

(c) Retention-time window range for the confirmation column was determined by the injection of a 3-ppm and 20-ppm standard within a 3-day period, and was calculated as the average retention time plus three standard deviations.

OG100R^{*(a)}, Rev 1

Analysis of Polychlorinated Biphenyls as Aroclors in Solid Radioactive Mixed Wastes

1.0 Scope and Application

- 1.1 This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in extracts from radioactive solid matrices and is suitable for extraction and cleanup in a glovebox or hot cell. Sample radioactivity has not been found to be carried over into the purified extracts, which can be analyzed in non-zoned laboratories.
- 1.2 This method is based upon adaptation of U. S. Environmental Protection Agency (EPA) (1992) SW-846 method 3550 (using water bath sonication), 3665 (cleanup), and 8081 (gas chromatography).

2.0 Summary of Method

- 2.1 Waste samples (0.5 g) are weighed out in a radiochemical glovebox or hot cell from larger samples collected in the field and transferred to small vials for analysis of PCBs. Samples are spiked with Aroclor standards (matrix-spiked samples only); surrogate standards, tetrachlorometaxylene (TCMX) and decachlorobiphenyl (DCBP), are added to all samples and blanks.
- 2.2 After evaporation of spike solvents, 5 mL of hexane are added to the sample, and extraction is carried out using an ultrasonic water bath.
- 2.3 Extracts undergo a cleanup step with concentrated H₂SO₄ (SW-846, Method 3665).
- 2.4 The Aroclor content is measured using capillary column gas chromatography (GC) with electron capture detection (ECD) (SW-846, Method 8081). The packed column GC method (SW-846, Method 8080) is also acceptable.

Caution: As required by the U.S. Department of Energy (DOE) "as low as reasonably achievable" (ALARA) principle to minimize radiation exposure and contamination of personnel and facilities, it is imperative to follow all radiochemical laboratory procedures for handling radioactive samples and for health physics monitoring. It is important that the purified extracts be analyzed for radioactivity before GC analysis.

* This method was originally issued as OG081R. It has been renumbered to OG100R.

(a) This method was supplied by G. A. Segal and W. H. Griest (Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee).

3.0 Interferences

- 3.1 The most common sources of interferences are co-extracted phthalate esters, organosulfur compounds, lipids, and waxes. The presence of high concentrations of co-eluting hydrocarbons will diminish detector response, while the high sensitivity of the electron capture detector often results in significant masking of analytes of interest by co-eluting phthalate esters, organosulfur, organophosphorus, or chlorinated hydrocarbon pesticides.
- 3.2 The sulfuric acid cleanup step included as an integral part of this procedure is effective in removing organophosphorus pesticides and significant amounts of unsaturated hydrocarbons.
- 3.3 Interferences by phthalate esters are often introduced during sample preparation due to the contact of reagents or samples with flexible plastics. Interferences from phthalate esters can best be minimized by avoiding contact with any plastic materials and checking all solvents and reagents for contamination. Reagents and glassware may be purified by solvent extraction or heating to 400°C for 1 h and storing in covered containers until use.
- 3.4 The presence of elemental sulfur will result in large peaks that obscure a significant portion of the chromatogram. It is recommended that SW-846 Method 3660 be used for removing sulfur.
- 3.5 Interferences will vary significantly from waste to waste. See SW-846 Method 8081 for additional guidance on interferences and cleanup procedures.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to organic solvents and contaminants. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Materials

- 5.1 Small glass vials (20 to 40 mL), with Teflon-lined caps, in which the extraction is carried out.
- 5.2 N-Evap Concentrator apparatus (Organomation Associates Inc., or equivalent).
 - 5.2.1 Concentrator tube - 10 mL graduated (Organomation Associates Inc., or equivalent).
- 5.3 Ultrasonic bath, Branson 5200 or equivalent.

- 5.4 Gas Chromatograph:** Analytical system complete with GC suitable for split-splitless injection and all required accessories including syringes, analytical columns, gases, ECD, and recorder/integrator or data system.

5.4.1 Narrow-Bore Capillary Columns

- DB-5 capillary column 30 m x 0.32 mm ID with a 0.25- μ m-thick film of 5%-phenyl-methylpolysiloxane (or equivalent).
- DB-1701 capillary column, 30 m x 0.32 mm ID with a 0.25- μ m-thick film of 14%-cyanopropylphenyl-methylpolysiloxane (or equivalent) may be used for confirmation.

6.0 Reagents

- 6.1** Solvents and reagents should all be of pesticide quality or equivalent. Each solvent/reagent lot should be checked for possible interferences.

- Hexane
- Methanol
- Sulfuric acid

7.0 Sample Collection, Preservation, and Handling

- 7.1** The radioactivity of the samples to be analyzed by this method requires that all applicable radiochemical laboratory procedures and health physics monitoring practices be followed to ensure that the DOE ALARA principle is observed.

- 7.2** Sample collection, preservation, and handling should be addressed in the planning process.

8.0 Procedure

- 8.1** Mixed waste samples (0.5 g) are weighed out in a radiochemical glovebox or hot cell from larger samples collected in the field and transferred to small vials for analysis of PCBs. Wet samples (>~50% water content) are first mixed with an equal weight of sodium sulfate to remove free water. Matrix-spiked samples are spiked with 0.2 mL of Aroclor standards (in hexane or methanol) to give a concentration of 5 μ g/g for each Aroclor analyzed. Surrogates of TCMX and DCBP (in 0.2 mL of hexane or methanol) are added to all samples and blanks to achieve concentrations of 300 ng/g and 1000 ng/g, respectively. These particular surrogates are used because they bracket the retention times of all PCBs.

- 8.2 After spike solvents are evaporated in a hood at room temperature for 1 to 2 h, the samples are transferred to a radioactive contamination zone laboratory and extracted with 5 mL of hexane in an ultrasonic water bath for 30 min. The extractions can be performed in a glovebox or hot cell if required by sample radioactivity.
- 8.3 **Cleanup/Fractionation:** Four milliliters of hexane extract are vortexed with 2 mL of concentrated H₂SO₄ (EPA SW-846, Method 3665). The hexane is removed, and 2 mL of fresh hexane are added to the H₂SO₄ for reverse extraction. The sulfuric acid extraction should be repeated if significant visible color or material is extracted into the acid until the acid extractions remove no additional color or material. The hexane solutions are combined and concentrated under a stream of nitrogen to the original 4-mL volume before analysis.
- 8.4 The purified extract is screened for radioactivity before GC analysis, using site-specific methods. This screen may include gross alpha activity, gross beta activity, or gamma spectroscopy.

8.5 Gas Chromatographic Analysis

8.5.1 GC Conditions

- DB-5 column, 30 m x 0.32 mm ID with a 0.25- μ m film thickness in a GC with ECD, automatic sample injection system, and chromatography data system.

Carrier gas:	He (~1 mL/min); N ₂ make up gas (~30 mL/min)
Injector temperature:	250°C
Detector temperature:	330°C
Temperature program:	
Initial temperature:	80°C
Program 1:	80°C to 180°C at 30°C/min
Program 2:	180°C to 280°C at 5°C/min
Final temperature:	280°C, hold for 10 min
Total time:	33.3 min.
Injection volume:	1 μ L

8.5.2 GC Analysis

- At least three concentrations of Aroclor standards spanning the expected range of sample concentrations are injected.
- The purified sample extracts, matrix-spiked samples, and blanks are injected.
- Aroclors are identified and quantitated. The PCB residues are quantitated by comparing the responses of three to five major peaks in each

appropriate Aroclor standard with the peaks obtained from the chlorinated biphenyls in the sample extract. The amount of Aroclor is calculated using each of the major peaks, and the results of the three to five determinations are averaged.

- If the identification of the sample chromatographic pattern with an Aroclor mixture on the primary column is suspect, the secondary column is used to aid in pattern recognition, or GC-mass spectrometry (GC-MS) is employed if concentrations are sufficiently high.

9.0 Quality Control

- 9.1 Modifications to this method should be supported by appropriate quality control (QC) methods (for example, as outlined in Chapter 3 of this document) and should meet the objectives of the project.
- 9.2 Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. If the daily check standard indicates greater than $\pm 15\%$ drift, then a new standard curve should be prepared. This should be conducted as in EPA SW-846, Method 8081.
- 9.3 The surrogate standard recovery is calculated on all samples, blanks, and spikes. It should be determined if the recovery is within established limits. If the recovery is not within limits, measurements and instrument performance should be verified. Re-extraction and analysis may be required.
- 9.4 A mid-concentration reference should be included after each group of 20 samples in the analytical sequence as a calibration check. If the results are greater than $\pm 30\%$ of the expected value, the analysis should be halted, the injector cleaned, the septum replaced, and the system re-calibrated before resuming the analysis.
- 9.5 A regular preventive maintenance program is needed to maintain instrument performance.
- 9.6 For each batch of samples processed, a laboratory reagent blank should be analyzed. The presence of PCBs or interferences should be evaluated for data impact before analyzing the samples.
- 9.7 The laboratory should document the effect of the sample matrix on method performance by analyzing at least one matrix spike and either one matrix duplicate or matrix-spike duplicate per analytical batch.

10.0 Method Performance

- 10.1** The extraction technique was applied to two surrogate radioactive mixed waste sludges, one characteristic of Oak Ridge National Laboratory (ORNL) nuclear waste-tank sludge and the other characteristic of Los Alamos National Laboratory (LANL) process water-treatment sludge. Figure 1 shows a typical GC chromatogram of PCBs recovered from a 0.5-g sample of the ORNL surrogate sludge spiked with 5 µg/g each of Aroclor 1221 and Aroclor 1260.

Tables 1 and 2 and Figure 2 show the recoveries of Aroclor 1221 and Aroclor 1260 recovered from the two surrogate sludges. Each Aroclor was spiked at a concentration of 5 µg/g. Recoveries were comparable with both sludges and ranged from 80 to 110%. Precision was 7 to 17% {relative standard deviation (RSD)}.

A variance component analysis estimated the variation among samples and among replicates within a sample. Estimated standard deviations for method duplicates by the maximum likelihood method showed that all estimates were zero for the four surrogate sludge/Aroclor combinations {i.e., (ORNL/Ar1221), (ORNL/Ar1260), (LANL/Ar1221), (LANL/Ar1260)}. These results indicate that variation due to measurement replication is the predominant source of variation. Estimated standard deviations for measured replicates for the four surrogate sludge/Aroclor combinations are given in Tables 1 and 2 under the "Reps within Aroclor" columns.

- 10.2** Tables 3 and 4 show the recoveries of the surrogate standards TCMX and DCBP from the surrogate sludges and sand blanks. Recoveries of TCMX ranged from 61 to 80% with a precision of 5 to 10% (RSD); DCBP recoveries ranged from 84 to 90% with a precision of 4 to 10% (RSD).

A variance component analysis for the TCMX and DCBP surrogate standards in the ORNL and LANL surrogate sludges estimated the variation due to method duplicates (i.e., sample to sample variation) and due to measured replicates. Estimated standard deviations for method duplicates and measured replicates by the maximum likelihood method are given in Table 5.

- 10.3** Table 6 shows the recoveries of Aroclor 1254 and the surrogate standards from actual radioactive mixed-waste samples that required extraction in a glovebox. Surrogate standard and matrix-spike recoveries were generally consistent with that of the surrogate radioactive mixed-waste sludges, in spite of the multiple sulfuric acid extractions that were required. The original samples were contaminated with plutonium (Pu) at levels up to 282 µCi (1.0×10^7 Bq)/g of sample. After hexane extraction and sulfuric acid cleanup, the gross α/β activities measured in the extracts were all at background levels, a reduction in activity levels of more than 10^6 .

- 10.4 Method Detection Limits.** The GC was calibrated with standards of Aroclor 1221 and Aroclor 1260 mixed together in hexane and each at 200-, 500- and 800-ng/mL

concentrations. This range of concentrations was used to bracket the expected concentration of the Aroclors in the hexane extracts for 100% recovery (500 ng/mL). Applying the method of Hubaux and Vos (1970) to the calibration curves, the method detection limits (MDLs) for Aroclor 1221 and Aroclor 1260 were 62 ng/mL and 48 ng/mL, respectively. Lower MDLs were obtained when a lower range of concentration standards were used. Thus, with Aroclor 1221 and Aroclor 1260 concentration standards at 50, 100, and 200 ng/mL, the MDLs were lowered to 28 ng/mL and 22 ng/mL, respectively.

11.0 References

U.S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Methods*, SW-846, 3rd Edition, Final Update I, SW-846. Office of Solid Waste and Emergency Response. Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Hubaux, A., and G. Vos. 1970. "Decision and Detection Limits for Linear Calibration Curves." *Anal. Chem.* 42: 849-855.

Figure 1. Recovery of PCBs from ORNL Surrogate Sludge Matrix. ORNL surrogate sludge spiked with Aroclor 1221 and Aroclor 1260 (each at 5 $\mu\text{g/g}$ in 0.5 g of matrix). The surrogate standard TCMX was spiked at 0.3 $\mu\text{g/g}$, and the DCBP was spiked at 1 $\mu\text{g/g}$. Extracted PCBs were in a total volume of 5 mL of hexane. Expanded regions of the chromatograph show peaks used for quantitation. {See text (8.5.1) for conditions.}

Table 1. Recovery of PCBs from ORNL Surrogate Sludge

Observation	Aroclor	Sample	Rep.	% Recovery	Reps within Sample		Reps within Aroclor		% Rel SD			
					Average	STD	Average	STD				
					% Recovery ^(a)		% Recovery					
1	Ar 1221	1	1.	90	84	6	79	6	8			
2	Ar 1221	1	2	78								
3	Ar 1221	1	3	83								
4	Ar 1221	2	1	75	79	5						
5	Ar 1221	2	2	84								
6	Ar 1221	2	3	77								
7	Ar 1221	3	1	78	76	6						
8	Ar 1221	3	2	69								
9	Ar 1221	3	3	81								
10	Ar 1260	1	1	137	117	18						
11	Ar 1260	1	2	114								
12	Ar 1260	1	3	101								
13	Ar 1260	2	1	111	112	8	110	13	12			
14	Ar 1260	2	2	120								
15	Ar 1260	2	3	104								
16	Ar 1260	3	1	107	101	9						
17	Ar 1260	3	2	91								
18	Ar 1260	3	3	106								

(a) Based on a true value of 500 ng/mL of each Aroclor.

Table 2. Recovery of PCBs from LANL Surrogate Sludge

Observation	Aroclor	Sample	Rep.	% Recovery	Reps within Sample		Reps within Aroclor		
					Average	STD	Average	STD	% Rel SD
					% Recovery ^(a)		% Recovery		
1	Ar 1221	1	1	55	80	22	87	16	18
2	Ar 1221	1	2	94					
3	Ar 1221	1	3	91					
4	Ar 1221	2	1	87	91	5			
5	Ar 1221	2	2	96					
6	Ar 1221	2	3	90					
7	Ar 1221	3	1	98	90	20			
8	Ar 1221	3	2	68					
9	Ar 1221	3	3	105					
10	Ar 1260	1	1	68	84	14			
11	Ar 1260	1	2	94					
12	Ar 1260	1	3	89					
13	Ar 1260	2	1	91	89	3	90	13	14
14	Ar 1260	2	2	89					
15	Ar 1260	2	3	86					
16	Ar 1260	3	1	101	99	17			
17	Ar 1260	3	2	81					
18	Ar 1260	3	3	114					

(a) Based on a true value of 500 ng/mL of each Aroclor.

Figure 2. Aroclor Recovery, 95% Confidence Intervals

Table 3. Recovery of Surrogate Standards from ORNL Surrogate Sludge

TCMX						
Observation	Sample	Rep	% Recovery TCMX	Average % Recovery TCMX	STD TCMX	Grand Average % Recovery TCMX
1	Sand blank	1	54	53	2	
2	Sand blank	2	52			
3	Sand blank	3	51			
4	1	1	72	67	4	
5	1	2	65			
6	1	3	65			
7	2	1	60	62	3	64
8	2	2	66			
9	2	3	61			
10	3	1	63	61	3	4 ^(a)
11	3	2	57			6 ^(b)
12	3	3	63			

DCBP						
Observation	Sample	Rep	% Recovery DCBP	Average % Recovery DCBP	STD DCBP	Grand Average % Recovery DCBP
1	Sand blank	1	101	100	2	
2	Sand blank	2	99			
3	Sand blank	3	99			
4	1	1	104	99	11	
5	1	2	86			
6	1	3	108			
7	2	1	87	87	7	86
8	2	2	94			
9	2	3	79			
10	3	1	77	73	7	14 ^(a)
11	3	2	66			16 ^(b)
12	3	3	78			

(a) Standard deviation of three samples, each with three replicates

(b) Relative standard deviation

Table 4. Recovery of Surrogate Standards from LANL Surrogate Sludge

<u>TCMX</u>									
<u>Observation</u>	<u>Sample</u>	<u>Rep</u>	<u>% Recovery</u> <u>TCMX</u>	<u>Average %</u> <u>Recovery</u> <u>TCMX</u>	<u>STD</u> <u>TCMX</u>	<u>Grand Average %</u> <u>Recovery</u> <u>TCMX</u>			
1	Sand blank	1	67	84	15	79			
2	Sand blank	2	87						
3	Sand blank	3	97						
4	1	1	55	74	16		11 (a) 14 (b)		
5	1	2	84						
6	1	3	82						
7	2	1	80	82	3			11 (a) 14 (b)	
8	2	2	85						
9	2	3	81						
10	3	1	87	81	14				11 (a) 14 (b)
11	3	2	64						
12	3	3	91						

<u>DCBP</u>									
<u>Observation</u>	<u>Sample</u>	<u>Rep</u>	<u>% Recovery</u> <u>DCBP</u>	<u>Average %</u> <u>Recovery</u> <u>DCBP</u>	<u>STD</u> <u>DCBP</u>	<u>Grand Average</u> <u>Recovery</u> <u>DCBP</u>			
1	Sand blank	1	79	88	10	83			
2	Sand blank	2	86						
3	Sand blank	3	99						
4	1	1	69	79	9		11 (a) 13 (b)		
5	1	2	86						
6	1	3	84						
7	2	1	79	76	3			11 (a) 13 (b)	
8	2	2	76						
9	2	3	74						
10	3	1	93	94	12				11 (a) 13 (b)
11	3	2	83						
12	3	3	106						

(a) Standard deviation of three samples, each with three replicates

(b) Relative standard deviation.

Table 5. Estimated Standard Deviations for the TCMX and DCBP Surrogate Standards

<u>Source of Variation</u>	<u>Surrogate Matrix/Surrogate Standard (%)</u>			
	<u>ORNL/DCBP</u>	<u>ORNL/TCMX</u>	<u>LANL/DCBP</u>	<u>LANL/TCMX</u>
Among Samples	9	2	6	0
Among Replicates	9	4	9	11

Table 6. Method Performance with Transuranic Mixed Waste Samples

<u>Sample</u>	<u>Number of Acid Washes</u>	<u>N^(a)</u>	<u>Average Recoveries $\pm$ STD (%)</u>		<u>Matrix Spike Recovery</u>	
			<u>TCMX</u>	<u>DCBP</u>	<u>Aroclor 1254</u>	<u>RPD (%)^(b)</u>
J2	1	3	90 $\pm$ 2.1	82 $\pm$ 3.2	76	34
Gasket 1	5	1	58	56	-	-
Gasket 2	16	4	102 $\pm$ 11	62 $\pm$ 6.9	68	16
Filter	11	3	61 $\pm$ 12	66 $\pm$ 12	-	-
Sand Blank	1	3	83 $\pm$ 5.3	90 $\pm$ 3.6	105	13

(a) Number of samples

(b) Relative percent difference of matrix spike and matrix spike duplicate

OH100R^(a)

Direct Analysis of TCLP Acidic Semivolatile Compounds in Radioactive Liquid Wastes or Leachates using HPLC with Ultraviolet Absorbance Detection

1.0 Scope and Application

- 1.1** This method describes the direct determination by high performance liquid chromatography (HPLC) of the toxicity characteristic leaching procedure (TCLP) acidic semivolatile compounds in leachates and aqueous liquid-waste samples. It is based upon U.S. Environmental Protection Agency (EPA) SW-846 method 8321 (EPA 1992), but incorporates different reverse-phase conditions and reagents for use in the analysis of TCLP acidic semivolatiles. No sample preparation is required beyond filtration (or pH adjustment, as needed); thus operator exposure to sample radioactivity and laboratory waste generation are minimized compared to methods based upon solvent extraction and gas chromatography. Compounds that can be determined using this method are found in Table 1.
- 1.2** This method may be applicable to the determination of other semivolatile or nonvolatile organic compounds that are present in aqueous samples or aqueous extracts of solid samples and that possess a chromophore sufficient for absorbance detection.

Table 1. Compounds Determined by HPLC

<u>Compound Name</u>	<u>Cas No.*</u>
o-Cresol	95-48-7
m-Cresol	108-39-4
p-Cresol	106-44-5
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7
Pentachlorophenol (PCP)	87-86-5
2,4,5-Trichlorophenol (2,4,5-TCP)	95-95-4
2,4,6-Trichlorophenol (2,4,6-TCP)	88-06-2
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	93-76-5
2-(2,4,5-Trichlorophenoxy)propionic acid (Silvex or 2,4,5-TP)	93-72-1

* Chemical Abstracts Service registry number.

(a) This method was supplied by R. L. Schenley, J. E. Caton, W. H. Griest, and C-h. Ho (Oak Ridge National Laboratory, Analytical Chemistry Division, Oak Ridge, Tennessee).

- 1.3 This method is restricted to use by or under the supervision of analysts experienced in HPLC.

2.0 Summary of Method

This method provides conditions for the determination of TCLP acidic semivolatile compounds using a mobile-phase composition gradient, and an isocratic mobile-phase version for the determination of only the herbicides. Aqueous liquid wastes and TCLP leachates are directly injected into a reverse-phase HPLC column and are eluted and detected using ultraviolet absorbance. Sample filtration and/or pH adjustment may be required before injection. Components are identified by their retention time on the primary column and are confirmed by either their ultraviolet (UV)-visible spectrum or their retention time on the secondary column. The herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), which is not a TCLP toxicity characteristic compound, may be used as a surrogate standard.

3.0 Interferences

- 3.1 Interferences may be encountered from other UV-absorbing compounds that co-elute with the target analytes from the reverse-phase column.
- 3.2 Highly alkaline samples may degrade some of the target analytes, or may interfere with their chromatographic separation.
- 3.3 Mass spectroscopy may be used as an option for more selective detection or structural confirmation.
- 3.4 Organic sample matrices are not appropriate for this procedure and may require other HPLC conditions.

4.0 Safety

When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Methods

5.1 High Performance Liquid Chromatography System

- 5.1.1 **HPLC:** Binary or ternary gradient HPLC system with UV absorbance detector (280 nm), injector with at least a 25- μ L volume, mobile-phase degassing system, and chromatography data system. A Hewlett-Packard model 1090 with diode array UV absorbance detector, automatic sample

injector, and ChemStation data acquisition and analysis software system (*HPLC ChemStation*, 1st Edition, Hewlett-Packard, Federal Republic of Germany, November 1987) were used in method development and performance evaluation.

5.1.2 Columns

- Primary column: Poly(styrene-divinylbenzene) HPLC column, 150 mm x 4.1 mm ID, 5- μ m particles, 75 Å pores (Hamilton PRP-1 or equivalent) with matching guard column.
- Confirmatory columns:
 - C-8 bonded silica HPLC column, 150 mm x 4.6 mm ID, 5- μ m particles (Econosphere C-8 or equivalent with 8% or greater carbon load) with matching guard column.
 - C-18 bonded silica column, 150 mm x 2.1 mm ID, 5- μ m particles (ZORBAX RX-C-18 or equivalent) with matching guard column.

5.1.3 Other Equipment

- Syringe: 1-mL gas tight (Hamilton 1001-LT or equivalent).
- Filter: Nylon filter, 13 mm OD, 0.22 μ m (Gelman or equivalent).

6.0 Reagents

- Water, HPLC grade
- Methanol, HPLC grade
- Acetonitrile, HPLC grade
- Glacial acetic acid, American Chemical Society (ACS) grade
- Sulfuric acid, ACS grade

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

8.0 Procedure

8.1 High Performance Liquid Chromatography Conditions

8.1.1 Primary Column 1

- TCLP acidic semivolatile compounds

Mobile phase: (see Table 2)
Flow rate: 1 mL/min
Injection volume: 25 μ L
Temperature: room temperature (ca 21°C)
Monitored wavelengths: 280 and/or 235 nm
Reference wavelength: 450 nm
Equilibration between runs: 9 min

Table 2: Mobile Phase Gradient for TCLP Acidic Semivolatile Compounds on Column 1

<u>Step or Run</u> <u>Time (min)</u>	<u>Volume %</u> <u>0.1 M Acetic Acid</u> <u>in 10/90 (v/v)</u>	
	<u>Acetonitrile/Water</u>	<u>Acetonitrile</u>
Initial	62	38
4.5	62	38
10.5	3.0	97
13.0	3.0	97
14.0	62	38
16.0	62	38

- TCLP herbicides only

Mobile phase: isocratic 55 vol % of 0.0 M acetic acid in 10/90 (v/v) acetonitrile/water and 45% acetonitrile
Flow rate: 1 mL/min
Injection volume: 25 μ L
Temperature: room temperature (ca. 21°C)
Monitored wavelengths: 280 and/or 235 nm
Reference wavelength: 450 nm

8.1.2 Confirmatory Columns

• C-8 confirmatory column

Mobile phase: see Table 3
 Flow rate: 1 mL/min
 Injection volume: 25 μ L
 Temperature: room temperature (ca. 21°C)
 Monitored wavelengths: 280 and/or 235 nm
 Reference wavelength: 450 nm
 Equilibration between runs: 10 min

Table 3. Mobile Phase Gradient for TCLP Acidic Semivolatile Compounds on C-8 Confirmatory Column

Step or Run Time (min)	Volume %		
	0.1 M Acetic Acid in 10/90 (v/v) Acetonitrile/Water	0.1 M Acetic Acid in Methanol	Acetonitrile
Initial	75	15	10
1.0	75	15	10
3.0	55	35	10
9.0	55	35	30
10.0	35	55	10
15.0	0	10	90
20	0	10	90
21	75	15	10
24	75	15	10

• C-18 confirmatory column

Mobile phase: see Table 4
 Flow rate: 0.57 mL/min
 Injection volume: 2.5 μ L
 Temperature: 40°C
 Monitored wavelengths: 235 and/or 280 nm
 Reference wavelength: 450 nm
 Equilibration between runs: 6 min

Table 4. Mobile Phase Gradient for TCLP Acidic Semivolatile Organic Compounds on C-18 Confirmatory Column

<u>Step or Run</u> <u>Time (Min)</u>	<u>Volume %</u>	
	<u>Acetonitrile</u>	<u>Water</u>
Initial	6	94
2.0	6	94
7.0	20	80
10.0	20	80
12.0	6	94
14.0	6	94

8.2 Calibration. Standard solutions of each analyte should be prepared in methanol over the range of concentrations expected in the sample, at least one of which must be at or below the TCLP Regulatory Limit. At least a 5-point calibration curve is recommended. Twenty-five microliter volumes of each standard should be injected. External standardization per SW-846 method 8000 should be performed.

8.3 Chromatographic Analysis

8.3.1 The samples should be prepared for analysis by acidifying alkaline samples to a pH of <3 using concentrated sulfuric acid and filtering out particles using the syringe and Nylon filter assembly. Acidic samples or leachates should be adjusted to pH 12 with NaOH, allowed to stand for 1 h, and then adjusted to pH 3 before filtration and analysis (EPA Method 515.1, Rev. 4). A known mass of 2,4,5-T (final concentration of 5.0 to 7.5 µg/mL) also may be added to the sample to serve as a surrogate standard. Other compounds may be used as a surrogate standard if their performance with respect to the analytes is documented.

8.3.2 Twenty-five microliters of the sample should be injected into the primary column, and analyte concentrations should be calculated using the method of external standards. Where TCLP acidic semivolatile compounds are tentatively identified by retention time on the primary column, their identifications are confirmed using either their UV absorbance spectra or their retention times on either of the confirmatory columns.

9.0 Quality Control

Chapter 3 of this document should be referred to for quality control (QC) guidelines. Modifications to this method should be supported by standard QC procedures (e.g., as outlined in Chapter 3 of this document) and should meet the objectives of the project.

10.0 Method Performance

10.1 Chromatographic Performance and Spectra of Analytes. Table 5 lists the chromatographic performance of the primary column. The PRP-1 column was chosen as the primary column because of its good efficiency, resolution of all analytes (except for m+p-cresols, which is permitted by the TCLP), and resistance to hydrolysis. The polystyrene packing is stable over the pH range of 1 to 13, versus the pH range of 2 to 8 for silica-based packings. A chromatogram of the analytes on the primary column is shown in Figure 1. Table 6 gives the retention times of the analytes on the confirmatory columns. Two columns are listed: a conventional C-8 column, and a 2.1-mm ID C-18 column. The latter reverses the relative retention times of the analytes and also reduces solvent consumption relative to the primary column and the C-8 confirmatory column. Figure 2 shows the separation of the TCLP acidic semivolatiles with the C-18 column. The UV absorbance spectrum of each analyte is included as Figure 3 (at the end of the method).

10.2 Detection Limits, Quantitation Limits, and Linear Range. Table 7 lists the instrument detection and quantitation limits calculated according to Hubaux and Vos (1970). The TCLP regulatory limits for each analyte can be met by using the appropriate detector wavelength. The linear ranges are only approximate, and probably extend above the upper limits listed. Two wavelengths can be used with this procedure (280 and/or 235). The 280-nm wavelength is preferred because of its generally superior sensitivity and the lower interference from solvent and sample impurities.

Table 5. Chromatographic Performance of the Primary Column 1

Compound	RT ^(a) (Min.)	Sym ^(b)	Width ^(c) (Min.)	K ^(d)	N ^(e)
p-Cresol	4.235	0.84	0.152	2.682	3105
m-Cresol	4.271	0.85	0.155	2.713	3037
o-Cresol	4.926	0.82	0.182	3.283	2930
2,4-D	5.375	0.75	0.207	3.673	2697
2,4,5-T	7.334	0.75	0.142	5.377	10670
Silvex	8.4111	0.71	0.119	6.313	19983
2,4,5-TCP	9.333	0.66	0.115	7.115	26346
2,4,6-TCP	9.753	0.60	0.136	7.480	20571
PCP	11.175	0.53	0.162	8.717	19034

(a) Retention time

(b) Peak symmetry = a complex function reflecting peak area before apex divided by peak area after apex^(f)

(c) Peak width = $0.3T + 0.7 A/H$, where T = time between peak inflection points; A = peak area; H = peak height^(f)

(d) Capacity factor

(e) Number of theoretical plates

(f) *HPLC Chemstation*, 1st Edition, Hewlett-Packard, Federal Republic of Germany, November 1987

Figure 1. Chromatogram of TCLP Acidic Semivolatiles on Primary Column 1

Table 6. Analyte Retention Times on the Confirmatory Columns		
Compound	Retention Time (min)	
	C-8	C-18
o-Cresol	—	8.995
m-Cresol	4.659	—
m + p Cresols	—	8.756
o + p-Cresols	4.676	—
2,4-D	6.354	1.551
2,4,5-T	7.991	3.785
Silvex	8.961	5.295
2,4,5-TCP	10.021	6.060
2,4,6-TCP	10.321	2.300
PCP	13.542	7.366

Figure 2. Chromatogram of TCLP Acidic Semivolatile Organic Compounds on C-18 Confirmatory Column

Table 7. Detection Limits, Quantitation Limits, and Approximate Linear Range for TCLP Acidic Semivolatile Organics by HPLC-UV Detection on Column 1^(a)

Compound	Detection Limit		Quantitation Limit		Approximate Linear Range
	235 nm	280 nm	235 nm	280 nm	
o-Cresol	4.6	2.6	8.9	5.2	2 - 100
m-Cresol	2.2	0.9	4.3	1.8	1 - 100
p-Cresol	2.5	2.1	5.0	4.2	2 - 100
m + p-Cresols	3.6	5.7	6.9	11.2	4 - 100
2,4-D	0.59	0.93	1.2	1.8	0.5 - 150
2,4,5-T	1.8	1.3	3.6	2.7	1 - 175
Silvex	0.97	0.81	1.9	1.6	1 - 250
2,4,5-Trichlorophenol	1.2	2.2	2.4	4.4	1 - 125
2,4,6-Trichlorophenol	0.74	0.46	1.5	0.91	0.5 - 125
Pentachlorophenol	7.3	3.7	14.3	7.4	4 - 350

(a) Detection limit and quantitation limit determined according to Hubaux and Vos (1970).

10.3 Analyte Recoveries. Two standard matrices (TCLP leaching fluid, nitrate liquid) were spiked with known concentrations of the analytes. The spikes were prepared at a concentration at or below the TCLP regulatory limit ("low spike"), and a concentration that was generally a factor of four higher than the regulatory limit ("high spike"). The measurement of each spiked sample was the average of triplicate injections on each of three days. The determined concentrations were compared with the prepared values. Table 8 shows the results for TCLP leaching fluid #2 (SW-846 Method 1311) (EPA 1992). A graphical representation of the recoveries is included in Figure 4 (at the end of the method). The recoveries were 87% or better for this sample matrix. Corresponding results for analysis in nitrate liquid (5 M NaNO₃) are shown in Table 9. The latter solution emulates the conditions found in many nuclear waste tanks. This matrix required acidification before analysis by HPLC. It is not surprising that spike recoveries are much lower for this hostile matrix than from the TCLP leaching fluid, and the results suggest that many of the TCLP acidic semivolatile compounds will not survive in some of the waste matrices. A small peak that disappeared during a relatively short period of storage time (less than 24 h) was observed in early range-finding analyses for pentachlorophenol.

Table 8. Average Recoveries of TCLP Acidic Semivolatile Organic Compounds and Their 95% Confidence Intervals from TCLP Leaching Fluid

Compound (Wavelength)	Low Spike		High Spike	
	Conc. ($\mu\text{g/mL}$)	Recy. ^(a) (%)	Conc. ($\mu\text{g/mL}$)	Recy. ^(a) (%)
m+p-Cresols (280)	10	102.0 $\pm$ 1.0	40	111.0 $\pm$ 2.2
o-Cresols (280)	5	88.6 $\pm$ 6.2	20	88.9 $\pm$ 8.7
2,4-D (235)	5	91.1 $\pm$ 7.7	20	106.8 $\pm$ 3.2
2,4,5-T (280)	5	89.4 $\pm$ 1.7	20	100.9 $\pm$ 2.0
Silvex (280)	1	97.5 $\pm$ 11.4	20	117.0 $\pm$ 4.0
2,4,5-Trichlorophenol (280)	5	96.2 $\pm$ 6.5	20	95.6 $\pm$ 3.5
2,4,6-Trichlorophenol (280)	2	128.2 $\pm$ 11.2	20	101.3 $\pm$ 4.0
Pentachlorophenol (280)	10	96.0 $\pm$ 8.9	40	103.9 $\pm$ 4.0

(a) Average statistics and confidence intervals are based on three replicates (days 1, 2, and 3).

10.4 Surrogate Standard Recoveries. The isocratic mobile-phase method has been used extensively for the determination of 2,4-D and silvex in TCLP leachates of wastes. A surrogate standard, 2,4,5-T, was spiked at concentrations of 5.0 to 7.5 $\mu\text{g/mL}$. The 95% confidence interval for the average recovery for 61 samples analyzed over the course of 12 months was 96.7 $\pm$ 3.8%. The standard deviation for an individual measurement was 14.8%.

Table 9. Average Recoveries of TCLP Acidic Semivolatile Organic Compounds and Their 95% Confidence Limits from Surrogate Nuclear Waste Tank Liquid (5 M NaNO₃)

Compound (Wavelength)	Low Spike		High Spike	
	Conc. (µg/mL)	Recy. ^(a) (%)	Conc. (µg/mL)	Recy. ^(a) (%)
m + p-Cresols (280)	10	91.2 ± 2.2	40	101.9 ± 0.7
o-Cresol (280)	5	77.4 ± 4.7	20	86.5 ± 5.5
2,4-D (235)	5	58.1 ± 2.5	20	66.5 ± 13.7
2,4-D (280)	5	41.5 ± 5.2	20	90.4 ± 5.0
2,4,5-T (280)	5	ND	20	63.6 ± 2.7
Silvex (280)	1	ND	20	33.4 ± 0.5
2,4,5-Trichlorophenol (280)	5	ND	20	28.7 ± 1.0
2,4,6-Trichlorophenol (280)	2	ND	20	66.0 ± 3.7
Pentachlorophenol (280)	10	ND	40	ND

^(a) Average statistics and confidence intervals are based on three replicates (days 1, 2, and 3).

ND = not detected.

10.5 Sources of Variation. Table 10 lists the standard deviations due to different experimental factors (i.e., sample matrices, spikes within the matrices, and replicates within spikes). Figure 5 (at the end of the method) is a graphical representation of the sources of experimental variation. It is clear that the instrumental method represented by the variation due to replicates within spikes is very reproducible, with standard deviations all less than 2.6%. Matrix effects are the main source of variation, and when hostile matrices such as concentrated sodium nitrate are encountered, variation can be large between different matrices.

10.6 Blanks. No peaks that could be quantitated were observed in reagent blanks of either sample matrix.

11.0 References

Hubaux, A., and G. Vos. 1970. "Decision and Detection Limits for Linear Calibration Curves." *Anal. Chem.*, 42:849-855.

U. S. Environmental Protection Agency (EPA). 1992. *Test Method for Evaluating Solid Waste. Physical/Chemical Methods*, SW-846. 3rd Edition, Final Update I. Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Table 10. Standard Deviations of Percent Recovery from Experimental Sources

<u>Compound</u>	<u>Experimental Sources</u>		
	<u>Between</u>	<u>Spikes Within</u>	<u>Replicates Within</u>
	<u>Matrices (%)</u>	<u>Matrices (%)</u>	<u>Spikes (%)</u>
o-Cresol	3.5	4.3	2.6
m,p-Cresol	5.0	7.0	0.7
2,4-D	12.0	17.9	2.0
PCP	70.6	3.8	2.0
2,4,5-TCP	56.8	14.3	1.5
2,4,6-TCP	52.0	35.6	2.5
2,4,5-T	38.5	32.3	0.8
Silvex	62.5	19.3	2.4

Figure 3. UV Absorbance Spectra of TCLP Acidic Semivolatile Compounds

(d)

(e)

(f)

Figure 3. (Contd)

Figure 3. (Contd)

Figure 4. Average Percent Recoveries for Direct HPLC Analysis of TCLP Acidic Semivolatile Compounds

Figure 5. Standard Deviations of the Experimental Sources for Direct HPLC Analysis of TCLP Acidic Semivolatile Compounds

Chapter 9

Inorganic Methods

Scope and Application

This chapter summarizes guidance pertinent to U.S. Department of Energy (DOE) sites for characterization of inorganic constituents in environmental and waste management (EM) samples. The general considerations, quality control (QC) concerns, and methods specific to inorganic analytical laboratories are provided. Inorganic analysis includes instrumental analysis, such as inductively coupled plasma-optical emission spectrometry (ICP-OES), ion chromatography (IC), and inductively coupled plasma-mass spectrometry (ICP-MS), as well as immunoassays, screening methods, and field methods. Sample preparation to remove interferents from specific matrices is an important part of inorganic analysis, and methods to accomplish separations are considered within this chapter. Suggested QC protocols for instrumental-analysis systems are identified. Additional QC checks may be specified in the individual procedures. Additionally, the nature of mixed waste may preclude the application of standard methods of analysis because of the chemical or radiochemical components contained within the sample. A summary of these associated constraints is included in this chapter.

Limitations

It is important to understand the limitations inherent in inorganic sample preparation and instrumental analysis. For a chosen technique, it is recommended that the client also be made aware of any associated limitations. For example, a specific detection limit may not be attainable due to the highly radioactive

nature of the original sample; to reduce exposure to the analyst, the sample may need to be greatly diluted.

The type of sample container, sample size, and transportation conditions should be commensurate with the nature of the analytes of interest and laboratory sampling needs. Refrigeration to 4°C may be required for several analytes {see SW-846 (EPA 1986), chapter 2}. However, refrigeration may not be possible for highly radioactive samples. Field sampling is subject to many factors that impact sample delivery time, such as special sample-handling precautions due to radioactivity and site locations for analytical services. Sampling may be done by personnel who are not a part of the laboratory organization. The analytical laboratory generally has no control over such sampling constraints. Therefore, sample hold times should be determined from the time of sample receipt at the analytical laboratory. If preliminary hot-cell work is required before sample analysis, sample preparation will probably be delayed, and hold times may need to be extended. These limiting factors should be negotiated with the concerned parties before sampling of the site. A data quality objective (DQO) process, such as outlined in Chapter 1, may be used to facilitate this process. Protocols for sample chain-of-custody may need to be observed. Samples may need to be stored in locked or otherwise protected areas.

Field analytical screening is subject to many uncontrolled factors that influence the quality of data collected; however, the use of field methods is encouraged when possible so that the sampling process

results in representative material for more definitive analysis in the laboratory.

Safety issues inherent to general chemistry laboratories are complicated by safety concerns that arise in analyzing radioactive samples. Radioactivity in samples might require using additional protection (supplied air, specialized clothing) or modifying facilities (special hoods or hot cells). Details of these safety-related issues may be found in Chapter 4 of this compendium. For analyzing samples that contain low-level or medium-level radioactivity, certain precautions should be taken to prevent any material from escaping into the laboratory. For example, vacuum pumps used in ICP-MS work should be vented through a high-efficiency particulate air (HEPA) filter system; exposed aspiration areas in AA spectrophotometers should be controlled and ventilated through a HEPA system. As required by the DOE "as low as reasonably achievable" (ALARA) principle, laboratory personnel should follow radiochemical laboratory procedures for handling radioactive samples and should ensure that health physics monitoring procedures are in place.

Standards established for subsampling (e.g., grinding, coning and quartering of soils) may not be practical for use with highly radioactive samples. No current standard exists to ensure homogeneity in tank sludges, though considerable variability exists in the horizons within radioactive waste tanks.

Laboratory protocols should be developed to ensure that representative samples are taken. The protocols should incorporate limitations imposed by the radioactive and/or hazardous nature of the samples as well as specific project needs. Refer to Chapters 5 and 7 for details on sampling.

Definitions

Continuing Calibration Blank (CCB) - A sample made with reagents or a simulated sample matrix. This sample is periodically run to confirm that the matrix or reagents used in the analysis do not contribute to a false-positive result for the analyte.

Continuing Calibration Verification (CCV) - A standard that is periodically run to confirm instrumental performance during a set of analyses.

Initial Calibration Verification (ICV) - A set of standards that are employed to determine instrumental performance before analyzing samples. Factors to consider in choosing an ICV-standard set include the dynamic range of the instrument used, expectations of detection and linearity, and the expected range of the analyte in the samples. Data from ICV should encompass the working range for the analysis so that the expected concentration of the sample analyte falls between two of the ICV standards used. For well-defined systems for which performance data have been compiled, the ICV may consist of a single standard that corresponds with the mid-range of the expected analyte concentration.

Quality Control

Quality Control for Inorganic Analysis

Chapter 3 defines QC objectives. A method includes all steps relating to sample preparation and analysis. Quality control samples need to follow all the method's steps to which a sample is subjected. The criteria given below are to be used as guidelines; the appropriate quality assurance project plan (QAPP) should take precedence. Statistics generated by

these QC sample analyses criteria should be judged against the appropriate QAPP and/or internal laboratory procedure requirements. General conditional elements for quality assurance (QA), such as method proficiency, control limits and control charting, laboratory control procedures, method blanks, matrix-specific bias, and matrix-specific precision, are adequately covered in chapter 3.

For certain field methods that rely on a subjective observation (e.g., a color change or color saturation of an indicator), the level and type of QC applied to the method will be somewhat different than that used in instrumental analysis. For example, multiple observations by independent observers may be an element of determining QC for a color-test method. Similarly, the QC data generated by immunoassays may depend on color saturations that may vary from batch to batch due to subtle differences in reagents or the conditions of the biomolecules that react in the assay. In these cases, QC samples are best run with each sample set, and should include method blanks, spiked blanks, and spiked samples to ensure that matrix, reagents, temperature, and other influences are not affecting the measurement. Appropriate QC controls should be included with each of these assays.

General information pertaining to the types of QC applied to each method is to be found within section 8 of the method; the data obtained from applying the method to samples and QC samples can be found in section 9 of the method.

Standards

Standards should be traceable to the National Institute of Standards and Technology (NIST) or other certified vendors. Storage conditions need to be considered to maintain standard integrity. Typically, standards are certified for 1 year past the bottling date.

Standard soil or sludge matrices of known inorganic analyte content may not be available. The NIST lists a few river-sediment standards with known concentrations of several metals. These, however, may not be of similar composition to the site-specific matrices. Furthermore, no satisfactory way exists to add inorganic analytes to these matrices to mimic the chemical and physical form of the analytes in the field sample.

Instrument Quality Control

A typical analytical session, during which one or more batches of samples are analyzed, may consist of the following activities:

1. instrument calibration
2. calibration verification/blank verification
3. analysis of samples
4. analysis of QC samples (e.g., duplicate).

Recommended protocols for each of these activities for both single-analyte analysis techniques {e.g., spectrophotometry, atomic absorption (AA) (graphite furnace AA, cold vapor AA, hydride generation AA)} and multi-analyte techniques (ICP-OES, ICP-MS, IC) are described below.

Instrument Calibration

Single-Analyte Technique. Calibration curves are typically generated using four concentrations of the analyte prepared by diluting a certified stock solution. One of the four calibration-standard concentrations may be zero (blank).

Multi-Analyte Technique. Calibration for ICP-OES and ICP-MS instruments can be done using 1)

a blank and 2) certified (mixed) standard(s) containing the target elements at a convenient concentration level (typically 10 ppm for ICP-OES and 100 ppb for ICP-MS), affording a two-point calibration. An initial multi-point calibration may be necessary.

Ion Chromatography. Mixed standards, prepared from certified stock standards of target analytes each at four or more different concentrations, are used for calibration. One of the “mixed standards” may be a blank.

Calibration Verification/Blank Verification

In the normal sequence of operations, a calibration verification standard (also regarded as a “check standard”) and blank are analyzed before sample analysis. If these results are outside of the tolerance (control) limits established by the procedure, the problem should be addressed and corrected if possible. Sample analysis may then proceed.

The ICV standard should be prepared from a certified standard different from the instrument calibration standards, if possible. The ICV should correspond to the approximate mid-range of the calibration curve.

A calibration verification standard CCV or ICV and blank (CCB) should be run periodically, as specified by the method, during an analytical session or run to ensure that the system remains in control. If results are outside the tolerance range, the situation should be corrected, and the samples since the last acceptable CCV (or ICV) should be analyzed. The CCB should be re-analyzed or appropriately flagged in the analysis report.

The standards should bracket the sample analyte concentration. The sample can be diluted if it is too highly concentrated to fall within the standard curve.

If the concentration of an analyte is less than 25% higher than the high standard, dilution may not be necessary; the analyte concentration can be reported with a qualifier that it was higher than the high standard by the appropriate percentage. This procedure should be acceptable if the analytical range in question remains within the linear working range of the analytical instrument.

For any matrix in which abnormal response of the analyte is suspected, a standard addition of analyte to the matrix (method of standard additions or matrix spike analysis) should be considered to establish the absence or level of these effects on the sample. Ordinarily, no correction for matrix effects should be involved in the reported values; however, the apparent yield from a spiked matrix may be very useful information to the client in determining the validity of the data.

Data Reporting

The client should specify what is needed in the data report. As a guideline, the following items should be included:

- identification and quantification of analyte(s)
- sample volume or weight analyzed (if chemical pretreatment was required)
- uncertainty - estimated or propagated error at the 1-sigma confidence level
- matrix specific detection limit - best estimate based on nominal sample size and analytical conditions.

If holding times are of concern, the sample receipt date and the sample digestion or analysis date should be specified, whichever is appropriate.

The following should be available in reference files for client review:

- QC data, demonstrating the quality of the measurement process, including available calibrations and control charts
- chain-of-custody information, if applicable
- run log for the analytical session
- date of sample preparation and analysis
- identification of measuring and test equipment
- identification of standards
- preparation method and analyte measurement methods or procedure(s) identification
- procedural deviations
- primary data (e.g., strip-chart recordings)
- results of performance evaluations done with known standards.

Summary of Methods

Methods for analyzing inorganic constituents in waste include previously accepted methods, such as those from SW-846 (EPA 1986) and new techniques applicable to DOE wastes as well as methods that have been modified to deal with problems posed by radioactive samples. Table 9.1 (at the end of this chapter) summarizes those methods provided in this chapter.

Reference

U.S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Method*. 3rd Edition, SW-846, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Table 9.1. Methods for Analyzing Inorganic Constituents in Waste

Method Number	Title	Summary
MS100	A Reflectometry Based Instrument for Reading Colorimetric Test Strips	A convenient reflectometric instrumental method is presented to increase the accuracy and reproducibility of test strip reactions used to determine specific analytes. Use of this instrument for lead and chromate test data is described and compared with data from test strip visual assay.
MS110	An Indicator Strip-Based Colorimetric Test for Chromate Ions (CrO_4^{2-}) in Aqueous Samples	Chromate is detected (1 to 60 mg/L) by a diphenylcarbazone color reaction bonded to test strips. Useful for field screening for relatively large amounts of chromate.
MS210	An Indicator Strip-Based Colorimetric Test for Lead (Pb^{2+}) in Water	Lead is detected (20 to 500 mg/L) by a rhodizonic acid color reaction on test strips. Useful for field screening for relatively large amounts of lead.
MS310	An Indicator Strip-Based Colorimetric Test for Nitrate Ions (NO_3^-) in Water and Soil	Nitrate is detected (5 to 500 mg/L) by diazotization color reaction bonded to test strips. Useful for field screening for relatively large amounts of nitrate.
MS410	An Indicator Strip-Based Colorimetric Test for Nickel (Ni^{2+}) in Aqueous Samples	Nickel is detected (5 to 500 mg/L) by a dimethylglyoxime color reaction bonded to test strips. Useful for field screening for relatively large amounts of nickel.
MB100, Rev. 1	Immunoassay for Mercury in Soils	Acid extracts of soils are plated and complexed with an Hg specific antibody. A secondary peroxidase antibody, peroxide, and oxidizable chromophore yield a colored product that is quantitated spectrophotometrically. The useful range of the assay is 5 ppm to 80 ppm Hg in soil.
MP100R	Solvent Extraction of Uranium and Thorium from Radioactive Liquid Wastes	After acid digestion, the sample is diluted then extracted with tri-n-octylphosphine oxide (TOPO) in cyclohexane. This treatment minimizes the U and Th and allows analysis of Resource Conservation and Recovery Act (RCRA) metals by standard methods.
MP110R	Cleanup of Transuranic Liquid Wastes using Extraction Chromatography	After acid digestion, the sample is passed through a TRU-Spec column to remove Th and U. The eluate can then be analyzed for RCRA metals by standard methods.

Table 9.1. Contd

<u>Method Number</u>	<u>Title</u>	<u>Summary</u>
MU012R	Total Cyanide by Remote Microdistillation and Argentometric Titration	Cyanide is determined in radioactive ferrocyanide wastes by microdistillation and colorimetry. The lower limit for usability is 0.1% cyanide by weight in the waste material.
MM100	Inductively Coupled Plasma-Mass Spectrometry for Radionuclide Analysis	General guidance is given for instrumental techniques useful in determining long-lived radionuclides by ICP-MS.
MM210	ICP-MS of ^{99}Tc , ^{230}Th , and ^{234}U using Flow Injection Preconcentration	ICP-MS coupled with flow-injection preconcentration is used to determine ^{99}Tc , ^{230}Th , and ^{234}U at sub pCi/g levels in soils. These levels are competitive with traditional radiochemical analytical methods.
MM800	Ion Chromatography and Inductively Coupled-Mass Spectrometry Determination of Uranium Concentration Isotopic Abundance in Groundwater and Drinking Water	Uranium concentration and isotopic abundance is determined by ICP-MS using a ^{233}U spike before sample preparation and concentrating the sample with Dowex anion exchange resin.

MS100^(a)**A Reflectometry-Based Instrument for Reading Colorimetric Test Strips****1.0 Scope and Application**

Indicator strip-based colorimetric tests are usually read by visually comparing the color of the test strip with a reference color chart (Waters et al, 1993a; Waters et al. 1993b). The RQflex meter is based on principles of reflectometry and is specifically designed to read colorimetric test strips. This instrument is the basis for the Reflectoquant™ Analysis System (E. Merck; Darmstadt, Germany - manufacturer/EM Science; Gibbstown, NJ - supplier). The use of such an instrument should significantly increase the accuracy and reproducibility of these methods of analysis. RQflex compatible test strips are currently available for ascorbic acid, chromate, copper, molybdenum, nitrate, nitrite, peracetic acid, peroxide, pH, silver, and lead. Test strips for aluminum, ammonia, calcium, chlorine, cobalt, cyanide, formaldehyde, iron, manganese, nickel, tin, and zinc are expected to be available in the future.

2.0 Summary of Method

The chemistry of the strip tests varies, depending on the analyte being measured (for examples, see Methods MS210 for lead or MS310 for nitrate). Test strips for use with the RQflex are different from the strips used in those methods in that they have two identical reaction zones instead of one. Test water samples are treated as required for the specific test, e.g., a pH adjustment. Test strips are immersed in the test samples, excess liquid is removed, and the color reaction is allowed to proceed for the period of time specified for the test strips being used. The strip is then inserted into the strip adapter of the RQflex instrument and read. The percent reflectance of both reaction zones, relative to a white standard blank, is determined and averaged. The results are converted to $\mu\text{g/mL}$, using a programmed reference concentration curve. They are immediately displayed on the screen and stored in Memory.

This method describes the use of the RQflex instrument to read test strips for lead and chromate in water. Its performance is compared with those described in Methods MS210 (lead) and MS110 (chromate) (Waters 1994) in which the usual visual method of reading the test strips was used.

(a) This method was supplied by L. C. Waters, R. A. Jenkins, and R. W. Counts (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

3.0 Interferences

Because the chemistry of the Reflectoquant™ test strips for lead and chromate is identical to that of the corresponding Merckoquant® test strips, potential chemical interferences are the same as those in the respective methods, MS210 and MS110.

Results of this evaluation have indicated a potential source of false-positive responses when lead-contaminated samples at less than 10 µg/mL are measured. Lead measurement with the RQflex has a threshold for detection of ~10 µg/mL, and samples with lower concentrations are indicated as being “Lo.” In using the recommended procedure of “shake off excess liquid from the test strip,” negative, blank samples were frequently indicated to contain 10 to 12 µg/mL Pb²⁺. This was traced to the presence of excess residual water on the test strip after the 2-min reaction time. By briefly blotting the strip against a paper towel, in addition to the recommended shake procedure, such samples consistently gave “Lo” readings. This “wetness” effect was not significant with strips that had color, i.e., samples with ≥10 µg/mL lead. Such an effect was not observed with the chromate test strips.

4.0 Safety

Lead, chromate, and sulfuric acid are known health hazards. Consequently, gloves and protective clothing should be worn when samples known or suspected to contain lead or chromate, and the sulfuric acid reagent, are being handled.

5.0 Apparatus and Materials

5.1 Instrument

- RQflex: The RQflex is a small (19 x 8 x 2 cm; 275 g), push-button controlled reflectometer. The light source is 4 light-emitting diodes (LEDs) producing wavelengths of 570 and 657 ± 10 nm and using double optics. It is powered by four AAA batteries (which will yield >1000 measurements). All necessary information to run the instrument is communicated via a barcode strip. This includes analyte-specific reaction times, wave-length corrections, and reference curves for concentration. Periodically, the instrument is blanked by the use of a barcode for calibration and a white standard calibration strip. The instrument can be preprogrammed, using separate barcodes, for up to 5 different methods (analytes). Up to 50 measurements for each method, with time and date, are stored in Memory. Data in Memory can be transferred to a personal computer (PC) via an available, special software program. The RQflex is designed to operate in humidity below 90% and at temperatures between 5 and 40°C.
- Barcode strip and white, standard calibration test strip: For blank calibration of the instrument.

- Merck RQflex© manual: The manual contains a description of the instrument and includes instructions for setting up the instrument, coding, measuring, handling measurement results, maintaining the instrument, and troubleshooting.

5.2 Strip Test Kits. The essential difference between the Reflectoquant™ test kits and the Merckoquant® test kits used in Methods MS110 and MS210 is that the Reflectoquant™ test strips have two, instead of one, identical reactive zones, adapting them to be read with the RQflex.

- Reflectoquant® 16999-1 Lead Test Kit
 - Instructions: Supplied with kit
 - Sampling vessel: Marked at 5 mL (disposable tubes and a 2-mL volume were used in the performance evaluation - see section 11.0)
 - Test strips (50): Impregnated with rhodizonic acid
 - Reagent (5% acetic acid): For acidifying test samples
 - Barcode strip: Code 991—to program instrument to measure lead
- Reflectoquant® 16988-1 Chromate Test Kit
 - Instructions: Supplied with kit
 - Sampling vessel: Marked at 5 and 10 mL (disposable tubes and a 2-mL volume were used in the performance evaluation - see section 11.0)
 - Test strips (50): Impregnated with diphenylcarbazide
 - Reagent (25% sulfuric acid): For acidifying test samples
 - Barcode strip: Code 310—to program instrument to measure chromate

6.0 Reagents

(The only reagents required are the acids supplied in the kits as listed in section 5.2.)

7.0 Sample Collection, Preservation, and Handling

(Refer to Methods MS210 and MS110.)

8.0 Procedure

8.1 RQflex Setup

8.1.1 **Setting Time and Date:** Follow RQflex manual instructions. (This is important so that measurement data stored in Memory can be identified.)

8.1.2 **Blank Recalibration:** The instrument should be recalibrated with the blank, white standard test strip if 1) measurements are suspect, 2) the strip adapter has been changed, e.g., cleaned (Note: the strip adapter should be removed and cleaned, with water or ethanol, whenever a different test is being run or if color carryover is suspected), 3) after mechanical mistreatment, e.g., a fall, or 4) in case of error display (ERR).

- The instrument should be stored for at least 30 min at 18 to 22°C.
- The instrument is switched on and the barcode strip is inserted for calibration. CAL is shown on the display.
- The white calibration strip is inserted. It should be checked carefully for proper alignment.
- The Start button should be pressed. The instrument is recalibrated when the CAL display disappears.

8.1.3 **Coding:** The instrument should be coded when 1) the instrument is new, 2) a new method is loaded (test), 3) the lot of Reflectoquant[®] strips is new, or 4) an existing method (or test) is being overwritten.

- The barcode should be chosen that is specific for the lot of Reflectoquant[®] strips being used.
- The instrument should be switched on (On/Off switch).
- The Test button is pressed until the arrow points to the corresponding method (1 through 5) where the new code is to be stored.

- The barcode is inserted from the left to the right until it disappears. Then the barcode is pulled out of the instrument.
- The coding process is successfully completed when the left three digits of the test strip lot number are displayed. A beeper will sound.
- A stored method (test) will be overwritten by inserting a new barcode and stored data for the first method will be deleted. A flickering MEM in the display indicates that measurement data are stored for the method indicated by the arrow.
- Some methods require two barcode strips (not those for lead and chromate described in this method); see manual for instructions.

8.2 Test Water Sample Preparation

- 8.2.1 Lead: 5 mL of sample are adjusted to a pH of 2 to 5 with the acetic acid reagent (~2 drops).
- 8.2.2 Chromate: 10 mL of sample are acidified with sulfuric acid reagent (10 drops).
Note: In Method MS110, the Merckoquant® 10012 Chromate Test procedure called for adjusting the pH of the sample to < 1, i.e., ~5 drops/mL instead of the 1 drop/mL called for in the Reflectoquant® 16988-1 Chromate Test procedure. Comparative strip tests of samples prepared in the two ways showed that the intensity of the colors produced was the same. However, the color produced with the less acidic sample was significantly more stable.
- 8.2.3 Preparation procedure used for RQflex evaluation

Lead - 2-mL samples in deionized water (DW) were acidified with 1 drop of reagent acidic acid.

Chromate - 2-mL samples in simulated groundwater (SGW) (Rocky Mt. 1989) were acidified with 2 drops of reagent sulfuric acid.

8.3 Sample Testing (RQflex Reader)

- 8.3.1 The instrument should be recalibrated (8.1.2) and/or coded (8.1.3) as appropriate before beginning a series of measurements.
- 8.3.2 The instrument is turned on (On/Off button).

- 8.3.3 The appropriate coded method (test) is chosen by pressing the Test button until the pointer addresses the correct method number. (The number of the correct method will correspond to the first three digits of the lot number of the Reflectoquant[®] test strips being used.)
- 8.3.4 The Start button is pressed one time. The test-specific reaction time is displayed (in seconds).
- 8.3.5 The Start button is pressed again (this activates the reaction timer 120 sec for lead, 30 sec for chromate), and the test strip is simultaneously immersed in the test sample for 1 to 2 sec.
- 8.3.6 The test strip is shaken (and blotted if appropriate - see section 3.0) to remove excess liquid.
- 8.3.7 A beeper sounds with 5 sec remaining on the timer to indicate that the test strip should be read.
- 8.3.8 The test strip is inserted all the way into the strip adapter with the reaction zones facing the display screen.
- 8.3.9 The measurement result is read from the display screen and is automatically stored in Memory.
- 8.3.10 The results are recorded in a notebook, with periodic notation of the time for reference (verify recorded results by scrolling through Memory after the analyses are completed).
- 8.3.11 The sample testing procedure is repeated until all samples have been measured.
- 8.3.12 The strip adapter should be removed and cleaned at the end of the workday, or at any time the possibility of color carryover is suspected.

9.0 Calculations

The mean and standard deviation were calculated using standard statistical formulas. The percent relative standard deviation (%RSD), also known as the coefficient of variation, expresses the standard deviation as a percent of the mean and is a useful measure of dispersion when the variation in the response increases as the concentration increases. The intercept, slope, and R2 value for the best-fit least-squares lines were estimated using the Statistical Analysis System (SAS) computer package. The R2 ($0 \leq R^2 \leq 1$) value obtained from the least-squares fit measures the fraction of the total variation in the response, which can be accounted for by the linear

regression between the response and the concentration. The R² value can be considered as a measure of reproducibility.

10.0 Quality Control

Samples of test strips from each batch should be tested using solutions of known analyte concentration (available from Merck). Batches that do not produce accurate readings with the RQflex, or true colors when compared with the Merckoquant® test kits' color charts (see 5.2), should not be used. Likewise, test samples that do not produce true colors should be suspected of containing interferants.

11.0 Method Performance

11.1 Lead. Spiked water samples were used to evaluate the RQflex for reading lead test strips. Two experiments were done using dilutions (in DW) of lead acetate stocks that contained 1164 and 994 µg/mL Pb²⁺, respectively, as determined by inductively coupled plasma/mass spectrometry (ICP/MS). Duplicate 2-mL aliquots of test samples in the range of 0 to 300 µg/mL were tested. Samples above ~200 µg/mL gave readings of "Hi" and were not used in the analysis of the data. Figure 1 shows the results obtained with the RQflex relative to the expected results.

11.1.2 Sensitivity: It was determined that samples with ≥10 µg/mL Pb²⁺ consistently gave a positive numerical reading while those with <10 µg/mL gave "Lo" readings, provided that the test strips were also blotted to remove excessive moisture (see section 3.0 - Interferences). A concentration of ≥20 µg/mL was required to consistently get a positive response when the visual method of reading the strips was used (see MS210).

11.1.3 Reproducibility: Test samples that were <10 µg/mL consistently gave "Lo" readings, if the strips were blotted. The reproducibility of the RQflex and the test strips for measuring positive samples was also tested. Five replicates of a sample at the nominal concentration of 100 µg/mL were tested. A mean value of 103.6 µg/mL with a percentage relative standard deviation (%RSD) of 10.3 was obtained. A similar experiment, with another sample, in which the strips were also blotted gave a mean value of 92.6 µg/mL with a %RSD of 7.4. These results suggest that blotting the strips may increase the reproducibility of the measurement throughout the working range of the test. The RQflex method of reading the strips (n=2 readings/concentration) is compared to visually reading the strips (n=12 readings/concentration) in Figures 1 and 2. As can be observed from the two figures, using the RQflex reader results in significantly better reproducibility. The best-fit least-squares line for the RQflex data yields an R² of 0.977 compared to an R² of 0.867, calculated from the data obtained by visually reading the test strips (see MS210).

Figure 1. Lead Strip Test Performance Using the RQflex Reader

Figure 2. Lead Strip Test Performance Using Human Readers

11.1.4 **Accuracy:** The best-fit line obtained from measurements using the RQflex (see Figure 1) has a slope of 1.21, indicating that the test slightly overestimates the lead content of water. In the same concentration range, visual readings of the strips (see Figure 2) resulted in a best fit line with a slope of 1.67. This comparison indicates that the RQflex method of reading strips is significantly more accurate than the visual method.

11.1.5 **Working Range:** The working range of the lead method is 20 to 200 $\mu\text{g/mL}$ Pb^{2+} .

11.2 **Chromate.** Spiked water samples were used to evaluate the RQflex for reading chromate test strips. Spiked samples in the range of 0 to 60 $\mu\text{g/mL}$ were prepared (in SGW) by diluting a stock of sodium chromate that contained 1010 $\mu\text{g/mL}$ as determined by ICP/MS. Duplicate 2-mL aliquots of each sample concentration were tested. Samples greater than ~ 40 $\mu\text{g/mL}$ gave readings of "Hi" and were not used in the analyses of the data. The results obtained relative to the expected values are shown in Figure 3.

11.2.1 **Sensitivity:** Chromate concentrations ≥ 0.5 $\mu\text{g/mL}$ were consistently distinguished from zero.

11.2.2 **Reproducibility:** Measurements of chromate concentration using the RQflex are very reproducible. Replicate measurements of blank ($n=8$) and nominally "5" ($n=5$) and "30" ($n=5$) $\mu\text{g/mL}$ samples gave mean readings of 0.075 ± 0.089 , 6.28 ± 0.13 , and 39.24 ± 0.84 $\mu\text{g/mL}$, respectively. The RQflex method of reading the strips ($n=2$ readings/concentration) is compared with visually reading the strips ($n=18$ readings/concentration) in Figures 3 and 4. As can be observed from the two figures, using the RQflex reader results in significantly better reproducibility. The best-fit least-squares line for the RQflex data yields an R^2 of 0.998 compared to an R^2 of 0.889 calculated from the data obtained by visually reading the test strips (see MS110).

11.2.3 **Accuracy:** The best-fit line obtained from measurements using the RQflex (see Figure 3) has a slope of 1.19, indicating that the test slightly overestimates the chromate content of water. In the same concentration range, visual readings of the strips (see Figure 2) resulted in a best-fit line with a slope of 1.61. Because the test strips used in this evaluation of the RQflex and the ones used in the validation of Method MS110 gave identical color intensities, and the concentrations were consistently overestimated with reference to the color chart, the possibility that the concentrations assigned to the hues on the reference chart were incorrectly assigned should be considered.

Figure 3. Chromate Strip Test Performance Using the RQflex Reader

Figure 4. Chromate Strip Test Performance Using Human Readers

11.2.4 **Working Range:** The working range of the chromate method is 1 to 45 $\mu\text{g/mL}$.

11.3 **Summary.** The RQflex is an effective, easy-to-use instrument for reading colorimetric test strips. It provides reproducible and accurate measurements without the potential for bias and error inherent in the visual method for reading such tests.

12.0 References

Rocky Mountain Arsenal. 1989. *Chemical Quality Assurance Plan*. Section 4-7, Commerce City , Colorado 80022-2180.

Waters, L. C., R. A. Jenkins, R. R. Smith, R. W. Counts, and J. H. Stewart. October 1993a. "Method MS210: An Indicator Strip-Based Colorimetric Test for Lead (Pb^{2+}) in Water" in *DOE Methods for Evaluating Environmental and Waste Management Samples*, DOE/EM-0089T, by S. C. Goheen, M. McCulloch, B. L. Thomas, R. G. Riley, D. S. Sklarw, G. M. Mong, and S. A. Fadeff. Pacific Northwest Laboratory, Richland, Washington.

Waters, L. C., R. A. Jenkins, R. R. Smith, R. W. Counts, and J. H. Stewart. October 1993b. "Method MS310: An Indicator Strip-Based Colorimetric Test for Nitrate Ions (NO_3^-) in Water and Soil" in *DOE Methods for Evaluating Environmental and Waste Management Samples*, DOE/EM-0089T, by S. C. Goheen, M. McCulloch, B. L. Thomas, R. G. Riley, D. S. Sklarw, G. M. Mong, and S. A. Fadeff. Pacific Northwest Laboratory, Richland, Washington.

Waters, L. C. April, 1994. "Method MS110: An Indicator Strip-Based Colorimetric Test for Chromate Ions (CrO_4^{2-}) in Aqueous Samples" in *DOE Methods for Evaluating Environmental and Waste Management Samples*, DOE/EM-0089T, by S. C. Goheen, M. McCulloch, B. L. Thomas, R. G. Riley, D. S. Sklarw, G. M. Mong, and S. A. Fadeff. Pacific Northwest Laboratory, Richland, Washington.

13.0 Further Reading

SAS Institute Inc. 1988. *SAS/STATTM User's Guide*, Release 6.03 Edition. Cary, North Carolina.

MS110^(a)

An Indicator Strip-Based Colorimetric Test for Chromate Ions (CrO_4^{2-}) in Aqueous Samples

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This is a field screening method to be used to test aqueous samples for the presence of chromate {Merckoquant[®] 10012; Merck; EM Science - supplier (E. Merck, Frankfurter Strasse 250, D-6100 Darmstadt 1, Germany; EM Science, 480 Democrat Road, Gibbstown, New Jersey 08027)}. It can be applied to surface, ground, and wastewater samples. It is also useful in the laboratory to determine appropriate dilutions of test water samples that will be analyzed by more standard laboratory methods, thereby eliminating costly reruns.

2.0 Summary of Method

The method is based on a redox reaction between chromate ions and diphenylcarbazide. Chromate ions oxidize diphenylcarbazide in acidic solution to produce diphenylcarbazone. The Cr^{3+} ions formed in this reduction react with the enolate form of diphenylcarbazone in a 1:1 molar ratio to produce a red-violet complex. In practice, the pH of the test sample is adjusted to <1 with sulfuric acid; then the reaction zone of the test strip is wetted in the test sample, removed, and "blotted" to remove excess liquid. After 15 sec, the chromate content of the sample is estimated by comparing the color of the test strip with a standard color chart. The white reaction zone remains white in the absence of chromate and changes to varying shades of red-violet in the presence of chromate. The color chart provides reference hues for concentrations of 0, 3, 10, 30, and 100 $\mu\text{g/mL}$ chromate. The test can detect chromate at $\geq 1 \mu\text{g/mL}$. The working range of the test is in the range of 1 to 60 $\mu\text{g/mL}$.

3.0 Interferences

Merck (Rapid Test Handbook. 1987. Merck, pp. 86,87) has examined a number of chemicals for their interference in the chromate test.

(a) Method submitted by L. C. Waters and R. A. Jenkins (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

Other anions: At concentrations less than 1000 µg/mL, Br^- , BrO_3^- , Cl^- , ClO_3^- , ClO_4^- , CN^- , F^- , I^- , N_3^- , NO_2^- , NO_3^- , OCN^- , PO_4^{3-} , SCN^- , SeO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_8^{2-}$, WO_4^{2-} , acetate, citrate, oxalate, succinate, or tartrate do not interfere. Interfering colorations are produced by more than 10 µg/mL IO_3^- or IO_4^- (pink to brown), 10 µg/mL MnO_4^- (grey-pink), 25 µg/mL molybdate (pink to violet), 5 µg/mL VO_3^- (brown to wine red), and 50 µg/mL $[\text{Fe}(\text{CN})_6]^{3-}$ (grey to greyish pink). Ascorbate, $[\text{Fe}(\text{CN})_6]^{4-}$, S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_4^{2-}$, and $\text{S}_2\text{O}_5^{2-}$ reduce CrO_4^{2-} to Cr^{3+} (see Note following).

Cations: At concentrations less than 1000 µg/mL, Ag^+ , Al^{3+} , Ba^{2+} , Be^{2+} , Ca^{2+} , Cd^{2+} , Ce^{3+} , Co^{2+} , Cr^{3+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Rb^+ , Sr^{2+} , Ti^{4+} , Tl^+ , Zn^{2+} , or Zr^{4+} do not interfere. In the presence of Pb^{2+} , relatively insoluble lead chromate is formed; therefore, less or no chromate will be detected. Interfering colorations are produced by more than 10 µg/mL Au^{3+} , 100 µg/mL Bi^{3+} , and Ce^{4+} or Cu^{2+} ; 25 µg/mL Fe^{3+} color the reaction zone of the test strip pink or brown. More than 25 µg/mL Hg^+ or 100 µg/mL Hg^{2+} color the test strip blue. Molybdenum blue interferes with the test due to its intrinsic color. Molybdenum blue, As^{3+} , Fe^{2+} , Sb^{3+} , Sn^{2+} , and VO^{2+} reduce CrO_4^{2-} to Cr^{3+} (see Note following).

Methods of treating the samples to overcome many of the interferences due to aberrant colors are given in Merck's Rapid Test Handbook, pp. 86 and 87.

Note: If they are oxidized to chromate according to the following method, Cr^{3+} ions can also be determined with the chromate strip test: 1) one spatula-tip of sodium peroxide or potassium peroxydisulfate is added to 5 mL of the solution ($\text{pH} > 5$); 2) the solution is boiled for 5 to 10 min, and the pH is adjusted to < 1 with 25% sulfuric acid; 3) the solution is diluted to a 5-mL volume with water and tested as usual.

4.0 Safety

Chromate and sulfuric acid are known health hazards. Consequently, gloves and protective clothing should be worn when samples known or suspected to contain chromate and sulfuric acid reagent are being handled.

5.0 Apparatus and Materials

- Timer - Capable of measuring in sec
- Pipettes - Plastic 5- or 10-mL disposables with filler bulb to measure water sample volume
- Test tubes - Plastic, disposable, 13 x 100 mm (Falcon 2027 or equivalent) to test multiple samples

- pH paper (0 to 14 range - For measuring pH of test samples
- Merckoquant® 10012 Chromate Test Kit - Instructions supplied with kit
- Sampling vessel - Marked at 5 mL, for measuring test sample (Disposable tubes and a 1-mL volume can be used when multiple or replicate samples are being tested—see section 8.2)
- Test strips (100 - Impregnated with diphenylcarbazide
- Reagent (25% sulfuric acid) - For acidifying test samples
- Color chart - Permanently affixed to the test-strip container—provides reference hues for values of 0, 3, 10, 30, and 100 µg/mL.

6.0 Reagents

Except for the reagents required to eliminate interferences, the only reagent required is 25% sulfuric acid (included with the kit).

7.0 Sample Collection, Preservation, and Handling

The test is designed to be performed in the field. Because the samples are not modified, except for pH adjustment, they may be disposed of at their collection source. Samples that are tested away from their collection source and are positive for chromate and/or are corrosive, as judged by pH, should be handled and disposed of as hazardous wastes.

8.0 Procedure (Merckoquant® 10012 Chromate Test Instructions)

8.1 Single Samples

- 8.1.1 Five mL of the sample to be tested are added to the measuring vessel.
- 8.1.2 The pH of the sample is adjusted to pH <1 with the 25% sulfuric acid reagent.
- 8.1.3 The test strip is immersed into the sample until the reaction zone is thoroughly moistened. The excess liquid is removed by wiping the test strip against the sample vessel rim.
- 8.1.4 After 15 sec, the color of the reaction zone is compared with the color chart. (If significant dilution is involved during pH adjustment, this should be taken into account in the final determination of the chromate concentration in the sample.)

8.2 Multiple Samples. In situations where multiple samples or replicates of single samples are to be tested, an alternate procedure is suggested.

8.2.1 An appropriate number of 13- x 100-mm plastic, disposable tubes and a corresponding number of test strips are labeled using a permanent-ink marker.

8.2.2 One-mL aliquots of the solutions to be tested are added to the tubes.

8.2.3 The acidity of the samples is adjusted to pH <1 with the 25% sulfuric acid reagent.

8.2.4 The strip tests are performed as indicated in sections 8.1.3 and 8.1.4. The strips should be read as quickly as possible after the 15-sec reaction period because the color begins to fade within 30 min.

9.0 Calculations

The chromate concentrations defined by the color chart are 0, 3, 10, 30, and 100 $\mu\text{g/mL}$. Assignments between those values can also be made. To evaluate the sensitivity and accuracy of the method, numerical values were assigned to the results obtained from each strip as follows: a result of 10 $\mu\text{g/mL}$ was given the value 10, a result of 10 to 30 was given the value 20, and so on. Assignments greater than 100 were arbitrarily given the value 150. The values were summed, averaged, and corrected for dilution to generate the calculated concentrations of chromate in the samples. Often a significant volume of reagent acid will be required to adjust the pH of the test samples to pH <1. Because the volume required may be different for different samples, it is suggested that this dilution be taken into account in the final estimate of chromate concentration. For example, in the evaluations of the method, 5 drops or about 0.143 mL of reagent acid per mL of sample were required to adjust the samples to pH <1; therefore, the calculated concentrations were multiplied by 1.14 to correct for this dilution.

10.0 Quality Control

Samples of test strips from each batch should be tested using solutions of known chromate concentration. Batches that do not produce true colors should not be used. Likewise, test samples that do not produce true colors should be suspected of containing interferants.

11.0 Method Performance

Spiked and wastewater samples were used to evaluate this method. Stock solutions of potassium dichromate and sodium chromate at nominal concentrations of 580 and 1000 $\mu\text{g chromate/mL}$, respectively, were made in simulated groundwater (SGW) {deionized water to which 0.165 g/L of sodium chloride and 0.148 g/L of sodium sulfate has been added (contains 100 $\mu\text{g/mL}$ each of SO_4^{2-} and Cl^- [Rocky Mtn. 1989])}. The concentrations of chromate in the stocks, as

determined by inductively coupled plasma/mass spectrometry (ICP/MS), were 535 $\mu\text{g/mL}$ in the $\text{K}_2\text{Cr}_2\text{O}_7$ stock and 1010 $\mu\text{g/mL}$ in the Na_2CrO_4 stock. Wastewater samples were taken from a metal-plating operation and had been treated by reverse osmosis as a method of extracting and concentrating the chromate from the wastewater. Fractions for each sample included FEED—the untreated waste stream, PERM—the permeate from the treatment, and CON—the concentrate from the treatment.

Spiked samples: Test samples were made by diluting the stock solutions to concentrations between 0.5 and 100 $\mu\text{g/mL}$. Triplicate (for $\text{K}_2\text{Cr}_2\text{O}_7$) and duplicate (for Na_2CrO_4) 1-mL samples were added to 13- x 100-mm tubes. The samples were acidified to a pH <1 with 0.143 mL (5 drops) of the reagent sulfuric acid. Samples were randomized and assayed using the test strips as described in section 8.0. Five or six analysts independently read the test strips and recorded the concentrations with reference to the color chart. The chromate concentrations defined by the color chart are 0, 3, 10, 30, and 100 $\mu\text{g/mL}$. Assignments between those values were also made. To evaluate the sensitivity and accuracy of the method, numerical values were assigned to the results obtained from each strip as follows: a result of 10 $\mu\text{g/mL}$ was given the value 10, a result of 10 to 30 was given the value 20, and so on. Assignments greater than 100 were arbitrarily given the value 150. The values were summed, averaged, and corrected for dilution to generate the data presented in the Tables and Figures.

Among the conclusions that can be made about the strip-test assay for chromate in spiked SGW are the following (see Table 1 and Figure 1):

Note: Only the tabular data for the $\text{K}_2\text{Cr}_2\text{O}_7$ spiked samples are given (Table 1); the graphic data (Figure 1) are a composite of data from both the $\text{K}_2\text{Cr}_2\text{O}_7$ and Na_2CrO_4 spiked samples.

1. False positive responses were not observed. None of the 96 analyses of blank samples were tested positive (Tables 1 and 2— Na_2CrO_4 data not shown).
2. One $\mu\text{g/mL}$ was consistently distinguished from zero. No false negatives were observed with samples that contained ≥ 1 $\mu\text{g/mL}$ (Tables 1 and 2— Na_2CrO_4 data not shown).
3. The strip-test assay consistently overestimated the actual chromate concentration by about a factor of 1.75 (see Table 1 and Figure 1). Two separate batches of test strips gave this same result.
4. Overall, with reference to ICP/MS, the strip-test assay gave a best-fit straight line with an $R^2 = 0.986$ and a slope of 1.741 (Figure 1). Individually, the experiments using $\text{K}_2\text{Cr}_2\text{O}_7$ gave an $R^2 = 0.984$ and a slope of 1.751; using Na_2CrO_4 gave an $R^2 = 0.987$ and a slope of 1.723.

Waste samples: Three waste samples—FEED, PERM and CON—were taken eight times each for a total of 24 samples. Each sample was diluted with SGW, if necessary, so that its concentration would fall within the working range of the strip test assay (done by comparing the intensity of the color, by eye, with standard solutions). Duplicate 1-mL aliquots were added to 13- x 100-mm tubes. The samples were acidified, randomized, and tested as described in section 8.0. Five analysts read the strips, and the data were treated as described above for the “spiked samples.” Final concentrations were obtained by correcting for sample dilution (Table 2). Nine of the 24 samples, including the least and most concentrated as determined by the strip-test assay, were analyzed by ICP/MS for comparison (Table 2 and Figure 2).

The following conclusions can be made about using the strip-test assay to test wastewater samples for chromate:

1. As was the case with spiked samples, the test overestimated the chromate concentration of the waste samples by a factor of about 1.74.
2. After compensating for the fact that chromate is overestimated in standard solutions, the test quite accurately indicated the concentration of chromate in the 9 samples for which both strip-test and ICP/MS data were obtained.
3. With reference to ICP/MS, the strip-test results gave a best-fit straight line with a slope of 1.738 with an $R^2 = 0.962$.

Taken together with the manufacturer’s claims concerning the lack of interferences by a wide variety of inorganic ions, this appears to be a time- and cost-effective method for screening water samples that contain ≥ 1 $\mu\text{g/mL}$ chromate. By correcting for the fact that the actual concentration is overestimated by a factor of about 1.75 times, a reasonably accurate measure of the actual chromate concentration in water samples can be made. The effective working range of the test is 1 to 60 μg chromate/mL.

12.0 Reference

Rocky Mountain Arsenal. 1989. *Rocky Mountain Arsenal Chemical Quality Assurance Plan*, section 4-7. Commerce City, Colorado 80022-2180.

Table 1. Strip-Test Assay for Chromate in Spiked Water Samples

Sample No.	Test No.	Chromate Concentration ^(a)						Calculated Conc. ^(b) $\mu\text{g/mL}$
		0-3 (1.5)	3-10 (6.5)	10-30 (20)	30-100 (65)	>100 (150)		
1	30	ABCDER ^(d)					0	
2	21	ABCDER					0	
3	19	ABCDER					0	
4	15	ABCDER					0	
5	4	ABCDER					0	
6	36	ABCDER					0	
7	26	ABCDER					0.54	
Sample No.	Test No.	0-3 (1.5)	3-10 (6.5)	10-30 (20)	30	Calculated Conc. ^(b) $\mu\text{g/mL}$	Actual Conc. ^(c) $\mu\text{g/mL}$	
8	33	DF				1.14	0.54	
9	29	F				1.42	0.54	
10	22	ABCE				2	1.07	
11	32	ABCE	F			2	1.07	
12	27	ABCE	F			2	1.07	
13	11	ABCE	DF			2.28	1.61	
14	34	ACD	BEF			2.56	1.61	
15	8	ABCE	DF			2.28	1.61	
16	18	ABE	ABE			3.42	2.68	
17	5	ABCE	ABCE			4.08	2.68	
18	12	ABCE	DF			4.75	2.68	
19	23	ABCE	ACDE			8.74	5.35	
20	7	ABCE	ACDE			8.07	5.35	
21	24		BOD			8.74	5.35	
22	6		E			17.1	10.7	
23	31					12.63	10.7	
24	13					13.3	10.7	
25	2					22.8	16.05	
26	26					22.8	16.05	

(a) Simulated groundwater was spiked with potassium dichromate. The chromate concentration (µg/mL) was estimated by comparison with the reference color chart.

(b) Includes a factor of 1.4 for dilution during sample acidification.

(c) Determined by ICP/MS analysis.

(d) Each strip (one strip per water sample) was independently read by six analysts (ABDCEFF) as indicated. Underlined letters indicate expected results.

Table 1. (contd)

Sample No.	Test No.	Chromate Concentration (a)					Calculated Conc. (b) $\mu\text{g/mL}$	Actual Conc. (c) $\mu\text{g/mL}$
		10-30 (20)	30	30-100 (65)	100	>150 (150)		
27	14	DF	B				20.9	16.05
28	9	ACE		ABDE			57	26.75
29	10	CE	B	ABD			50.35	26.75
30	1	CE	D	ABE			50.35	26.75
31	16	CE		AB	CDEF		100.7	53.5
32	3			C	ABDEF		107.35	53.5
33	28			ACDE	BE		87.4	53.5
34	17				ABCD	E	123.5	80.25
35	20				AD	BCDF	152	80.25
36	36				BCDF	AE	133	80.25

(a) Simulated groundwater was spiked with potassium dichromate. The chromate concentration ($\mu\text{g/mL}$) was estimated by comparison with the reference color chart.

(b) Includes a factor of 1.14 for dilution during sample acidification.

(c) Determined by ICP/MS analysis.

Figure 1. Strip Test Assay for Chromate in Spiked Water.

Table 2. Strip-Test Assay for Chromate in Waste Water Samples

			Chromate Concentration ^(a)				Calculated Conc.	Actual Conc. ^(b)
Sample No.	Sample ID	Test No.	0-3 (1.5)	3-10 (6.5)	10 (20)	30-100 (65)	Conc. corrected for dil. $\mu\text{g/mL}$	Conc. $\mu\text{g/mL}$
1	PERM-1	42		ABCE ^(c)	D		410	
2	PERM-1	17		ABC	DE		4500	
3	FEED-1	36			BD	ACD	36480	
4	FEED-1	9		C	ABDE		2120	
5	CON-1	37				ABCD	25080	
6	CON-1	50			C	ABC	27360	
7	PERM-2	15		ABCE	D	E	251	118
8	PERM-2	16		BE	ACD	DE	274	118
9	FEED-2	26				DE	1642	937
10	FEED-2	30					1961	937
11	CON-2	27				ABC	13680	6690
12	CON-2	8				ABCE	11400	6690
13	PERM-3	53				ABC	137	62
14	PERM-3	2				ABCE	114	62
15	FEED-3	22		ABCE			741	401
16	FEED-3	23	A	BCDE			661	401
17	CON-3	25		A	BCD	E	6441	4237
18	CON-3	14		C	ABDE		6301	4237
19	PERM-4	44			ABCE		114	
20	PERM-4	33			ABCD		13.7	
21	FEED-4	36				E	125	
22	FEED-4	13			ABCD	ABCD	125	
23	CON-4	5	C	ABDE			616	
24	CON-4	24		CDE			1163	
25	PERM-5	40		ABCE	D		8.2	

(a) Concentrations in $\mu\text{g/mL}$. Field samples were diluted so that their chromate concentrations fell within the range of the reference color chart. "Calculated concentrations" are the estimated concentrations of the diluted samples multiplied by the dilution factor.

(b) Determined by ICP/MS analysis

(c) Each strip (one strip per water sample) was independently read by five analysts (ABCDE) as indicated.

Table 2. (Contd)

Sample No.	Sample ID	Test No.	Chromate Concentration ^(a)					Calculated Conc. corrected for dil. $\mu\text{g/mL}$	Actual Conc. $\mu\text{g/mL}$
			0	0.3 (1.5)	3	3-10 (6.5)	10	10-30 (20)	
26	PERM-5	41			ABCE	D		8.2	
27	FEED-5	3			BC	ADE		98	
28	FEED-5	47				ABCE	D	137	
29	CON-5	39			D	ABCE			1322
30	CON-5	46				ABCE	D		1642
31	PERM-6	20					ABC	DE	
32	PERM-6	55				ABCE	AD	ECE	16
33	FEED-6	52				ABCE	D		
34	FEED-6	43			E	ABCE		18	
35	CON-6	29				ABCE		410	
36	CON-6	31				ABCE		370	
37	PERM-7	45				ABCE		3306	
38	PERM-7	10			D	ABCE	D	3705	
39	FEED-7	18						8.2	3.6
40	FEED-7	19					A	6.6	3.6
41	CON-7	48					A	102.6	49
42	CON-7	34					ABC	102.6	49
43	PERM-8	51						1596	825
44	PMER-8	11		C		BC		2508	825
45	FEED-8	28			ADE			5	
46	FEED-8	4			ABDE			3.1	
47	CON-8	7				C	AB	75.8	
48	CON-8	38				C	ABDE	53	
						C	ABDE	1060	
						C	ABD	1288	

(a) Concentrations in $\mu\text{g/mL}$. Field samples were diluted so that their chromate concentrations fell within the range of the reference color chart. "Calculated concentrations" are the estimated concentrations of the diluted samples multiplied by the dilution factor.

(b) Determined by ICP/MS analysis

Table 2. (Contd)

Sample No.	Sample ID	Test No.	Chromate Concentration ^(a)					Calculated Conc. corrected for dil. $\mu\text{g/mL}$	Actual Conc. ^(b) $\mu\text{g/mL}$
			0	0.3 (1.5)	3 (6.5)	10 (20)	30		
49	SGW	49	ABCD					0	
50	SGW	32	ABCD					0	
51	SGW	1	ABCD					0	
52	SGW	6	ABCD					0	
53	SGW	56	ABCD					0	
54	SGW	21	ABCD					0	
55	SGW	12	ABCD					0	
56	SGW	54	ABCD					0	

(a) Concentrations in $\mu\text{g/mL}$. Field samples were diluted so that their chromate concentrations fall within the range of the reference color chart. "Calculated concentrations" are the estimated concentrations of the diluted samples multiplied by the dilution factor.

(b) Determined by ICP/MS analysis.

Figure 2. Strip Test Assay for Chromate in Waste Water

MS210^(a)**An Indicator Strip-Based Colorimetric Test for Lead (Pb²⁺) in Water****1.0 Scope and Application**

This is a field screening method to be used to test aqueous samples for ionic lead {Merckoquant[®] 10077 (E. Merck, Frankfurter Strasse 250, D-6100 Darmstadt 1, Germany), EM Science - supplier (E. M. Science, 480 Democrat Road, Gibbstown, New Jersey 08027)}. It does not detect organic forms of lead. Because of its measuring range {20 to 500 µg/mL (ppm)}, the test is not suitable for checking compliance with drinking water and discharging limits. Nevertheless, the kit is still useful in the field for rapidly identifying highly contaminated surface and groundwaters. Another valuable use of this and other strip tests is in the laboratory to determine an appropriate dilution of water samples to be used for their analysis by more standard laboratory methods, thereby eliminating costly reruns.

2.0 Summary of Method

The basis for this test is that in acidic solution, lead ions react with rhodizonic acid to form a red-colored complex. The intensity of the color is proportional to the amount of Pb²⁺ in the sample. In practice, 5 mL of the test sample are adjusted to a pH of 2 to 5 with the reagent (acetic acid) supplied. The rhodizonic acid-impregnated reaction zone of the test strip is wetted by brief immersion in the sample, removed, and "blotted" to remove excess liquid. The orange-colored reaction zone changes to white for <15 µg/mL (ppm) lead or to varying shades of red if the lead content is in the 15 to 500 µg/mL (ppm) range. After 2 min, the lead content of the sample is estimated by comparing the color of the strip with a standard color chart. The intensity of the color increases in proportion to the lead concentration in the range of 15 to 500 µg/mL (ppm).

3.0 Interferences

Merck (Merckoquant[®] 10077 Lead Test Instructions) has determined that there are no interferences by the following anions at less than

- 1000 µg/mL (ppm): Br⁻, BrO₃⁻, BO₃²⁻, Cl⁻, ClO₃⁻, ClO₄⁻, CO₃²⁻, CN⁻, CrO₄²⁻, F⁻, I⁻, MoO₄²⁻, NO₂⁻, NO₃⁻, OCN⁻, PO₄³⁻, P₂O₇⁻, SCN⁻, SO₄²⁻, S₂O₃²⁻, S₂O₈²⁻, SeO₃²⁻, WO₄²⁻, acetate, ascorbate, citrate, tartrate

(a) This method was supplied by L. C. Waters, R. A. Jenkins, R. R. Smith, R. W. Counts and J. H. Stewart (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

- 100 µg/mL (ppm): IO_3^- , oxalate
- 10 µg/mL (ppm): S^{2-} , SO_3^{2-}

and cations at less than:

- 1000 µg/mL (ppm): Al^{3+} , As^{3+} , Ca^{2+} , Cd^{2+} , Cr^{3+} , Co^{2+} , Hg^{2+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Na^+ , NH_4^+ , Ni^{2+} , Rb^+ , Sb^{3+} , Te^{4+} , Tl^{3+} , V^{5+} , Zn^{2+} , Zr^{4+}
- 300 µg/mL (ppm): Ag^+ , Be^{2+} , Bi^{3+} , Sn^{2+} , Ti^{4+} , Fe^{2+}
- 100 µg/mL (ppm): Ce^{3+} , Cu^{2+} , Sr^{2+} , Fe^{3+}
- 10 µg/mL (ppm): Ba^{2+}

Although these ions apparently do not produce colors that would interfere with that produced by lead, several of the anions do produce relatively insoluble precipitates with lead and in that sense would have interfered by removing lead from the sample (see section 9.0). Very acidic solutions interfere with the test by discoloring the reaction zone of the strip (see section 8.0).

4.0 Apparatus and Materials

- 4.1 Timer
- 4.2 Pipettes. Plastic, disposable, 5 or 10 mL, with filler bulb to measure water sample volume
- 4.3 Test tubes. Plastic, disposable, 13 x 100 mm (Falcon 2027 or equivalent)
- 4.4 Permanent ink marking pen. For labeling test strips and tubes
- 4.5 pH paper (0 to 14 range). For measuring pH of test sample
- 4.6 Merckoquant[®] (10077 Lead Test Kit)
 - Instructions: Supplied with kit
 - Sampling vessel: Marked at 5 mL (Disposable tubes and a 2 mL volume should be used when multiple samples are being tested—see 7.2.)
 - Test strips (100): Impregnated with rhodizonic acid

- Reagent (5% acetic acid): For acidifying test samples
- Color chart: This chart, permanently affixed to the test strip container, provides reference hues for values of 0, 20, 40, 100, 200, and 500 $\mu\text{g/mL}$ (ppm).

5.0 Reagents

Except in cases of strongly acidic or basic samples, all required reagents are included in the test kit. In these cases, the samples should be adjusted with 1 N NaOH or 1 N HNO_3 , as required, to pH 2 to 5 before testing.

6.0 Sample Collection, Preservation, and Handling

The test is designed to be performed in the field. Because the samples are not modified, except for pH adjustment, they may be disposed of at their collection source. Samples that are tested away from their collection source and are positive for lead and/or are corrosive, as judged by pH, should be handled and disposed of as hazardous wastes.

7.0 Procedure (Merckoquant® 10077 Lead Test Instructions)

7.1 Single Samples

- 7.1.1 Five milliliters of the solution to be tested are added to the measuring vessel.
- 7.1.2 The sample is adjusted to pH 2 to 5 by the dropwise addition of acetic acid reagent, 1 N NaOH or 1 N HNO_3 as required (pH paper should be used for monitoring).
- 7.1.3 The test strip is immersed into the sample until the reaction zone is thoroughly moistened (about 1 sec). The excess liquid is removed by wiping the test strip against the sample vessel rim.
- 7.1.4 After 2 min, the color of the reaction zone should be compared with the color chart. (If significant dilution is involved during pH adjustment, this should be taken into account in the final estimate of lead concentration in the sample.)

- 7.2 **Multiple Samples.** In situations where multiple samples or replicates of single samples are to be tested, an alternate procedure is suggested.

- 7.2.1 An appropriate number of plastic, disposable tubes, 13 x 100 mm, and a corresponding number of test strips are labeled using a permanent-ink marker.
- 7.2.2 Two milliliters of the solutions to be tested are added to the tubes.
- 7.2.3 One drop of reagent is added to each tube and mixed. (The recommendation in section 7.1.2 should be followed if the pH of the samples is outside the 2 to 5 range at this point.)
- 7.2.4 The strip test should be performed as indicated in sections 7.1.3 and 7.1.4. The results should be read as quickly as possible after the 2-min reaction period. (Consistent readings are obtained when made within a 30-min time period.)

8.0 Quality Control

Samples of test strips from each batch should be tested using solutions of known lead concentration. Batches that do not produce true colors should not be used. Likewise, test samples that do not produce true colors should be suspected of containing interferants. For example, strips used to test lead-containing water samples whose acidity is below pH 2 will be red at the edges, but faded dramatically in the centers.

9.0 Method Performance

Spiked water samples were used to evaluate this method. Attempts to locate contaminated field samples for use in the evaluation were unsuccessful. Stock solutions of lead acetate, at a nominal concentration of 1000 µg/mL (ppm) Pb^{2+} , were made in either deionized water (DW) or simulated groundwater (SGW). Simulated groundwater is DW to which 0.165 g/L of sodium chloride and 0.148 g/L of sodium sulfate has been added {contains 100 µg/mL (ppm) each of SO_4^{2-} and Cl^- } (Rocky Mt. 1989). Soluble lead in the DW and SGW stocks was determined by inductively coupled plasma (ICP) assay to be 1100 and 900 µg/mL (ppm), respectively.

Dilutions to be tested were made in the same type water as was used to make the stocks. Duplicate 2-mL samples were added to 13- x 100-mm tubes, acidified, randomized, and tested using test strips as described in section 7.2. Four to six analysts independently read the strips and recorded the concentration with reference to the color chart. The lead concentrations defined by the color chart are 0, 20, 40, 100, 200, and 500 µg/mL (ppm). Analysts also used increments between and above these values. To evaluate the accuracy of the method, numerical values were assigned to the results from each strip as follows: a result of 20 µg/mL (ppm) was given the value 20; a result of 20 to 40 was given the value

30, and so on. A result of >500 was arbitrarily given the value 550. The values were summed and averaged to give the data presented in Table 1 and Figure 1.

Several conclusions can be made about the strip-test assay for lead as tested in DW:

1. False positive results are rare; only 2 of 32 analyses were positive in assays of unspiked DW (and SGW).
2. Samples at 20 $\mu\text{g/mL}$ (ppm) or greater consistently tested positive.
3. Above 30 to 40 $\mu\text{g/mL}$ (ppm), the actual concentrations of lead are overestimated by the test.

The results observed in SGW are obviously complicated because lead is removed from the sample by the precipitation of lead sulfate {e.g., 20 $\mu\text{g/mL}$ (ppm) tested negative}. Because it is unlikely that equilibria between precipitation and solubilization of lead sulfate were reached in any of these samples, it would be nonproductive to attempt to explain the shape of the concentration curve obtained. Suffice it to say that it is consistent with the expected decrease in the amount of soluble lead in the sample, particularly at the lower concentrations.

Taken together with the manufacturer's claims concerning the lack of interferences by a wide variety of inorganic ions, this method appears to be a rapid and effective field method for screening water samples that contain lead at $\geq 20 \mu\text{g/mL}$ (ppm).

Because the method does overestimate the lead content of water throughout most of the concentration range, an appropriate use of the method would be to have standard lead solutions (with concentrations set at the action level desired) and to directly compare the color produced by the test samples with that of the known standards. In this way, the lead content of the field sample can be defined relative to the level of concern.

Assay sensitivity and range: Lead ions at $\geq 20 \mu\text{g/mL}$ (ppm) were consistently detected. A 15 $\mu\text{g/mL}$ (ppm) sample was determined to be positive in about 50% of the tests. Ten-ppm samples always tested negative. The working range of the test is 20 to 500 $\mu\text{g/mL}$ (ppm).

10.0 Reference

Rocky Mountain Arsenal. 1989. *Chemical Quality Assurance Plan*. Section 4-7, Commerce City, Colorado 80022-2180.

Table 1. Strip Test Assay for Lead in Water

Sample No.	Test No.	Nominal µg/mL (ppm)	Actual(b) µg/mL (ppm)	Calculated µg/mL (ppm)	Average µg/mL (ppm)	Lead Concentration(a)			
						0	0-20 (10)	20-40 (30)	40-100 (70)
In deionized water									
1	15	0	0	1.7		ABCEG	F		
2	14	0	0	0		ABCEG			
3	9	0	0	0		ABCEG			
4	12	0	0	0	0.4	ABCEG			
5	18	10	11	0	0	ABCEG			
6	16	10	11	0	0	ABCEG			
7	5	15	16.5	5	0	ABCEG	BDF		
8	10	15	16.5	3.3	4.2	ACE	AF		
9	23	20	22	10		BCDE	ABCEG		
10	21	20	22	10	10	BCDE	ABCEG		
11	6	30	33	30				ABCEG	
12	13	30	33	43.7	30.8			ABCEG	
13	22	40	44	41.7				ABCEG	
14	4	40	44	63.3	52.5			ABCEG	
15	20	75	82.5	136.7				ABCEG	
16	24	75	82.5	145	140.8			ABCEG	
17	47	100	110	203.3				ABCEG	
18	19	100	110	128.3	165.8			ABCEG	

(a) The lead concentration (ppm) was estimated by comparing the test strip color with the reference color chart.

(b) Determined by ICP.

(c) Each test strip (one strip per water sample) was independently read by 4 or 6 analysts (A, B, C, D, E, F) as indicated.

Table 1. (contd)

Sample No.	Test No.	Nominal µg/mL (ppm)	Actual ^(b) µg/mL (ppm)	Calculated µg/mL (ppm)	Average µg/mL (ppm)	Lead Concentration (a)			
						100 (150)	100-200	200 (350)	200-500
In deionized water									
14	4	40	44	41.7		B ^(c)			
15	20	75	82.5	136.7		E	ACD	B	
16	24	75	82.5	145	140.8	E	AD	BC	
17	17	100	110	203.3				ABDE	
18	19	100	110	128.3	165.8	D,E	AC	B	C
19	1	150	165	291.7			F	E	ABCD
20	11	150	165	258.3	275		BF	D	ACE
21	7	200	220	350					ABCEDEF
22	2	200	220	341.7	345.8		F		ABCE
23	3	300	330	425					ABCE
24	8	300	330	425	425				ABF
									AEF
									B
									BCD
									BCD

(a) The lead concentration (ppm) was estimated by comparing the test strip color with the reference color chart.

(b) Determined by ICP

(c) Each test strip (one strip per water sample) was independently read by 4 or 6 analysts (A,B,C,D,E,F) as indicated.

Table 1 (cont'd)

Sample No.	Test No.	Nominal (µg/mL (ppm))	Actual ^(a) (µg/mL (ppm))	Calculated ^(b) (µg/mL (ppm))	Average (µg/mL (ppm))	Lead Concentration ^(a)
in simulated groundwater						
3	1	0	0	0		0-20 (10)
4	5	0	0	2.5	125	A
7	2	20	18	0		A,B,C,D
8	22	20	18	0	0	A,B,C,D
11	18	40	36	12.5		A,B,C,D
12	15	40	36	15	13.75	C
15	12	100	90	37.5		A,B,D
16	8	100	90	37.5		B,D
						A,C
						A,B,D
						A,B,D
						C
						E
in simulated groundwater						
Sample No.	Test No.	Nominal (µg/mL (ppm))	Actual ^(a) (µg/mL (ppm))	Calculated ^(b) (µg/mL (ppm))	Average (µg/mL (ppm))	Lead Concentration ^(a)
						100 (150)
						100-200 (350)
						200 (350)
						200-500
						500
						>500
19	24	200	180	162.5		A ^(c)
20	9	200	180	162.5	162.5	D
23	13	500	450	512.5		B,C
24	23	500	450	437.5	475	A,B,D
						C
						B
						A,C,D
						C,D
						A

(a) The lead concentration (ppm) was estimated by comparing the test strip color with the reference color chart.

(b) Determined by ICP.

(c) Each test strip (one strip per water sample) was independently read by 4 or 6 analysts (A,B,C,D,E,F) as indicated.

Figure 1. Strip Test Assay for Lead in Water

MS310^(a)**An Indicator Strip-Based Colorimetric Test for Nitrate Ions (NO_3^-) in Water and Soil****1.0 Scope and Application**

This is a field screening method to be used to test aqueous samples and soils for the presence of nitrate {Merckoquant[®] 10020 (E. Merck, Frankfurter Strasse 250, D-6100 Darmstadt 1, Germany); EM Science - supplier (E. M. Science, 480 Democrat Road, Gibbstown, New Jersey 08027)}. It is also a useful method for laboratory use to determine an appropriate dilution of test water samples to be used for their analysis by more standard laboratory methods, thus eliminating costly reruns.

2.0 Summary of Method

The outer reaction zone of the test strip contains a reducing agent that reduces nitrate to nitrite. In the presence of an acid buffer, the nitrite is then converted to nitrous acid, which diazotizes an aromatic amine (sulfanilic acid). The diazotized sulfanilic acid couples with N-[naphthyl(1)]-ethylenediamine (NNEDDC) to produce a red-violet azo dye. In practice, the reaction zone of the test strip is wetted in the test sample, removed, and "blotted" to remove excess liquid. The pale yellow-colored reaction zone changes to white for negative samples and to varying shades of red-violet in the range of 5 to 500 $\mu\text{g/mL}$ (ppm) nitrate. After 1 min, the nitrate content of the sample is estimated by comparing the color of the strip with a standard color chart. The intensity of the color is proportional to the nitrate concentration in the range of 5 to 500 $\mu\text{g/mL}$ (ppm).

Soils are tested by extracting the soil with an equal amount of deionized water and testing the extract as described for aqueous samples.

3.0 Interferences

Merck (Rapid Test Handbook, Merck, pp. 191, 192. 1987) has examined a number of chemicals for their interference in the nitrate test.

Nitrite: As little as 0.5 $\mu\text{g/mL}$ (ppm) nitrite produces a false-positive reaction. The test strip contains two reaction zones. The zone at the very end indicates both nitrate and nitrite, while the other reacts only to nitrite. A pink to red-violet coloration in the latter zone indicates the presence of nitrite, which interferes with the nitrate determination. Interference by nitrite can be eliminated by mixing 1 mL of test sample solution ($\text{pH} < 10$) with one drop of an aqueous 10%

(a) This method was supplied by L. C. Waters, R. A. Jenkins, R. R. Smith, R. W. Counts and J. H. Stewart (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

amidosulfonic acid solution. The solution is shaken several times and then tested for nitrate after 2 min as described in the procedure (section 7.0). This method allows the detection of 10 µg/mL (ppm) nitrate in the presence of 1000 µg/mL (ppm) nitrite.

Other anions: At concentrations less than 1000 µg/mL (ppm) Br⁻, BrO₃⁻, Cl⁻, ClO₃⁻, ClO₄⁻, CN⁻, F⁻, I⁻, Mo₇O₂₄⁶⁻, N₃⁻, OCN⁻, PO₄³⁻, SO₄²⁻, SeO₃²⁻, WO₄²⁻, acetate, ascorbate, citrate, oxalate, succinate, and tartrate do not interfere. In the presence of more than 100 µg/mL (ppm) [Fe(CN)₆]⁴⁻, 25 µg/mL (ppm) S²⁻, 100 µg/mL (ppm) SCN⁻, 500 µg/mL (ppm) SO₃²⁻, 250 µg/mL (ppm) S₂O₃²⁻, 100 µg/mL (ppm) S₂O₄²⁻, or 250 µg/mL (ppm) S₂O₅²⁻, the nitrate concentration indicated is less than that actually present. Oxidizing anions turn the reaction zone light brown to orange brown. This type of interference is caused by more than 20 µg/mL (ppm) CrO₄²⁻, 100 µg/mL (ppm) [Fe(CN)₆]³⁻, 500 µg/mL (ppm) IO₃⁻, 10 µg/mL (ppm) MnO₄⁻, 100 µg/mL (ppm) S₂O₈²⁻, or 25 µg/mL (ppm) VO₃⁻. These interferences can be largely overcome by adding approximately 50 mg of hydrazine sulfate to 5 mL of test sample solution, mixing and testing according to the procedure (section 7.0). The quantity of nitrate indicated will, however, be less than is actually present.

Cations: At concentrations less than 1000 µg/mL (ppm), the following cations do not interfere: Al³⁺, As³⁺, Ba²⁺, Ca²⁺, Co²⁺, Cr³⁺, K⁺, Li⁺, Mg²⁺, Mn²⁺, Na⁺, Ni²⁺, Pb²⁺, Rb⁺, Sb³⁺, Sn²⁺, Ti⁴⁺, and Zn²⁺. The color is less intense in the presence of more than 500 µg/mL (ppm) Fe²⁺, 50 µg/mL (ppm) Fe³⁺, 50 µg/mL (ppm) VO²⁺, or 500 µg/mL (ppm) Zr⁴⁺. More than 50 µg/mL (ppm) Ag⁺, 50 µg/mL (ppm) Hg⁺, or 100 µg/mL (ppm) Hg²⁺, interferes by turning the reaction zone grey.

pH: The test is independent of pH in the range of 1 to 12. More strongly acidic solutions should be buffered with sodium acetate and more strongly basic solutions with tartaric acid.

4.0 Apparatus and Materials

- Timer: Capable of measuring in seconds
- Pipettes: Plastic 5- or 10-mL disposables with filler bulb to measure water sample volume
- Test tubes, plastic, disposable, 13 x 100 mm (Falcon 2027 or equivalent)
- Permanent ink marking pen: For labeling test strips and tubes
- pH paper (0 to 14 range): For measuring pH of test sample
- Merckoquant® 10020 Nitrate Test Kit (E. Merck, Frankfurter Strasse 250, D-6100 Darmstadt 1, Germany E. M. Science, 480 Democrat Road, Gibbstown, New Jersey 08027):

- Instructions: Supplied with kit.
- Test strips (100): Impregnated with nitrate-specific color reagents. A separate reaction zone indicates whether nitrite is present.
- Color chart: This chart, permanently affixed to the test strip container, provides reference hues for values of 0, 10, 25, 50, 100, 250, and 500 $\mu\text{g/mL}$ (ppm). A separate chart provides an indication of the amount of nitrite present.

5.0 Reagents

Except in cases of strongly acidic or basic samples, all required reagents are included in the test kit (section 4.0). In these cases, the samples should be adjusted as indicated in section 3.0.

6.0 Sample Collection, Preservation, and Handling

The test is designed to be performed in the field. Because the samples are not modified, they may be disposed of at their collection source.

7.0 Procedure (Merckoquant® 10020 Nitrate Test Instructions)

7.1 Single Samples

- 7.1.1 Two to three milliliters of the solution to be tested are added to a clean test tube.
- 7.1.2 The pH is tested with pH paper. If outside the 1 to 12 range, an adjustment should be made to that range with sodium acetate or tartaric acid (section 3.0, paragraph 5).
- 7.1.3 The test strip is immersed into the sample until the reaction zone is thoroughly moistened (about 1 sec). The excess liquid is removed by wiping the test strip against the test-tube rim.
- 7.1.4 After 1 min, the color of the reaction zone at the very end of the strip should be compared with the color chart. Coloration of the second reaction zone indicates nitrite, which must be removed from the sample to obtain an accurate measure of nitrate (section 3.0, paragraph 2). (If significant sample dilution has occurred during pH adjustment, this should be taken into account in the final estimate of the nitrate concentration in the sample.)

7.2 Multiple Samples: In situations where multiple samples or replicates of single samples are to be tested, an alternate procedure is suggested.

7.2.1 An appropriate number of disposable, plastic tubes and a corresponding number of test strips should be labeled using a permanent-ink marker.

7.2.2 Two to three milliliters of the solutions to be tested are added to the tubes.

7.2.3 The pH is tested and adjusted as required.

7.2.4 The strip test is performed as indicated in sections 7.1.3 and 7.1.4. The strip should be read as quickly as possible after the 1-min reaction period. (Consistent readings are obtained when made within a 30-min time period.)

8.0 Quality Control

Samples of test strips from each batch should be tested using solutions of known nitrate concentration. Batches that do not produce true colors should not be used. Likewise, test samples that do not produce true colors should be suspected of containing interferants.

9.0 Method Performance

9.1 Spiked and naturally contaminated water samples were used to evaluate this method. A stock solution of sodium nitrate, at a nominal concentration of 1000 $\mu\text{g/mL}$ (ppm), was made in simulated groundwater (SGW) {deionized water to which 0.165 g/L of sodium chloride and 0.148 g/L of sodium sulfate has been added (contains 100 $\mu\text{g/mL}$ [ppm] each of SO_4^{2-} and Cl^-) (Rocky Mtn. 1989)}. Nitrate in the stock solution was determined by ion chromatography to be 1050 $\mu\text{g/mL}$ (ppm). Results of tests made using deionized water were essentially identical to those presented below using SGW.

Test solutions were made by diluting the stock solution to various concentrations with SGW. Triplicate 2.5-mL samples were added to 13- x 100-mm tubes (a single sample was used to test the 1:10 dilutions of contaminated water). The samples were randomized and tested using the test strips as described in section 7.2. Four or five analysts independently read the strips and recorded the concentrations with reference to the color chart. The nitrate concentrations defined by the color chart are 0, 10, 25, 50, 100, 250, and 500 $\mu\text{g/mL}$ (ppm). Increments between these values were also used. To evaluate the accuracy of the method, numerical values were assigned to the results obtained from each strip as follows: a result of 50 $\mu\text{g/mL}$ (ppm) was given the value 50; a result of 50 to 100 was given the value 75 and so on. The values were summed and averaged to produce the data presented in Tables 1 and 2 and Figures 1 and 2.

Among the conclusions that can be made about the strip-test assay for nitrate in spiked SGW are the following (see Table 1 and Figure 1):

1. False positives occurred at a very low frequency. Two of 52 analyses of blank samples were tested positive (see Tables 1 and 2).
2. Five ppm were consistently distinguished from zero. There were no false-negative results with samples that contained ≥ 5 ppm (Table 1).
3. Below 100 $\mu\text{g/mL}$ (ppm), good agreement existed between the estimates made with the strip test and the results obtained by ion chromatography (Table 1 and Figure 1).
4. Above 200 $\mu\text{g/mL}$ (ppm), the test appears to overestimate the nitrate concentration (Table 1 and Figure 1).
5. Overall with reference to ion chromatography, the strip-test assay gave a best-fit straight line with an $R^2 = 0.959$ and a slope of 1.188 (Figure 1).

The strip-test assay was very accurate in estimating the nitrate content of 10 contaminated water samples (see Table 2 and Figure 2). Only above 350 $\mu\text{g/mL}$ (ppm) did the results deviate significantly from those determined by ion chromatography. Regression analysis of the strip-test data with reference to ion chromatography (Figure 2) gave a best-fit straight line with an $R^2 = 0.972$ and a slope of 0.898. These results clearly indicate the potential of using this test in the laboratory as a prescreen to determine the appropriate sample dilutions to be used in standard laboratory analysis.

Taken together with the manufacturer's claims concerning the lack of interferences by a wide variety of inorganic ions, this method appears to be a rapid and effective field method for screening water samples that contain nitrate at ≥ 5 $\mu\text{g/mL}$ (ppm).

- 9.2 Assay sensitivity and range: Nitrate was consistently detected in samples with ≥ 5 $\mu\text{g/mL}$ (ppm) nitrate. The working range of the test is 5 to 500 $\mu\text{g/mL}$ (ppm).

10.0 Reference

Rocky Mountain Arsenal. 1989. *Rocky Mountain Arsenal Chemical Quality Assurance Plan*, section 4-7. Commerce City, Colorado 80022-2180.

Table 1. Strip Test Assay for Nitrate in Spiked Water

					Nitrate Concentration (a)						
Sample No.	Test No.	Actual Conc. µg/mL (ppm)	Calculated Conc. µg/mL (ppm)	Average Conc. µg/mL (ppm)	0	0-10 (5)	10	10.25 (17.5)	25	25-50 (37.5)	50
Experiment I											
1	27	0	0	A,B,C,D ^(b)	A,B,C,D						
2	34	0	0		A,B,C,D						
3	36	0	0		A,B,C,D						
4	10	0	12	B	A,C,D						
5	23	0	12		A,C,D						
6	5	0	0	A,B,C,D	A,B,C,D						
7	37	525	88		A,B,C,D						
8	35	525	5	A,B,C,D	A,B,C,D						
9	29	525	5		A,C,D						
10	13	10.5	62	B	A,C,D						
11	21	10.5	5		A,B,C,D						
12	24	10.5	62	A,C,D	A,C,D						
13	26	21	138		A,B						
14	20	21	17.5	C	C						
15	14	21	17.5		A,D						
16	16	31.5	19.4	A	A						
17	1	31.5	34.4		B,D						
18	39	31.5	21.2	C,D	C,D						
19	9	52.5	40.6		B,D						
20	22	52.5	40.6	A,C	A,C						
21	6	52.5	34.4		D						
22	19	78.75	68.8	C	A,B,D						
23	18	78.75	68.8		A,B,D						

(a) The nitrate concentration (µg/mL) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography.

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

(a) The nitrate concentration (µg/mL) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography.

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

Table 1. (contd)

Sample No.	Test No.	Actual Conc. (b) ($\mu\text{g/mL}$)	Calculated Conc. ($\mu\text{g/mL}$)	Average Conc. ($\mu\text{g/mL}$)	Nitrate Concentration (a)				
					50-100 (75)	100 (175)	100-250 (175)	250 (375)	500 (375)
Experiment-1									
22	19	78.75	68.8		A,B,D				
23	18	78.75	65.6		A	D			
24	7	78.75	100	78.1	A,C,D		B		
25	33	105	93.8		A	B,C,D			
26	12	105	93.8		A	B,C,D			
27	38	105	93.8	93.8	A	B,C,D			
28	31	210	193.8				A,B,D	C	
29	25	210	293.8				A	B,D	
30	11	210	231.2	239.6			A	B,C,D	
31	28	262.5	387.5				A		D
32	4	262.5	312.5					A,C	
33	32	262.5	375	358.3				B,D	C
34	30	420	437.5					B	B,C
35	3	420	437.5					A,D	B,C
36	8	420	468.8	447.9				A,D	B,C,D
								A	

(a) The nitrate concentration ($\mu\text{g/mL}$) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

(a) The nitrate concentration ($\mu\text{g/mL}$) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

Table 1. (contd)

		Nitrate Concentration (µ)																
		Actual (b) Conc.		Calculated Conc.		Average Conc.												
Sample No.	Test No.	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	0	0-10	10	10-25	25	25-50	50				
Experiment 2																		
1	8	0	0	0	0	0	0	A,B,C,D	(5)	(17.5)	(37.5)							
2	2	0	0	0	0	0	0	A,B,C,D										
3	7	10.5	8.8	8.8	8.8	8.8	8.8	D	A,B,C									
4	12	10.5	6.2	6.2	6.2	6.2	6.2	A,B,D	C									
5	4	52.5	45	45	45	45	45				D		G	B				
6	3	52.5	32.5	32.5	32.5	32.5	32.5				D		C	A				
7	6	105	131.2	131.2	131.2	131.2	131.2						B	A				
8	11	105	84.4	84.4	84.4	84.4	84.4						D					
		Nitrate Concentration (µ)																
		Actual (b) Conc.		Calculated Conc.		Average Conc.												
Sample No.	Test No.	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	50-100	100	100-250	250	250-500	500					
Experiment 2																		
5	4	52.5	45	45	45	45	45	(75)	(175)	(375)								
6	3	52.5	32.5	32.5	32.5	32.5	32.5	A										
7	6	105	131.2	131.2	131.2	131.2	131.2	D	C	A,B								
8	11	105	84.4	84.4	84.4	84.4	84.4	A,B,C			D							
9	1	262.5	325	325	325	325	325	D										
10	5	262.5	406.2	406.2	406.2	406.2	406.2					A,B,C						
														A,B,C	B			

(a) The nitrate concentration (µg/mL) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

(a) The nitrate concentration (µg/mL) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

Figure 1. Strip-Test Assay for Nitrate in Spiked Water.
Strip test versus ion chromatography.

Table 2. Strip Test Assay for Nitrate in Contaminated Water

Sample No.	Sample ID	Test No.	Actual Conc.		Calculated Average Conc.		Nitrate Concentration (a)			
			µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	µg/mL (ppm)	0	0-10 (5)	250-500 (17.5)	500 (37.5)
1	SGW46	36	0	0	0	0	A,B,C,D,E (c)			
2	SGW	4	0	0	0	0	A,B,C,D,E			
3	SGW	21	0	0	0	0	A,B,C,D,E			
4	125	10	2835	0	0	0		A		B,C,D,E
5	125	14	2835	475	475	475		A		B,C,D,E
6	125	33	2835	475	475	475				
7	126	9	3082	500	500	500				A,B,C,D,E
8	126	15	3082	450	450	450			A,D	B,C,E
9	126	24	3082	475	475	475			A	B,C,D,E
10	127	18	3545	450	450	450		A,D		B,C,E
11	127	30	3545	450	450	450		A,C		B,D,E
12	127	13	3545	475	475	475		A		B,C,D,E
13	128	1	2722	475	475	475		A		B,C,D,E
14	128	23	2722	475	475	475		A		B,C,D,E
15	128	9	2722	475	475	475		A		B,C,D,E
16	129	17	2738	475	475	475		A		B,C,D,E
17	129	29	2738	475	475	475		A		B,C,D,E
18	129	12	2738	425	425	425		A		B,C,D,E
28	133	19	224	0	0	0	A,B,C,D,E		A,C,D	B,E
29	133	5	224	0	0	0	A,B,C,D,E			
30	133	16	224	0	0	0	A,B,C,D,E			
42	SGW	42	0	0	0	0	A,B,C,D,E			

(a) The nitrate concentration (µg/mL) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

Table 2. (contd)

Sample No.	Sample ID	Test No.	Actual (b)		Average Conc.	Nitrate Concentration (a)					
			Conc. $\mu\text{g/mL}$ (ppm)	Conc. $\mu\text{g/mL}$ (ppm)		25-50 (37.5)	50 (7.5)	100 (17.5)	250 (175)	250-500 (375)	500
19	130	11	179.4	185		A			DE	BC	
20	130	7	179.4	170	179		CDE	B			
21	130	2	179.4	190					A,CDE	B	
22	131	28	350.9	335							
23	plus sed(d)	6	350.9	360			A				
24	plus sed(d)	8	350.9	335	343				A		
25	132	31	456.9	360					A		
26	132	26	456.9	385					A		
27	132	35	456.9	385	379				A		
31	134	22	142	155					A		
32	134	25	142	140					CE	B	
33	134	34	142	140	145				B,CB		
34	131	27	350.9	340					B,CB		
35	minus sed(4)	32	350.9	360							
36	minus sed(d)	20	350.9	375							
37	125 dil 1:10	37	141.7	140							
38	minus sed(4)	38	154.1	175					A		
39	127 dil 1:10	39	177.2	190					A,B,C		
40	128 dil 1:10	40	136.1	125					A,CB		
41	129 dil 1:10	41	136.9	160					A,CDE		
									B,C		
									CE		

(a) The nitrate concentration ($\mu\text{g/mL}$) (ppm) was estimated by comparison of the test strip color with the reference color chart.

(b) Determined by ion chromatography

(c) Each test strip (one strip per water sample) was independently read by four evaluators (A,B,C,D) as indicated.

Figure 2. Strip-Test Assay for Nitrate in Contaminated Water.
Strip test versus ion chromatography.

MS410^(a)**An Indicator Strip-Based Colorimetric Test for Nickel (Ni²⁺) in Aqueous Samples**

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This field screening method is suitable for analyzing aqueous samples, e.g., waste water, for the presence of nickel {Merckoquant[®] 10006; Merck; EM Science - supplier (E. Merck, Frankfurter Strasse 250, D-6100 Darmstadt 1, Germany; E. M. Science, 480 Democrat Road, Gibbstown, New Jersey 08027)}. It may also be useful in the laboratory for estimating the proper dilution for solutions to be analyzed by standard methods. This would eliminate costly reruns.

2.0 Summary of Method

The strip test is based on the reaction of nickel (Ni²⁺) ions with dimethylglyoxime to form a bright-red complex. The reaction proceeds practically quantitatively if the resulting hydrogen ions are taken up by a buffer. The accuracy of the detection is independent of the pH of the test sample in the range of 2 to 7. In general, the pH is determined using pH paper and is adjusted only if it is outside the mentioned range. The test strip is immersed briefly in the solution to be tested, making sure that the reaction zone is completely wetted. Excess liquid is removed by touching the walls of the test tube with the edge of the strip. The pale beige-colored reaction zone changes to white for negative samples and to various shades of pink-red in the range of 5 to 500 µg nickel/mL. After 30 sec, the reaction zone is compared with the color chart. The intensity of the color is proportional to the nickel concentration up to 500 µg/mL. Nickel at concentrations ≥5 µg/mL is detected by the test. The working range of the test is 5 to 500 µg/mL.

3.0 Interferences

Merck (Rapid Test Handbook, Merck, pp. 191, 192. 1987) has examined a number of chemicals for their interference in the nickel test.

(a) Method submitted by L. C. Waters, R. Jenkins, and L. J. Hernandez (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

Other cations: At a concentration of less than 1000 $\mu\text{g/mL}$, Ag^+ , Al^{3+} , Au^{3+} , Ba^{2+} , Be^{2+} , Bi^{3+} , Ca^{2+} , Cd^{2+} , Ce^{4+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , K^+ , Li^+ , Mg^{2+} , Mn^{2+} , Mo^{2+} to Mo^{5+} , NH_4^+ , Na^+ , Pb^{2+} , Rb^+ , Sb^{3+} , Sn^{2+} , Sr^{2+} , Ti^{4+} , Ti^+ , VO^{2+} , Zn^{2+} , and Zr^{4+} do not interfere with the determination. Some ions may cause the resulting color of the reaction zone to differ from the color scale. If after 1 min, the correlation is still impossible, then the ions should be masked as follows, then tested. Reagents are added in mg amounts (a spatula tip).

If color is	it has more than	and it should be masked by
Orange/brown	4500 $\mu\text{g/mL}$ Fe^{3+}	adding potassium fluoride
Orange	4000 $\mu\text{g/mL}$ Cu^{2+}	adding sodium thiosulfate
Yellow	750 $\mu\text{g/mL}$ Hg^{2+}	adding sodium chloride
Gray	220 $\mu\text{g/mL}$ Hg^+	adding sodium chloride
Yellow/brown	50 $\mu\text{g/mL}$ Co^{2+}	bathing in 10% ammonia solution
Blue	traces of Molybdenum blue	adding potassium permanganate until a pink color persists.

These masking reagents may be purchased from Merck.

Anions: The determination is not disturbed by less than 1000 $\mu\text{g/mL}$ Br^- , BrO_3^- , Cl^- , ClO_3^- , ClO_4^- , CrO_4^{2-} , F^- , I^- , IO_3^- , IO_4^- , MnO_4^- , $\text{Mo}_7\text{O}_{24}^{6-}$, N_3^- , NO_2^- , NO_3^- , OCN^- , PO_4^{3-} , SCN^- , SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_4^{2-}$, $\text{S}_2\text{O}_5^{2-}$, $\text{S}_2\text{O}_8^{2-}$, SeO_3^{2-} , VO_3^- , WO_4^{2-} , acetate, ascorbate, succinate, tartrate, oxalate (read after 1 min) or citrate (read after 1 min), less than 50 $\mu\text{g/mL}$ CN^- , or less than 10 $\mu\text{g/mL}$ $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Fe}(\text{CN})_6]^{4-}$. The following ions form complexes with Ni^{2+} that are destroyed in the usual manner by fuming with concentrated sulfuric acid: CN^- , $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$.

4.0 Safety

Nickel is a known health hazard. Consequently, gloves and protective clothing should be worn when handling samples suspected to contain nickel.

5.0 Apparatus and Materials

- 5.1 Timer. Capable of measuring in sec
- 5.2 Pipettes. Plastic 5- or 10-mL disposable with filler bulb to measure water sample volume
- 5.3 Test tubes. Plastic, disposable, 13 x 100 mm (Falcon 2027 or equivalent)
- 5.4 Permanent-ink marking pen. For labeling test strips and tubes
- 5.5 pH paper (0 to 14 range). For measuring pH of test sample

5.6 Merckoquant® 10006 Nickel Test Kit:

- Instructions. Supplied with kit
- Test strips (100). Impregnated with nickel-specific color reagents
- Color chart. Permanently affixed to the test-strip container (provides reference hues for values of 0, 10, 25, 100, 250, and 500 ppm)

6.0 Reagents

Except in cases of strongly acidic solutions, all required reagents are included in the test kit. In these cases ($\text{pH} < 2$), the solutions should be buffered with sodium acetate.

7.0 Sample Collection, Preservation, and Handling

The test is designed to be used in the field. Because the samples are not modified, they may be disposed of where they were collected.

8.0 Procedure (Merckoquant® 10006 Nickel Test Instructions)

8.1 Single Samples

- 8.1.1 Two to three milliliters of the solution to be tested are added to a clean test tube.
- 8.1.2 The pH is tested with pH paper. The accuracy of the determination is independent of the pH value of the test solution in the range 2 to 7. If strongly acidic ($\text{pH} < 2$), sodium acetate is added.
- 8.1.3 The test strip is immersed into the sample for at least 10 sec. The excess liquid is removed by wiping the test strip against the test-tube rim.
- 8.1.4 After 30 sec, the reaction zone is compared with the color chart. If the nickel concentration exceeds 500 $\mu\text{g/mL}$, the sample is diluted until the red color produced is within the range of the color chart. Significant sample dilution should be taken into account in the final estimate of the nickel concentration in the sample.

- 8.2 **Multiple Samples:** An alternate procedure to be used when multiple samples or replicates of single samples are being tested.

- 8.2.1 An appropriate number of disposable plastic tubes and a corresponding number of test strips are labeled using a permanent-ink marking pen.
- 8.2.2 Two or three milliliters of the solutions to be tested are added to the tubes.
- 8.2.3 The pH is tested and adjusted as required.
- 8.2.4 The strip test is performed as indicated in sections 8.1.3 and 8.1.4. The test strip should be read as quickly as possible (even though the color is stable for at least a week, it does fade somewhat as it dries).

9.0 Calculations

The nickel concentrations defined by the color chart are 0, 10, 25, 100, 250, and 500 µg/mL. Assignments between those values can also be made. To evaluate the sensitivity and accuracy of the method, numerical values are assigned to the results obtained from each strip as follows: a result of 10 µg/mL was given the value 10, a result of 10 to 25 was given the value of 17.5, and so on. Assignments greater than 500 were arbitrarily given the value 550. The values were summed and averaged to generate the calculated concentrations of nickel in the samples. Because the samples being tested in this evaluation were within the 2 to 7 pH range and were not otherwise diluted, corrections for dilutions were not necessary.

10.0 Quality Control

Samples of test strips from each batch should be tested using solutions of known nickel concentration. Batches that do not produce true colors should not be used. Test samples that do not produce true colors must be suspected of containing interferants.

11.0 Method Performance

Spiked water samples were used to evaluate this method. Efforts to locate contaminated field samples appropriate for use in evaluating the method were unsuccessful. A stock solution of nickel chloride, at a nominal concentration of 1000 µg/mL, was made in simulated groundwater (SGW) {deionized water to which 0.165 g/L of sodium chloride and 0.148 g/L of sodium sulfate has been added, and therefore contains 100 µg/mL of each SO_4^{2-} and Cl^- (Rocky Mtn. 1989)}. Nickel in the stock solution was determined by inductively coupled plasma/mass spectrometry (ICP/MS) analysis to be 940 µg/mL.

Test solutions were made by diluting the stock solution to various concentrations with SGW. Triplicate and duplicate 1.5-mL samples (in experiments 1 and 2, respectively) were added to 13-

x 100-mm tubes. The samples were randomized and tested using the test strips as described in section 8.2. Seven or eight analysts independently read the strips and recorded the concentrations with reference to the color chart. The nickel concentrations defined by the color chart are 0, 10, 25, 100, 250, and 500 $\mu\text{g/mL}$. Samples with concentrations between these values were also used. To measure the accuracy of the test, numerical values were assigned to every analysis. That is, if a test strip was read as having a concentration of 25 $\mu\text{g/mL}$, it was given a value of 25, and a reading between 25 and 100 was given a value of 62.5. This system of averaging was applied to all samples. The averaged values for the combined experiments are presented in Table 1. A graphic comparison of the results obtained with the strip-test assay with those obtained by ICP/MS analysis is shown in Figure 1.

Some conclusions that can be made about the strip-test assay for nickel in spiked SGW include the following (refer to Table 1 and Figure 1):

1. At $\geq 5 \mu\text{g/mL}$, no false negatives were observed.
2. False positives were infrequent. Only 2 out of 74 analyses of negative samples were positive.
3. There was a good correlation between strip-test estimates and actual concentrations in the samples.
4. Statistically, and with reference to ICP/MS, the strip-test data gave a best-fit straight line with an $R^2 = 0.980$ and a slope of 0.945, showing good agreement between the two methods (Figure 1).
5. Regression analyses of results of the individual experiments gave R^2 values of 0.980 and 0.980 and slopes of 0.948 and 0.941 for experiments 1 and 2, respectively.

Considering the manufacturer's claims regarding the lack of interferences by many inorganic ions and this evaluation, the method seems to be a rapid and effective field test for screening water samples containing $\geq 5 \mu\text{g/mL}$ nickel.

12.0 Reference

Rocky Mountain Arsenal. 1989. *Rocky Mountain Arsenal Chemical Quality Assurance Plan*, section 4-7. Commerce City, Colorado 80022-2180.

Table 1. Strip Test Assay for Nickel in Spiked Water Samples/Nickel Concentration^(a)

Sample No.	Test No.	Calculated Conc. $\mu\text{g/mL}$	Actual Conc. $\mu\text{g/mL}$	0-10 (5)	10 (17.5)	25	25-100 62.5
Experiment 1							
1	20	0	0	ABCD ^(b)			
2	5	0	0	ABCD ^(b)			
3	32	0	0	ABCD ^(b)			
4	25	0	0	ABCD ^(b)			
5	13	0	0	ABCD ^(b)			
6	12	0	0	ABCD ^(b)			
7	30	5	4.7	ABCD ^(b)			
8	4	5.7	4.7	ABCD ^(b)			
9	23	5	4.7	ABCD ^(b)			
10	6	11.8	9.4	AB	CG	BDF	
11	19	9.6	9.4	AB	CEFG	D	
12	27	9.3	9.4	B	ACDEFG		
13	26	29.3	23.5			ABDEFG	C
14	2	30.4	23.5			ACDEFG	B
15	33	28.2	23.5			ABDEFG	D
Experiment 2							
1	21	0	0	ABCD ^(b)			
2	3	0	0	ABCD ^(b)			
3	12	0.7	0	ACDEFGH			
4	8	0.7	0	BCDEFGH			
5	4	10.9	4.7	ABCEFGH			
6	9	5	4.7	ABCD ^(b)			
7	16	11.2	9.4	C	E	D	
8	10	10.3	9.4	A	BDEH	AG	
9	20	28.7	23.5		BCDEH	G	
10	19	28.7	23.5			D	
						ABCEHH	G
						ABCEHH	G

(a) Simulated groundwater was spiked with nickel chloride. The nickel concentration ($\mu\text{g/mL}$) was estimated by comparison with the reference color chart.

(b) Determined by ICP/MS analysis

(c) Each strip (one strip per water sample) was independently read by 7 or 8 analysts (A to G or H) as indicated. Underlined letters indicate expected results.

Table 1. (contd.)
Nickel Concentration^(a)

Sample No.	Test No.	Calculated Conc. $\mu\text{g/mL}$	Actual Conc. ^(b) $\mu\text{g/mL}$	25	25-100 (62.5)	100	100-250 (175)	250-500 (375)	500	>500 (550)
Experiment 1										
16	24	78.6	56.4		<u>BDEG</u>	<u>ACF</u>				
17	29	83.9	56.4		<u>DEG</u>	<u>ABCE</u>				
18	10	67.9	56.4	B	<u>CDEG</u>	<u>AF</u>				
19	31	116.1	94		G	<u>BCDE</u>	AC			
20	17	83.9	94		<u>BFG</u>	<u>ACDE</u>				
21	11	105.4	94		G	<u>BCDEF</u>				
22	14	153.5	164.5			<u>FG</u>	<u>ABCDE</u>			
23	1	214.3	164.5			G	<u>DEF</u>	BC	A	
24	16	148.2	164.5		F	G	<u>ABCDE</u>			
26	22	217.9	235				<u>BDG</u>	<u>ACDE</u>		
27	15	196.4	235			F	<u>BEG</u>	<u>ACD</u>		
28	18	364.3	352.5					<u>ABDEG</u>	C	
29	3	410.7	352.5					<u>BDEFG</u>	<u>AC</u>	
30	9	321.4	352.5					<u>ABDG</u>		
31	7	410.7	470					<u>BCG</u>	<u>ADE</u>	
32	8	428.6	470					BG	<u>ACDE</u>	
33	28	464.3	470					BG	<u>ACDEF</u>	

(a) Simulated groundwater was spiked with nickel chloride. The nickel concentration ($\mu\text{g/mL}$) was estimated by comparison with the reference color chart.

(b) Determined by ICP/MS analysis

(c) Each strip (one strip per water sample) was independently read by 7 or 8 analysts (A to G or H) as indicated. Underlined letters indicate expected results.

Table 1. (contd.)
Nickel Concentration^(a)

Sample No.	Test No.	Calculated Conc. (µg/mL)	Actual Conc. (b) (µg/mL)	25-100 (62.5)	100-250 (175)	250-500 (375)	>500 (550)
Experiment 2:							
11	7	67.2	56.4	A	BCFGH	DE	
12	14	90.6	56.4	BCFGH	CDE	A	
13	17	104.7	94	G	ABCEFH	E	
14	1	104.7	94	A	BCDEFGH	E	
15	22	193.9	164.5		BCGH	ACD	
16	11	212.5	164.5		BCGH	ACDE	
17	5	212.5	285		EG	CDEEH	
18	15	231.2	235		EG	ACDEEH	
19	13	390.6	352.5			ABCEFGH	E
20	6	293.7	352.5			DEEH	G
21	2	418.7	470		A	BCD	BFH
22	18	450	470			BF	ADH

- (a) Simulated groundwater was spiked with nickel chloride. The nickel concentration (µg/mL) was estimated by comparison with the reference color chart.
- (b) Determined by ICP/MS analysis.
- (c) Each strip (one strip per water sample) was independently read by 7 or 8 analysts (A to G or H) as indicated. Underlined letters indicate expected results.

Figure 1. Strip-Test Assay for Nickel in Spiked Water Experiments 1 and 2

MB100^(a), Rev 1**Immunoassay for Mercury in Soils****Part I - Using Microplates****1.0 Scope and Application**

- 1.1 This is a field method for the quantitative determination of inorganic Hg (as Hg²⁺) in soils using the BioNebraska BiMelyze™ Mercury Assay Kit^(b). Note that the method described appears to be suitable for screening radioactive and hazardous chemical mixed wastes. However, procedures in this method are described assuming the absence of significant quantities of radioactivity in the samples.

2.0 Summary of Method

- 2.1 A 1-g soil sample is extracted with 3 mL of an acid mixture (1 part concentrated nitric acid and 2 parts concentrated hydrochloric acid) by intermittent shaking for 10 min. The extract is then buffered and diluted (1:10,000) for immunoanalysis. The diluted samples are plated in wells of a 96-well microtiter plate where the Hg is bound by sulfhydryl-rich proteins coating the wells. Bound Hg is then complexed with a Hg-specific antibody. The amount of Hg/antibody complex formed is visualized via the action of a peroxidase conjugated to a secondary antibody that reacts with the Hg-specific antibody. In the presence of appropriate substrates, hydrogen peroxide and an oxidizable chromophore, a colored product which is in proportion to the amount of Hg originally present in the well is formed. The color produced is measured spectrophotometrically and can be directly related to the *log* of the Hg concentration. The mercury content of the soils is determined by reference to standard Hg concentrations run simultaneously. Quantitative results can be obtained if the Hg content of the diluted samples is in the range of 0.5 to 8 ng/g (ppb), i.e., equivalent to 5 to 80 µg/g (ppm) in the soil.

3.0 Interferences

- 3.1 A number of metal ions that might be expected to interfere with the immunoanalysis of Hg have been tested (Wylie et al. 1991). In the linear range of the assay, i. e., 0.5 to 8 ng/g (ppb), the following metals (and the fold excess at which they were tested) showed negligible interference: Ba²⁺(≥ 338 x), Cd²⁺(5 x), Cr³⁺(25 x), Pb²⁺(≥ 338 x),

(a) Submitted by L. C. Waters, R. A. Jenkins, R. Smith, J. Stewart, and R. Counts (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

(b) BiMelyze™ Mercury Assay - Protocol for twelve 8-well strips. BioNebraska, Inc.

Ag^+ (25 x) and Au^+ (≥ 338 x). Chloride ions at 1 mM ($\geq 27,000$ x) inhibited Hg detection by ≥ 2 fold whereas 10 μM had no effect. None of these metal ions gave a positive response when tested alone in the assay.

It is important to consider the applicability of this assay, and bioassays in general, for testing mixed radioactive/hazardous chemical waste—in particular, the adverse effects on the immunoassay performance that may be expected in the presence of radioactivity. Several factors can influence the effect of radiation on biomolecules such as enzymes. The most important factor is the radiation dose. It is known that thousands of rads are required to significantly reduce the catalytic activity of enzymes. Therefore, considering the large sample dilution, small volumes assayed, and short incubation times involved, bioassays should remain effective even with very highly radioactive samples. With this particular test, the sample extracts are rinsed away before adding antibody and/or peroxidase (see section 7.3) so that the exposure of antibody and peroxides to radioactivity should be minimal.

4.0 Apparatus and Materials

- 4.1 Timer
- 4.2 Permanent ink marking pen
- 4.3 Gloves
- 4.4 Paper towels
- 4.5 Laboratory tissue
- 4.6 Liquid waste container
- 4.7 BiMelyze™ Soil Extraction Kit^(a)
 - Plastic extraction bottles: 15- to 20-mL capacity, one bottle per sample containing two 6-mm glass dispersion balls, one bottle per sample containing 7-mL dilution/neutralization buffer
 - Sample diluent (M-2), 10 mL per sample
- 4.8 Balance - Portable and capable of accurately weighing to 0.01 g (Ohaus Model CT 200 or its equivalent)

(a) BiMelyze™ Mercury Extraction Kit - Protocol, BioNebraska, Inc.

- plastic weighing boats
- wooden spatulas

4.9 Pipets/pipettors

- 10-mL plastic or glass disposable pipets with filler bulb
- micropipettors which meet the following requirements:
 - adjustable to cover range 10 to 1000 μ L
 - repeating, with 8-channel adapter for repetitive pipetting into 96-well microtiter plates. Eppendorf models or their equivalents.

4.10 Microcentrifuge tubes (1.5-mL capacity): for storing extracts

4.11 BiMelyze™ Mercury Assay Kit^(a)

- a 96-well microtiter plate; contains 12 strips of protein-coated wells
- antibody (A-1): lyophilized powder
- antibody diluent (A-2): 12 mL
- conjugate concentrate (C-1); 20 μ L
- conjugate diluent (C-2): 12 mL
- substrate (S): 12 mL
- mercury standard concentrate (M-1) 100 mg/L (ppm): 4 mL
- mercury standard diluent (M-2): 12 mL
- buffered well rinse (10 x concentrate): 50 mL
- stop solution: 12 mL
- diagram of 96-well plate

(a) BiMelyze™ Mercury Assay - Protocol for twelve 8-well strips, BioNebraska, Inc.

- 4.12 Glass or plastic disposable tubes with caps (15-mL capacity): for diluting sample extracts
- 4.13 Glass vials with caps (2-mL capacity): for diluting mercury standard
- 4.14 An 8-place manifold, adaptable to wash bottle or syringe: for washing microtiter plate wells
- 4.15 Microtiter plate reader: portable and capable of reading at 405 nm to 410 nm. Dynatech Laboratories model MR 250 or equivalent.

5.0 Reagents

- 5.1 Deionized water
- 5.2 Hydrochloric acid: concentrated, J. T. Baker ULTREX or equivalent
- 5.3 Nitric acid: concentrated, J. T. Baker ULTREX or equivalent
- 5.4 All other required reagents are supplied in the test kit and are covered in the preceding sections, i. e., section 4.7 - BiMelyze™ Soil Extraction Kit and section 4.13 -BiMelyze™ Mercury Assay Kit. Reagents in these kits should be stored at 4°C until used.

6.0 Sample Collection, Preservation, and Handling

- 6.1 Soil samples should be collected and stored in screw-capped containers. Soils should be considered to contain hazardous substances and handled in such a manner as to minimize contamination and exposure. Samples should be analyzed within 28 days of collection. The acid extracts of the soils, generated in the assay, should be neutralized and, together with the diluted samples, handled and disposed of as hazardous wastes.

7.0 Procedure

- 7.1 Sample weighing and extraction (with BiMelyze™ Mercury Extraction Kit)
 - 7.1.1 A quantity of 1 ± 0.01 g of soil is weighed onto a plastic weighing boat.
 - 7.1.2 The soil is transferred quantitatively to an extraction bottle that contains the dispersion balls.
 - 7.1.3 Then 2 mL conc HCl and 1 mL conc HNO₃ are added to the soil sample. (If large numbers of samples are to be tested, this step can be facilitated by premixing the acids and dispensing 3 mL of the mixture via a mechanical dis-

penser. Long-term storage of this mixture is not recommended.) Loosen lid one-half turn to prevent pressure buildup.

- 7.1.4 The soil is extracted by swirling the sample once every min for 10 min or by shaking on a mechanical shaker for 10 min.
- 7.1.5 The contents are carefully poured into an extraction bottle that contains 7 mL of the dilution/neutralization buffer. The particulates are swirled for mixing and allowed to settle. (This extraction has effected a 1:10 dilution of the soil sample.) Extracts that are difficult to transfer can be effectively mixed, neutralized, and diluted by repeatedly (carefully) pouring the mixture back and forth between the two bottles.
- 7.1.6 For convenience in subsequent handling and storage (and for repeat analysis if necessary), a small amount of the extract is poured into a microcentrifuge tube. (Extracts can be stored in this state.)

7.2 Mercury Standard and Sample Dilution: (Note that highly diluted Hg is readily adsorbed to container walls, so dilutions should be made just before the assay.)

7.2.1 **Mercury Standard:** The assay is linear in the range of 0.5 to 8 ng/g (ppb). Standards in this range are conveniently prepared in 2-mL vials by the method of serial dilution:

- 10 μL M-1 {100 mg/L (ppm)} + 990 μL M-2 (diluent) $\rightarrow$ 1 mL {1000 $\mu\text{g/L}$ (ppb)} (primary dilution)
- 10 μL 1000 $\mu\text{g/L}$ (ppb) (primary dilution) + 1240 μL M-2 $\rightarrow$ 1.25 mL {8 $\mu\text{g/L}$ (ppb)}
- 200 μL 8 $\mu\text{g/L}$ (ppb) + 600 μL M-2 $\rightarrow$ 800 μL {2 $\mu\text{g/L}$ (ppb)}
- 200 μL 2 $\mu\text{g/L}$ (ppb) + 600 μL M-2 $\rightarrow$ 800 μL {0.5 $\mu\text{g/L}$ (ppb)}.

7.2.2 **Samples:** 10 mL of M-2 (diluent) are added to prelabeled dilution tubes. A quantity of 10 μL of extract (see 7.1.5 and 7.1.6) is then added, i.e., a 1:1000 dilution. Total sample dilution at this point is 1:10,000 (see 7.1.5). Samples known or believed to contain greater than 80 $\mu\text{g/mL}$ (ppm) Hg should be further diluted. Samples that test higher than 80 $\mu\text{g/mL}$ (ppm) can be retested by going back to the original extract (7.1.6) and using an appropriately higher dilution.

7.3 Immunoassay (using BiMelyze™ Mercury Assay)

7.3.1 **Reagent Preparation:** All reagents should be allowed to warm to ambient temperature before use.

7.3.1.1 **Antibody:** 10.5 mL of antibody diluent (A-2) are added to the bottle of lyophilized antibody (A-1) and gently agitated to redissolve the antibody. Dissolved antibody should be stored at 4°C and should be used within 7 days.

7.3.1.2 **Conjugate:** The conjugate concentrate (C-1) is diluted with conjugate diluent (C-2), 1 µL C-1 per mL C-2. (Note that at least 9.6 mL are required per plate.) Diluted conjugate is less stable than redissolved antibody (7.3.1.1). However, the conjugate concentrate is very stable at 4°C (> 6 months). It is recommended that the required amount of diluted conjugate be prepared each day.

7.3.1.3 **Buffered well rinse** is prepared by diluting the concentrate 1:10 with deionized water.

7.3.2 **Sample Plating:** The 96-well plate diagram (4.11.11) is used to assign each sample's location on the plate. Each sample (100-µL aliquot), including a negative blank (M-2 solution), Hg standards {0.5, 2, and 8 µg/L (ppb)}, and diluted sample extracts should be plated at least in duplicate. Plating should be carefully organized to minimize the time required to plate all the samples. After all samples are plated, the plate is gently agitated to remove any air bubbles that might prevent contact of the sample with the well wall. The sample is incubated for 30 min at ambient temperature (20 to 30°C). After incubation, the wells are emptied by shaking the liquid into a waste container. Unbound Hg is washed off by rinsing each well three times with deionized water. Excess water is removed by slapping the inverted plate against several layers of paper towels.

7.3.3 **Antibody Binding:** 100 µL of redissolved antibody (7.3.1.1) are added to each well. The plate is agitated to remove air bubbles, and the plate is incubated for 30 min at ambient temperature. After the incubation, the wells are emptied of antibody. The wells are rinsed three times with diluted buffered well rinse (7.3.1.3) and then three times with deionized water to remove unbound antibody. Excess water is removed as described in 7.3.2.

7.3.4 **Conjugate Binding:** 100 µL of diluted conjugate (7.3.1.2) are added to each well. Air bubbles are removed, and the plate is incubated for 30 min. After

incubation, unbound conjugate is removed by rinsing, and excess water is removed from the wells as described in 7.3.2.

7.3.5 Substrate Addition: 100 μL of substrate, hydrogen peroxide and a chromophore, are added to each well, and the peroxidase reaction is allowed to proceed for 15 min. (Shielding the plate during this time with aluminum foil or paper is suggested to prevent potential bleaching of the chromophore by light.) Absorbance measurements should be made immediately after the 15-min incubation period, or the reaction can be stopped by adding 100 μL of stop solution (4.11.10) and delaying measurements by up to 2 h.

7.3.6 Absorbance Measurements: A bluish-green color in a well indicates that Hg is in the sample. The intensity of the color is proportional to the *log* of the Hg concentration. Absorbance at 405 to 410 nm is determined for each well using a microtiter plate reader.

7.4 Determination of Hg Concentration in Soil Samples

7.4.1 A standard Hg concentration curve is generated by plotting the absorbance versus the Hg concentration of the standards on 2-cycle semilog graph paper or using commercial plotting software (using the *log* scale for Hg concentration).

7.4.2 The concentration of Hg in the diluted, unknown soil samples is determined by referring to the linear portion of the standard curve. These values are multiplied by 10,000 (the dilution factor) to give the actual concentration in the soil.

8.0 Quality Control

8.1 Because this is an assay based on the performance of biomolecules, and the reactions depend strongly on temperature and the integrity of the reagents, absolute absorbance values for control samples may not be reproduced. Therefore, negative and positive Hg controls must be included with each assay. The effects of these factors should, however, be independent of the Hg concentration if the assay is to be valid. This evaluation has included 10 independent analyses of Hg standards. The absorbance values obtained for the 2- $\mu\text{g/L}$ (ppb) and 0.5- $\mu\text{g/L}$ (ppb) standards, relative to the absorbance values for the 8- $\mu\text{g/L}$ (ppb) standard, were relatively constant at $57 \pm 10 \%$ and $27 \pm 3 \%$, respectively. These relative values are consistent with those published by the vender (Wylie et al. 1991). Relative standard values that are outside this range might invalidate the assay.

9.0 Method Performance

9.1 Evaluation: Two studies were done to evaluate the capacity of this method to quantify Hg levels in soils. One study analyzed 29 contaminated soil samples whose Hg contents had been previously measured by neutron activation analysis (NAA) or X-ray fluorescence (XRF) analysis or both. The second study used 15 samples of a standard reference soil that had been spiked with Hg at levels ranging from 0 to 80 µg/g (ppm). No false positive or false negative results occurred in either study.

9.1.1 The 29 samples studied (Table 1) were independently assayed three times with two replicates/assay. Values obtained with the immunoassay (IA) that were below 5 µg/g (ppm), i.e., below the linear range of the absorbance versus *log* concentration plot, are reported as < 5 µg/g (ppm). The averaged values from data < 5 ppm were given a value of 2.5 µg/g (ppm) for purpose of calculation. Values above the linear range, i.e., > 80 µg/g (ppm), were determined by using appropriate dilutions of those samples. Results were then compared with those obtained by NAA (see also reference 2) and XRF. Statistical comparisons of the methods were performed with the data given in Table 1. For this analysis, IA and NAA "less than" values were given one-half that value and XRF and IA values used were the averages of the respective two (XRF) and 4 to 6 (IA) determinations). When compared with NAA, the results obtained by immunoassay gave a best-fit straight line with an $R^2 = 0.977$ and a slope of 1.20. When compared with XRF, an $R^2 = 0.971$ and a slope of 1.10 were obtained. When results obtained by XRF were compared with those obtained by NAA, a straight line with an R^2 of 0.978 and a slope of 1.08 were produced. These results are interpreted to indicate that soil Hg contents determined by the immunoassay method correlate well with those determined by NAA and XRF and that the correlation of the immunoassay with either of the chemical/physical methods is as good as those two methods are with each other.

9.1.2 The 15 samples that were studied (Table 2) consisted of two soil samples at each of the following Hg concentrations in µg/g (ppm): 2.5, 5.0, 10.0, 20.0, 40.0, and 80.0 plus three soil samples with no added Hg. The data, presented in Table 2, are the actual absorbance values obtained. Selected extracts, with standards, were reassayed the next day. The data in this table provide an assessment of the sensitivity and reproducibility of the method. Several points can be made from the data: 1) precision of replicate assays of extracts is good, 2) 2.5 ppm can be distinguished from zero, and 3) sometimes a poor agreement exists between values obtained for duplicate samples, e.g., soils 12, 13, 14, and 15. A second assay (day 2) of these samples showed better agreement. This tends to indicate that the observed differences between duplicate samples are not due to the extraction process, but rather may involve variation in other parameters. The basis for this variation is under investigation.

Table 1. Immunoanalysis of Mercury in Contaminated Soil Samples: Comparison with Neutron Activation and X-ray Fluorescence Methods

Neutron ^(a) Activation	X-ray ^(b) Fluorescence	Analytical Technique $\mu\text{g/g}$ {(ppm) Hg}								Standard Deviation	
		Immunoassay									
		Assay 1 Replicates		Assay 2 Replicates		Assay 3 Replicates		Average			
		1	2	1	2	1	2				
<7.6	-	<5	<5	<5	<5	<5	<5	2.5	-		
8.6	13,15	18.0	-	15.0	23.0	11.0	15.0	16.4	4.4		
19	-	33.0	38.0	57.0	66.0	31.0	54.0	46.5	14.4		
<5	7,30	9.7	11.0	8.3	8.0	9.2	7.9	9.0	1.2		
<2.1	-	<5	<5	<5	<5	<5	<5	2.5	-		
8.3	23,33	-	-	38.0	32.0	30.0	35.0	33.8	3.5		
56	63,81	75.0	112.0	46.0	113.0	67.0	54.0	77.8	28.7		
<5.3	22,52	65.0	39.0	25.0	43.0	23.0	39.0	39.0	15.1		
12	19,24	32.0	24.0	39.0	71.0	20.0	33.0	36.5	18.2		
57	31,33	61.0	95.0	61.0	59.0	29.0	74.0	63.2	21.6		
46	56,69	102.0	76.0	33.0	76.0	77.0	84.0	74.7	22.7		
73	56,59	86.0	79.0	53.0	69.0	74.0	78.0	73.2	11.4		
12	12,20	30.0	-	24.0	28.0	9.1	8.9	20.0	10.3		
<1.5	-	<5	<5	<5	<5	<5	<5	2.5	-		
18	24,24	20.0	23.0	34.0	33.0	29.0	35.0	29.0	6.2		
<1.2	-	5.3	5.8	<5	<5	<5	<5	3.5	-		
<1.3	-	<5	<5	<5	<5	<5	<5	2.5	-		
<3.3	-	<5	<5	<5	<5	<5	<5	2.5	-		
17	15,31	66.0	37.0	45.0	30.0	31.0	22.0	38.5	15.5		
<7.7	-	<5	<5	<5	<5	<5	<5	2.5	-		
11	-	45.0	46.0	72.0	34.0	34.0	22.0	42.2	17.0		
121	118,122	120.0	170.0	132.0	130.0	118.0	82.0	125.3	28.4		
166	202,233	132.0	-	129.0	174.0	300.0	135.0	174.0	72.8		
589	601,684	795.0	705.0	690.0	780.0	660.0	810.0	740.0	62.7		
116	90,116	105.0	160.0	92.0	78.0	88.0	92.0	102.5	29.5		
87	150,159	156.0	150.0	178.0	142.0	100.0	112.0	139.7	28.9		
206	235,259	344.0	264.0	240.0	372.0	168.0	188.0	262.7	82.0		
94	80,106	92.0	124.0	49.0	108.0	204.0	82.0	109.8	52.7		
121	131,131	92.0	174.0	74.0	164.0	92.0	50.0	107.7	50.0		

(a) One determination
(b) Two determinations

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9.2

Assay Sensitivity: Mercury is detectable in soils that contain as little as 2 to 2.5 µg/g (ppm), i.e., 0.2 to 0.25 ng/g (ppb) in the assay. At this level, the absorbance values are 50 to 70% above background. It is recommended, however, that application of quantitative estimates be limited to those soil samples whose diluted concentrations lie within the linear portion of the standard curve, i.e., 0.5 to 8 ng/g (ppb) { 5 to 80 µg/g (ppm) in the soil}. Samples with greater than 80 µg/g (ppm) can be quantified by appropriate further dilution beyond the 1:10,000 used in the assay, thus indefinitely extending the range of the assay. For example, all the contaminated soil samples used in this evaluation (section 9.1.1) could be brought into the assay's effective range by an additional 1:10 dilution. Using lesser dilutions (< 1:10,000) to quantify samples containing less than 5 µg/g (ppm) Hg should be done with caution and with due consideration of the increased acidity of such samples. For example, while the pH of a 1:10,000 diluted extract is in the range of 6 to 8, the pH of a 1:1,000 diluted extract is 4 to 6, which might

Table 2. Immunoanalysis of Mercury in Spiked Soil Samples: Reproducibility and Sensitivity of Immunoassay Method

(a) Data shown are the actual absorbance values measured

Sample (soil)	Hg, µg/g (ppm)	Day 1	Day 2	Replicates
1	0	0.158	0.160	4
2	0	0.128	0.140	3
3	0	0.163	0.170	1
4	2.5	0.264	0.267	4
5	2.5	0.163	0.226	1
6	5.0	0.270	0.226	1
7	5.0	0.302	0.309	1
8	10.0	0.307	0.327	1
9	10.0	0.427	0.403	1
10	20.0	0.461	0.434	1
11	20.0	0.420	0.434	1
12	40.0	0.717	0.710	1
13	40.0	0.530	0.530	1
14	80.0	0.771	0.709	1
15	80.0	1.081	1.068	1
(Standard)	ppb			
1	0	0.200	0.231	4
2	0.5	0.212	0.275	3
3	2.0	0.495	0.526	1
4	8.0	1.044	1.083	1
1	0	0.124	0.190	4
2	0.5	0.206	0.288	3
3	2.0	0.423	0.469	1
4	8.0	0.744	1.092	1
1	0	0.117	0.129	4
2	0.5	0.207	0.207	3
3	2.0	0.384	0.384	1
4	8.0	0.833	0.833	1

Immunoassay (A₄₁₀)^(a)

denature the SH-rich proteins to which the Hg binds in the first step of the assay (see section 7.3.2).

- 9.3 Time Considerations:** The 15 sample study (see 9.1.2) involved one analyst, and, in addition to the 16 soil samples, other samples including blanks and standards were also assayed—a total of 48 wells. Approximately 5.5 h (from weighing the soil samples to recording the data) were required to perform this assay. A trained analyst could be expected to analyze 20 to 40 soil samples with this method in a working day.

10.0 References

Wylie, D. E., L. D. Carlson, R. Carlson, F. W. Wagner, and S. M. Schuster. 1991. "Detection of mercuric ions in water by ELISA with a mercury-specific antibody." *Anal. Biochem.* 194:381-387.

BiMelyze™ Mercury Extraction Kit - Protocol, BioNebraska, Inc.

BiMelyze™ Mercury Assay - Protocol for 12 8-well strips, BioNebraska, Inc.

Part II - Using Test Tubes

1.0 Scope and Application

The scope and application are the same as in Part I. The BiMelyze™ Mercury Assay Kit described in Part I using 96-well microplates is now referred to by the manufacturer as the “BiMelyze™ Mercury Microplate Immunoassay Kit,” and the modified kit using tubes is the BiMelyze™ Mercury tube Immunoassay Kit.”

2.0 Summary of Method

In principle, the BiMelyze assay for Hg is the same as the plate assay described in Part I, section 2.1. In practice, the significant difference is that the assay is performed in 12- x 75-mm plastic test tubes instead of in 96-well microplates. Reference standards of Hg-spiked soil are supplied, instead of a standard solution of Hg. Reaction times are significantly shortened. The colored reaction product is measured with a differential photometer instead of the more expensive microplate reader. In general, the tube assay is a more fieldable version of the method than the plate assay.

3.0 Interferences (see Part I, section 3.1)

4.0 Safety (see Part I, section 6.1)

5.0 Apparatus and Materials

5.1 User Supplied

- Balance: (see Part I, section 4.1)
- Differential photometer: to read at 405 to 410 nm
- Hydrochloric acid: (see Part I, section 5.2)
- Nitric acid: (see Part I, section 5.3)
- Liquid waste container
- Timer
- Permanent marking pen
- Paper towels

- Laboratory tissue
- Deionized water: 1 L in wash bottle
- 500-mL wash bottle: for diluting buffer rinse
- 500-mL graduated cylinder: for diluting buffer rinse

5.2 BiMelyze™ Soil Extraction Kit

- 3 soil sample bottles with glass dispersion balls: containing 1.0-g samples of soil with reference Hg concentrations of 0, 5, and 15 $\mu\text{g/g}$ (ppm)
- 13 soil sample bottles with glass dispersion balls: empty, for test soil samples
- 16 filter tops: for soil sample bottles
- 16 extract dilution bottles: with filter tops and containing a 35-mL buffer
- 14 weigh boats: for weighing soil
- Spatula: for weighing soil
- 60-mL bottle: for mixing acids
- 120-mL sample stabilizer (ss): for neutralizing sample extract
- 2 syringes: for adding acid mixture to soil and ss to soil extracts

5.3 BiMelyze™ Mercury Assay Tube Kit

- Sixteen 12- x 75-mm assay tubes: coated with SH-rich protein
- Reference photometer tube
- Foam tube holder with rubber bands
- Vial lyophilized antibody (A-1)
- Dropper bottle containing antibody diluent (A-2)

- Dropper bottle containing conjugate (C)
- Bottle containing 40 mL 10x buffered rinse
- Dropper bottle containing substrate (S)
- Dropper bottle containing stop solution

6.0 Reagents (see section 5)

7.0 Sample Collection, Preservation, and Handling (see Part I, section 6.0)

8.0 Procedure

8.1 Sample Extraction and Dilution. The soil samples, test, and reference are extracted with acid, and the extracts are diluted essentially as described in Part I, section 7.1, except for the following modifications: 1) 7 mL of ss is slowly added to the soil/acid mixture instead of vice versa to partially neutralize the extract and effect a 1:10 dilution of the soil extract and 2) the additional 1:1000 dilution is effected by adding 1 drop (35 μ L) of the once diluted extract via the use of a filtered dropper top to a dilution bottle that contains 35 mL of buffer. Thus diluted, the soil extracts should be quickly analyzed to avoid losses of Hg on the container walls.

{**Note:** Although it was not used in this evaluation, modifications have recently been made to the Soil Extraction Kit and the extraction procedure that improve the detection of Hg using the BiMelyze™ Mercury Tube Assay. These changes increase the sensitivity of the assay to 1 μ g/g (ppm) of Hg in soil and also increase assay reproducibility. The modifications are as follows: five grams (instead of 1) of soil are added to a soil sample bottle and extracted with 4 mL of a 2:1:1 mixture of concentrated HCl, concentrated HNO₃, and water. After shaking the sample for ten min, 10 mL of sample stabilizer are added to the extract. Three drops of filtered extract are added to a dilution bottle, and the diluted sample is then assayed as indicated below.}

8.2 Immunoassay

Preparation: The assay tubes are labeled to correspond to the labels given to the test and reference soil samples. The tubes are mounted around the black-foam tube holder using the rubber bands. The 40 mL of 10x buffered rinse are diluted to 400 mL with water and transferred to a wash bottle. The antibody (A-1) is prepared for use by adding the antibody diluent (A-2) to it, mixing it thoroughly, and transferring it back to the diluent bottle (A-2), which is equipped with a dropper top.

Mercury binding: The diluted test and reference soil extracts are added dropwise {up to the black line (500 μL)} to the appropriate assay tube. The contents are gently mixed and incubated at ambient temperature for 5 min to allow for Hg to bind to the SH-rich proteins. After the incubation, the tubes are emptied and rinsed three times with water (the tubes are filled about 1/2 full each time). After rinsing, residual water is removed by tamping the tubes on a paper towel.

Antibody binding: Reconstituted antibody is added to each tube—up to the black line. The contents are gently mixed and incubated for 5 min at ambient temperature to allow the antibody to bind to the Hg. The tubes are rinsed three times with the 1x buffered rinse and three times with water as described above.

Conjugate binding: Conjugate is added to each tube—up to the black line. The contents are gently mixed and incubated for 5 min at ambient temperature to allow the conjugate to bind to the antibody. Again, the tubes are rinsed with the buffered rinse and water as described above.

Substrate addition: Substrate (S) is added to each tube—up to the black line. The contents are mixed and incubated for 5 min at ambient temperature to allow for color development. The reaction is stopped by adding 3 drops of stop solution to each tube.

Absorbance measurements: A bluish-green color in a tube indicates the presence of Hg in a sample (the greater the intensity of the color, the more Hg is present). To quantitate the amount of Hg present, each tube is read at 405 to 410 nm in a differential photometer with reference to a tube containing substrate—up to the black line—and 3 drops of stop solution. (Because standards are routinely included in the assay, it is also appropriate to use water in the reference tube.) The content of Hg in the test samples is determined by referencing the absorbance of those samples to that of the three standard samples, i.e., 0, 5, and 15 $\mu\text{g/L}$ (ppm), included in the assay.

9.0 **Quality Control** (see Part I, section 8.1)

10.0 **Method Performance**

Accuracy and reproducibility: Two independent experiments were done to evaluate this method. Experiment 1 included 10 field samples and 3 spiked samples, in addition to the 3 standard samples supplied in the kit. Experiment 2 consisted of 8 field samples, 5 spiked samples and the 3 kit samples. Four of the field samples were common to both experiments. Instead of measuring absorbances directly in the assay tubes using a differential photometer, they were measured in 96-well microplates using an available microplate reader. Aliquots of 200 μL were read in Experiment 1, and 100 μL aliquots were read in Experiment 2. Test samples were referenced against the kit standards and could be categorized as having Hg

concentrations of 0, 0 to 5, 5, 5 to 15, 15, or >15 $\mu\text{g/g}$ (ppm). Results are given in Table 1. Wherever possible, analytical data obtained previously by neutron activation analysis (NAA), X-ray fluorescence (XRF) analysis, and immunoassay (IA) are given for comparison.

Except for one sample, No. 14 in Experiment 1, the tube assay gave the expected results with all of the samples tested. It appears, on the basis of previous data obtained by IA (in Part I) and that shown in Table 1, that the Hg content of sample No. 6 (both experiments) was significantly underestimated by NAA. Similarly, the Hg content of sample No. 8 (Experiment 1) also appears to have been underestimated by NAA. Like the microplate assay (Part I), the tube assay appears to be as accurate as either NAA or XRF for measuring Hg in soil. (It should be noted that data that are relevant to any particular remedial action level can be obtained by simply changing the concentrations of the reference standards used.) Results obtained for the four field samples that were analyzed in both experiments showed good reproducibility of the method.

Sensitivity: The method will detect as little as 5 $\mu\text{g/g}$ (ppm) Hg in soil. With the modified extraction procedure (see section 8.1), the sensitivity is increased to 1 $\mu\text{g/g}$ (ppm).

Working range: The method has a working range of 5 to 50 $\mu\text{g/g}$ (ppm) Hg in soil. At concentrations above 50 $\mu\text{g/g}$ (ppm), color formation is no longer proportional to concentration, and therefore, differences that exist in highly concentrated soil samples may not be indicated by the test. However, an accurate estimate of the Hg content of such samples can be made by retesting the extracts after further dilution to within the working range of the assay.

General comments: The tube assay for Hg is well suited for field screening use. It is rapid and easy to use. The tube assay avoids some of the potential problems of using the microplate assay in the field, e.g., 1) the requirement for an absolutely level working surface, 2) the requirement for a microplate reader, 3) the requirement for pipettors, and 4) the greater chance for spillage from the plate. The microplate assay still remains a rapid and cost-effective alternative to standard laboratory methods for screening large numbers of samples in the laboratory.

Table 1. Analysis of Mercury in Soils Using the BiMelyze™ Mercury Assay Tube Kit

Sample No.	Spiked (ppm)	NAA	Field (ppm) by: XRF	IA ^a	Absorbance @ 410 nm	Concentration (by tube assay)
Experiment 1 ^b						
1	0 ^c	—	—	—	0.077	0
2	5 ^c	—	—	—	0.131	5
3	15 ^c	—	—	—	0.216	15
4	—	116	90-116	102	0.357	>15
5	—	>3.3	—	<2.5 ^f	0.104	0-5
6	—	11	—	42	0.293	>15
7	—	<2.1	—	<2.5 ^f	0.096	0-5
8	—	<5.3	22-52	39	0.292	>15
9	—	<1.5	—	<2.5 ^f	0.127	0-5
10	—	<7.7	—	<2.5 ^f	0.088	0-5
11	—	87	150-159	140	0.337	>15
12	—	19	—	46.5	0.259	>15
13	—	121	118-122	125	0.264	>15
14	7.5 ^d	—	—	—	0.122	0-5
15	12.5 ^d	—	—	—	0.164	5-15
16	100 ^d	—	—	—	0.264	>15
Experiment 2 ^c						
1	0 ^e	—	—	—	0.046	0
2	5 ^e	—	—	—	0.068	5
3	15 ^e	—	—	—	0.097	15
4	—	116	90-116	102	0.159	>15
5	—	<3.3	—	<2.5 ^f	0.055	0-5
6	—	11	—	42	0.134	>15
7	—	<2.1	—	<2.5 ^f	0.056	0-5
8	—	<1.5	—	<2.5 ^f	0.065	5
9	—	0 ^f	—	—	0.059	0-5
10	—	—	—	—	0.054	0-5
11	—	—	—	—	0.050	0-5
12	0 ^d	—	—	—	0.054	0-5
13	2.5 ^d	—	—	—	0.054	0-5
14	5 ^d	—	—	—	0.066	5
15	7.5 ^d	—	—	—	0.071	5-15
16	25 ^d	—	—	—	0.118	>15

a Results presented in Part I.

b A 200-μL aliquot was read.

c Standard soils provided with kit.

d Soils spiked in the laboratory.

e A 100-μL aliquot was read.

f Stated to be "below detection limits of NAA method"

MP100R^(a), Rev. 1

Solvent Extraction of Uranium and Thorium from Radioactive Liquid Wastes

1.0 Scope and Application

1.1 This extraction procedure is used to lower uranium and thorium levels in radioactive liquid wastes containing U.S. Environmental Protection Agency (EPA) target analyte list elements to be analyzed by inductively coupled plasma (ICP) and graphite furnace atomic absorption (GFAA). Tri-n-octylphosphine oxide ($C_8H_{17}_3PO$) (TOPO) readily extracts U and Th from acidic solutions, lowering the solution concentration to <100 mg/L of U and Th. This minimization eliminates severe spectral/matrix interferences caused by high concentrations of these two elements. Plutonium is also extracted from acidic solutions by TOPO.

1.2 Samples prepared by this method may be analyzed by ICP and GFAA for the following EPA target analytes:

Aluminum	Cobalt	Potassium
Antimony	Copper	Selenium
Arsenic	Iron	Silver
Barium	Lead	Sodium
Beryllium	Magnesium	Thallium^(c)
Cadmium	Manganese	Vanadium
Calcium	Mercury^(b)	Zinc
Chromium	Nickel^(c)	

Elements in bold print are the Resource Conservation and Recovery Act (RCRA) metals.

2.0 Summary of Method

2.1 Samples to be analyzed are first acid digested by SW-846 Method 3050 (EPA 1986) using nitric acid (HNO_3) alone or by the alternate microwave acid digestion procedure, SW-846 Method 3051 (EPA 1990).

(a) This method was submitted by A. M. Swafford, and J. M. Keller (Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee).

(b) If Mercury Cold-Vapor Atomic Absorption method, SW-846 Method 7471, is employed, separation of U and Th from the solution is not necessary. Interferences from U and Th are not observed.

(c) Nickel and Thallium are proposed RCRA metals

- 2.2 The digested sample is diluted with HNO_3 and extracted with an equal volume of TOPO in cyclohexane for five minutes. After discarding the organic layer, an aliquot of the aqueous layer is brought to a known volume using a 5% HNO_3 solution. If an internal standard is employed, it is added at the time the sample is brought to a known volume. The U and Th levels are now minimized, and the sample can be analyzed for concentration of the target analytes.

3.0 Interferences

- 3.1 The use of hydrochloric acid (HCl) is avoided here due to extensive use of stainless steel in radiochemical laboratories and glovebox fabrication. Only HNO_3 is used throughout this procedure.
- 3.2 Using HNO_3 during sample digestion instead of HCl eliminates the possibility of extracting As(III), Cd, Hg(II), and Cr(VI) (see Table 3).
- 3.3 Lead is not extracted from nitric acid.
- 3.4 An emulsion layer may form in the aqueous layer during extraction, which is caused by entrained organics. Further separations and dilutions should be performed on the aqueous layer.
- 3.5 Entrained organics in the aqueous samples being analyzed for ICP can affect particle-size distribution produced in the nebulizer system and cause high recovery results. This interference can be reduced by pouring the aqueous solution through an EIChroM™ pre-filter column for removing organics before analyzing by ICP. In addition, the technique described in section 8.2 should be applied.

4.0 Apparatus and Materials

- 4.1 Volumetric glassware
- 4.2 5.0 mL, 10.0 mL pipettes
- 4.3 Separatory funnel
- 4.4 Beakers

5.0 Reagents

- 5.1 **2 M HNO₃:** This solution is prepared by adding 127 mL of concentrated HNO₃ to a 1-L volumetric flask and diluting to volume with distilled water.
- 5.2 **5% HNO₃:** 72 mL of concentrated HNO₃ is added to a 1-L volumetric flask. It is diluted to volume with distilled water.
- 5.3 **0.1 M TOPO/Cyclohexane:** This solution is prepared by adding 38.7 g of tri-n-octylphosphine oxide (Kodak, Cat. no. 119 3036 or equivalent) to a 1-L volumetric flask and diluting to volume with cyclohexane (reagent spectro grade).

6.0 Sample Collection, Preservation, and Handling

- 6.1 Sample collection and preservation should be performed according to most recent SW-846 approved methods.
- 6.2 Radioactive samples should be handled according to local applicable standards for handling radioactive materials.

7.0 Procedure

- 7.1 Using SW-846 Method 3050 or SW-846 Method 3051, the sample is digested in HNO₃ alone. Some elements are extracted by HCl, and furthermore, the corrosive effect of HCl on stainless steel facilities indicates that HCl should not be used in the procedure.
- 7.2 Then 5.0 mL of the sample is pipeted into a 10.0 mL volumetric flask. It is diluted to volume with 2 M HNO₃. The diluted sample is transferred to a separatory funnel. Then 10.0 mL of 0.1 M TOPO in cyclohexane is added to the funnel and extracted for five minutes. Complete separation of phases should be allowed.
- 7.3 The organic layer obtained from the extraction is discarded according to local applicable standards for organic waste disposal. An appropriate aliquot^(a) of the aqueous layer is pipeted into a 25.0-mL volumetric flask and diluted to volume with 5% HNO₃. Initial aliquot volume must be noted in order to determine the dilution factor. If an internal standard for ICP is desired, it should be added in this step before diluting with HNO₃ (10 mg/L scandium is recommended). The U and Th levels are now minimized to below 100 mg/L, and the sample may be analyzed by ICP and GFAA for target analyte concentration.

(a) An appropriate aliquot of sample would include a sufficient concentration of analytes for efficient detection by ICP analysis.

8.0 Quality Control

- 8.1 A quality control (QC) protocol sufficient for the needs of a particular sample request should be implemented to include duplicate samples so that precision may be determined, as well as standard spikes to the samples for determining accuracy based on percent recovery.
- 8.2 A matrix match standard containing known concentrations of the elements of interest should be prepared for each batch of samples being analyzed at a particular time by simulating the sample extraction using pure cyclohexane without TOPO present, and then sampling an aliquot of the aqueous phase. Calibration of the instrument with this standard accounts for the effects of entrained organics on the particle size distribution produced by the nebulizer for an ICP-atomic emission spectroscopy (AES) sample introduction system.
- 8.3 Instrument calibration and application of blanks for analyzing the cleaned-up samples should be followed as instructed in the particular analysis method being used.

9.0 Method Performance

- 9.1 Up to 23 mg of Th and 60 mg of U are extracted from 1 M HNO_3 with 0.5 millimole of TOPO (White and Ross 1961).
- 9.2 Table 1 lists the typical spike recoveries of the RCRA metals in the aqueous phase from the TOPO extraction on typical waste samples in the sludge form and containing U and Th (Autrey et al. 1990).
- 9.3 In another single laboratory evaluation, the recoveries of the EPA target analyte list elements being left behind in the TOPO extraction were determined. This study was performed on aqueous samples consisting of a HNO_3 and high nitrate matrix which were spiked with the target analytes. The extraction was performed at three different acid concentrations (1 M, 2 M, and 3 M HNO_3) and one nitrate concentration (0.4 M NaNO_3). The varying acid concentrations were applied to determine any trend in recoveries of the analytes. The samples were evaluated in triplicate, and averages with standard deviations were determined. Before analysis, standards and blanks were checked on the instrument to be used to ensure quality results.

Table 1. Typical Spike Recoveries with TOPO Extraction

Element	Spike recovery (%)	RSD (%)
As	100	11
Ba	100	2
Cd	96	5
Cr	100	7
Hg	72	24
Ni	98	3
Pb	96	11
Se	100	9
Tl	86	25

Table 2. Recovery of EPA Target Analyte List Elements from TOPO Extraction

Element	Tracer	0.1 M TOPO/Cyclohexane Extraction					
		1 M R	HNO ₃ RSD	2 M R	HNO ₃ RSD	3 M R	HNO ₃ RSD
Aluminum	-	102	1	100	1	99	2
Antimony	¹²⁵ Sb	88	3	86	6	88	<1
Arsenic	⁷⁶ As	98	4	90	2	93	3
Barium	¹³³ Ba	99	2	103	6	99	1
Beryllium	-	208	1	108	1	105	1
Cadmium	¹⁰⁹ Cd	99	<1	104	2	102	3
Calcium	-	206	1	102	1	101	1
Chromium	⁵¹ Cr	104	6	97	10	96	4
Cobalt	⁶⁰ Co	101	<1	101	2	102	1
Copper	-	99	1	98	2	95	2
Iron	⁵⁹ Fe	103	2	100	<1	100	<1
Lead	²¹⁰ Pb	95	9	89	1	106	2
Magnesium	-	105	2	107	1	106	5
Manganese	⁵⁴ Mn	101	3	102	4	102	1
Mercury	²⁰³ Hg	90	19	100	18	111	5
Nickel	⁶³ Ni	91	3	88	5	85	4
Potassium	⁴² K	100	1	98	2	101	<1
Selenium	⁷⁵ Se	100	5	99	5	98	7
Silver	^{110m} Ag	102	2	102	1	99	2
Sodium	²⁴ Na	100	3	99	4	101	1
Thallium	²⁰⁴ Tl	100	6	100	1	100	2
Vanadium	-	97	2	107	1	108	2
Zinc	⁶⁵ Zn	96	1	102	2	100	<1

R = average percent recovery of element in the aqueous phase.

RSD = relative standard deviation (percent) based on three replicates.

Table 3. Extraction of Metals from Acid Solutions with 0.1 M- TOPO/Cyclohexane^(a)

Element		Hydrochloric Acid		Nitric Acid	
		1M	7M	1M	7M
Aluminum	Al ⁺³	N	N	N	N
Antimony	Sb ⁺³	P	E	P	P
Arsenic	As ⁺⁵	N	N	N	N
Barium	Ba ⁺²	N	N	N	N
Beryllium	Be ⁺²	N	N	N	N
Bismuth	Bi ⁺³	P	N	P	N
Boron	B ⁺³	N	N	N	N
Cadmium	Cd ⁺²	P	P	N	N
Calcium	Ca ⁺²	N	N	N	N
Cerium	Ce ⁺³	N	N	N	N
Chromium	Cr ⁺³	N	N	N	N
Chromium	Cr ⁺⁶	E	E	E	E
Cobalt	Co ⁺²	N	N	N	N
Copper	Cu ⁺²	N	P	N	N
Dysprosium	Dy ⁺³	N	N	N	N
Erbium	Er ⁺³	N	N	N	N
Europium	Eu ⁺³	N	N	N	N
Gadolinium	Gd ⁺³	N	N	N	N
Gallium	Ga ⁺³	N	E	N	N
Germanium	Ge ⁺⁴	*	P	*	*
Gold	Au ⁺	E	E	E	P
Hafnium	Hf ⁺⁴	E	E	E	P
Holmium	Ho ⁺³	N	N	N	N
Indium	In ⁺³	P	P	N	N
Iron	Fe ⁺³	E	E	N	N
Lanthanum	La ⁺³	N	N	N	N
Lead	Pb ⁺²	N	N	N	N
Magnesium	Mg ⁺²	N	N	N	N
Mercury	Hg ⁺²	P	N	N	N
Molybdenum	Mo ⁺⁶	E	E	N	P
Neodymium	Nd ⁺³	N	N	N	N
Nickel	Ni ⁺²	N	N	N	N
Palladium	Pd ⁺²	N	N	N	N
Platinum	Pt ⁺²	P	P	N	N
Praseodymium	Pr ⁺²	N	N	N	N
Ruthenium	Ru ⁺²	N	N	N	N
Samarium	Sm ⁺³	N	N	N	N
Silver	Ag ⁺	N	N	N	N

(a) - Grindler 1962

Table 3. Contd.

Element	Hydrochloric Acid				Nitric Acid			
Sroutium	Sr+2	N	N	IM	N	N	N	IM
Terbium	Tb+3	N	N	N	N	N	N	N
Thorium	Th+4	N	N	N	N	N	N	N
Thulium	Tm+3	N	N	N	N	N	N	N
Tin	Sn+4	N	N	N	N	N	N	N
Titanium	Ti+4	N	N	N	N	N	N	N
Uranium	UO ₂ +2	N	N	N	N	N	N	N
Vanadium	V+4	N	N	N	N	N	N	N
Ytterbium	Yb+3	N	N	N	N	N	N	N
Yttrium	Y+3	N	N	N	N	N	N	N
Zinc	Zn+2	N	N	N	N	N	N	N
Zirconium	Zr+4	N	N	N	N	N	N	N

(E = complete extraction, P = partial extraction, N = no extraction, * = data incomplete)

a - Grindler 1962

Results of the evaluation show that the EPA analytes are not extracted by TOPO under the stated conditions, with the exception of antimony, which is partially extracted. No overall trends were concluded in recoveries of the analytes at the varying acid concentrations. Table 2 lists the recoveries observed in the aqueous phase.

9.4 Table 3 categorizes the degree of extraction of the analytes by TOPO from HNO₃ media and HCl media (Grindler 1962).

10.0 References

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White, J. C., and W. J. Ross. 1961. *Separations by Solvent Extraction with Tri-n-octylphosphine Oxide*/U.S. Atomic Energy Commission, Oak Ridge, Tennessee.

MP110R^(a)**Clean-up of Transuranic Liquid Wastes using Extraction Chromatography****1.0 Scope and Application**

- 1.1** The purpose of this method is to provide a procedure for cleaning-up radioactive liquid waste samples to be analyzed for the U.S. Environmental Protection Agency (EPA) target analyte list elements by inductively coupled plasma (ICP) and graphite furnace atomic absorption (GFAA). This procedure applies extraction chromatography using an EIChroM™ transuranic specific (TRU•Spec®) column which absorbs transuranic elements at high acid concentrations, but elutes them under low acid conditions. The TRU•Spec® can be obtained as a pre-packed column consisting of an extractant, octyl(phenyl)-N-N-diisobutyl-carbamoyl-methylphosphine oxide (CMPO) dissolved in tri-butyl phosphate supported on an inert substrate. Its use is important to eliminate emission interferences by removing the actinides, U, and Th, or for easier sample handling by removing most alpha emitters.
- 1.2** Samples prepared by this method may be analyzed by ICP and GFAA for the following EPA target analytes:

Aluminum	Cobalt	Potassium
Antimony	Copper	Selenium
Arsenic	Iron	Silver
Barium	Lead	Sodium
Beryllium	Magnesium	Thallium^(c)
Cadmium	Manganese	Vanadium
Calcium	Mercury^(b)	Zinc
Chromium	Nickel^(c)	

Elements in bold print are the Resource Conservation and Recovery Act (RCRA) metals.

- (a) Submitted by A. M. Swafford and J. M. Keller (Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee).
- (b) If Mercury Cold-Vapor Atomic Absorption method, SW-846 Method 7471, is employed, separating U and Th from the solution is not necessary. Interferences from U and Th are not observed.
- (c) Nickel and Thallium are proposed RCRA metals.

2.0 Summary of Method

- 2.1 Samples to be analyzed are first acid digested by SW-846 Method 3050 using HNO_3 alone or by the alternate microwave acid digestion procedure, SW-846 Method 3051.
- 2.2 The pre-packed column is conditioned by passing a high acid solution (4 M HNO_3) through it.
- 2.3 A sample aliquot corresponding to the working capacity of the column is loaded on the column in a small amount of the high acid solution followed by a larger volume "wash" of high acid solution. All of the eluate is collected. An aliquot of the eluate is brought to a known volume using a 5% HNO_3 solution. If an internal standard is employed, it is added at the time the sample is brought to a known volume. The sample can now be analyzed for the EPA target analytes.

3.0 Interferences

- 3.1 To achieve efficient extraction of the actinides, the sample aliquot should correspond to the working capacity (maximum possible loading) of the column. Literature recommends loadings of 10% to 20% of capacity to ensure minimum analyte loss. A useful loading is 2 to 4 mg of actinide based on Am-241 studies. If capacity is a concern for a particular sample, a dilution of the sample should be performed and analyzed by ICP to determine if the capacity of the actinides has been met.
- 3.2 According to literature, breakthrough of the actinides can occur after passage of 65 free column volumes (1 F.C.V. = 1.3 mL/col.) through the column. To prevent breakthrough, the total volume passed through the column should be maintained below 65 mL.
- 3.3 Ferric iron is absorbed by the TRU•Spec® column and inhibits the retention of Am. Ferric should be reduced to ferrous iron to prevent this effect. This can be achieved by titrating the sample to endpoint with 1 M ascorbic acid using ammonium thiocyanate as an indicator. Thiocyanate forms a red complex with ferric iron. Reduction of ferric iron is indicated when the red color dissipates, and the sample is colorless.
- 3.4 The use of HCl is avoided here due to extensive use of stainless steel in radiochemical laboratories and glovebox fabrication. Only HNO_3 is used throughout this procedure.

4.0 Apparatus and Materials

- 4.1 EIChroM™ TRU•Spec® pre-packed column EIChroM Industries Inc., cat. no. TR-C50 or TR-C200
- 4.2 Column rack
- 4.3 Volumetric glassware
- 4.4 Pipettes

5.0 Reagents

- 5.1 4 M HNO_3 - This solution is prepared by adding 254 mL of concentrated HNO_3 and diluting to 1 L with distilled water.
- 5.2 5% HNO_3 - This solution is prepared by adding 72 mL of concentrated HNO_3 to a 1-L volumetric flask. It is diluted to volume with distilled water.

6.0 Sample Collection, Preservation, and Handling

- 6.1 Sample collection and preservation should be performed according to most recent SW-846 approved methods.
- 6.2 Samples should be handled according to local applicable standards for handling radioactive materials.

7.0 Procedure

- 7.1 Using SW-846 Method 3050 or SW-846 Method 3051, the sample is digested in HNO_3 alone. Use of HCl should be avoided (see item 3.4). The digested sample is adjusted to 4 M HNO_3 .
- 7.2 The tip and the cap of the TRU•Spec® column are removed. The frit is lowered to just above the top of the resin. The column is conditioned by passing 15 to 20 mL of 4 M HNO_3 through the column.
- 7.3 An amount of sample that meets the restrictions stated in item 3.1 is loaded on the column. A wash of 4 M HNO_3 follows, being sure to maintain a total volume of less than 65 mL (see item 3.2). All of the eluate is collected.

- 7.4 A sample aliquot that is expected to be within the detection range of the instrument to be used for analysis is pipeted into a 25.0-mL volumetric flask. It is diluted to volume with 5% HNO₃. If an internal standard for ICP is desired, it should be added in this step before diluting with HNO₃ {10 mg/L (ppm) scandium is recommended}. The sample may now be analyzed by ICP and GFAA for target analyte concentration.
- 7.5 The used TRU•Spec[®] column should be disposed of according to local applicable standards for handling solid transuranic waste.

8.0 Quality Control

- 8.1 A quality control (QC) protocol sufficient for the needs of a particular sample request should be implemented to include duplicate samples for determining standard deviation as well as spikes to the samples for the determining accuracy based on percent recovery.
- 8.2 Blank samples consisting of nitric acid media alone should be applied to the TRU•Spec[®] procedure and used in the instrument calibration along with appropriate standards. Instrument calibration and subtraction of blanks should be followed as instructed in the particular analysis method being used. This will account for effects of the TRU•Spec[®] matrix.

9.0 Method Performance

- 9.1 In a single laboratory evaluation, the recoveries of the EPA target analyte list elements being eluted from the TRU•Spec[®] under high acid conditions were determined. In this study, a 5-mL 4 M HNO₃ solution was spiked with an analyte and loaded on the column followed by a 15-mL wash with 4 M HNO₃. This was performed in duplicate at room temperature under gravitational flow. The recoveries of the analytes in the 4 M HNO₃ eluate were determined and averaged. These averages along with their relative standard deviations are shown in Table 1. None of the analytes were found to be retained by the TRU•Spec[®] column.
- 9.2 Table 2 is a reconstruction of a table presented in a product brochure by EIChroM Industries, Inc. titled "Extraction Chromatographic Material for Rapid Separation of the Transuranic Elements."

Table 1. Recovery of EPA Target Analyte List Elements From TRU-Spec[®] Extraction

Element	Radioactive Tracer	TRU-Spec ^(a) (ORNL) 4 M HNO ₃	TRU-Spec ^(b) (ANL) 2 M HNO ₃
		% recovery (% RSD)	% recovery
Aluminum	-	101 (9)	100
Antimony	¹²⁴ Sb	100 (<1)	NA
Arsenic	⁷⁶ As	100 (<1)	NA
Barium	¹³³ Ba	94 (2)	100
Beryllium	-	101 (11)	NA
Cadmium	¹⁰⁹ Cd	104 (5)	100
Calcium	-	100 (9)	100
Chromium	⁵¹ Cr	93 (2)	100
Cobalt	⁶⁰ Co	103 (3)	100
Copper	-	101 (10)	100
Iron	⁵⁹ Fe	NA	100
Lead	²¹⁰ Pb	108 (6)	100
Magnesium	-	99 (10)	100
Mercury	²⁰³ Hg	101 (19)	-
Nickel	⁶³ Ni	86 (5)	100
Potassium	⁴² K	95 (6)	82
Selenium	⁷⁵ Se	100 (NA)	NA
Silver	^{100m} Ag	96 (4)	100
Sodium	²⁴ Na	96 (5)	93
Thallium	²⁰⁴ Tl	99 (1)	NA
Vanadium	-	99 (11)	NA
Zinc	⁶⁵ Zn	97 (2)	100

(a) Data obtained from Oak Ridge National Laboratory (ORNL) with radioactive tracers and inactive tracers.

(b) Data obtained from Argonne National Laboratory (ANL) by ICP-atomic emission spectroscopy (AES).

Table 2. Elution of Selected Elements on a TRU-Spec® Column

Fraction Eluting (%) by number of free column volumes

Element	1-5	6-10	11-15	16-20	21-25	26-30	31-40
Li	98.4	<9	-	-	-	-	-
Na	92.8	<1.2	-	-	-	-	-
X ^(a)	100	-	-	-	-	-	-
Al	99.8	<2.9	-	-	-	-	-
K	81.8	40.9	-	-	-	-	-
Fe	102	12.3	-	-	-	-	-
Y	23.4	76.8	-	-	-	-	-
Zr	-	-	-	-	-	-	75
Ru	82.6	<19	-	-	-	-	-
La	-	-	-	-	-	30.0	72.0
Ce	-	-	-	-	-	<25	75.0
Pr	-	-	-	-	-	-	100
Nd	-	-	-	-	-	-	96.0
Sm	-	-	-	-	-	-	100
Eu	-	-	-	-	-	-	<99
Hg	(100)	(60)	(19)	-	-	-	-
Am ^(b)	-	-	-	-	-	-	<99

(a) X represents the following elements: Mg, Ca, Cr, Mn, Co, Ni, Cu, Zn, Sr, Rh, Ag, Cd, Ba, Pb.

(b) radiometric.

1-30 f.c.v. : 2 N HNO₃.31-40 f.c.v. : 0.05 N HNO₃.

Note: These results were obtained from Inductively Coupled Plasma-Atomic Emission Spectroscopy. Due to uncertainties inherent in this analysis, the fractions for each element may not total 100%. Values in parenthesis hold considerable uncertainty and should only be used as a rough guide.

10.0 References

Horwitz, E. P., M. L. Dietz, D. M. Nelson, J. J. Larosa, and W. D. Fairman. 1990 "Concentration and Separation of Actinides from Urine Using a Supported Bifunctional Organophosphorus Extractant." *Anal. Chim. Acta* 238:263-271.

U. S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Method*, 3rd Edition. EPA/SW-846. Office of Solid Waste and Emergency Response. Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

U. S. Environmental Protection Agency (EPA). 1990. *Test Methods for Evaluating Solid Waste: Volume 1B, Physical/Chemical Method*, 3rd Edition, SW-846. Office of Solid Waste and Emergency Response. Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

MU012R(a)

Total Cyanide by Remote Microdistillation and Argentometric Titration

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This procedure provides a method for determining total cyanide in radioactive waste tank matrices where the concentration of total cyanide is greater than approximately 0.1% by weight (concentrations greater than 1 g CN⁻/kg). The method as written has general utility for moderately high levels of cyanide, but was specifically developed for samples that must be handled in a hot cell.

2.0 Summary of Method

Cyanide is released from most of its complexes and converted to hydrogen cyanide by treatment with acid in the presence of magnesium ions. Hydrogen cyanide (HCN) is distilled from acidified samples and captured with sodium hydroxide. Standard silver nitrate is used to titrate the cyanide using rhodamine indicator. The detection limit for this procedure is approximately 20 µg cyanide per sample. Single laboratory quality control (QC) indicates that spike recoveries range from 93 to 99% of the expected value using a simulated tank-waste matrix. Results obtained from hot-cell samples demonstrate a comparable spike recovery using a tank-waste matrix spiked with an approximately equal amount of CN⁻ as sodium nickel ferrocyanide.

3.0 Interferences and Limitations

No significant interferences were encountered with samples containing complexed ferrocyanides in the range indicated. The following interferences are known to occur in cyanide determinations, especially with cyanide in the mg/kg range.

3.1 Cobalticyanide complexes are known to be incompletely converted to HCN by distillation from acid.

(a) This method was supplied K. H. Pool (Pacific Northwest Laboratory, Richland, Washington).

- 3.2 Nitrate/nitrite may interact with certain organic materials, creating species that will decompose to HCN when distilled. If matrices contain nitrate and/or nitrite and significant ketone or organic acid content, then pretreatment with sulfamic acid will eliminate this interference.

4.0 Safety

Radiochemical safety protocol and requisite training in the use of associated equipment (e.g., hot cell procedures) are assumed for highly radioactive samples.

5.0 Apparatus and Materials

- Micro-distillation tubes (Lachat[®] part no. 1700-001 or equivalent)
- Temperature controlled heating block designed to accommodate at least five micro-distillation tubes simultaneously
- Micro-distillation tube assembler/disassembler (MDTA/D)
- Pipets (adjustable or fixed volume)
- Disposable pipet tips
- Repipetor, 500 mL
- Analytical four-place balance
- Buret, 10 mL, readable to nearest 0.02 mL
- Magnetic stirrer
- Vials, glass, 15 mL
- Stir bars, glass
- Ice cream cartons (sample transfer containers)
- Cardboard cartons (secondary containment vessels)
- Tissue or Kleenex[®] (secondary containment vessel packing)
- Silicone grease

6.0 Reagents

- 6.1 A solution of 0.0192 N AgNO_3 (titer: 1.00 mg CN^- /mL): A 3.2647 ± 0.0002 -g quantity of crushed primary standard grade (99.9% or better) AgNO_3 , which has been dried to constant weight at 40°C , should be weighed, dissolved in deionized water (DIW), and diluted to 1000 mL. Alternatively, a certified AgNO_3 solution from a commercial source may be used.
- 6.2 Sample pretreatment solution: Acid form EDTA and Ethylenediamine. Five grams of acid form EDTA and 5.0 g Ethylenediamine in DIW are dissolved to a total volume of 100 mL.
- 6.3 Releasing solution: 7.11 M H_2SO_4 + 0.79 M MgSO_4 : A 47.5-g quantity of MgSO_4 (anhydrous) is dissolved in approximately 150 mL of DIW. A 350-g quantity of concentrated H_2SO_4 is added slowly to avoid overheating to the point of boiling. The sample is diluted to 500 mL final total volume. If undissolved solids persist, the sample should be filtered.
- 6.4 Deionized water, greater than 15 megohm/cm, as indicated by the deionizer meter readout.
- 6.5 Rhodanine Indicator Solution: Two grams of p-dimethylamino-benzalrhodanine are dissolved in 100 mL of acetone.
- 6.6 Stock Standard CN^- spiking solution(s): A solution of $\text{K}_4\text{Fe}(\text{CN})_6$ and/or $\text{Na}_2\text{NiFe}(\text{CN})_6$ is dissolved in the sample pretreatment solution. Concentration 1 mg CN^- /mL.
- 6.7 A 0.25 M NaOH solution: A 10.0 ± 0.2 -g quantity of reagent grade NaOH pellets are dissolved in 1.0 L of DIW.

7.0 Sample Collection, Preservation, and Handling

No current information supplied.

8.0 Procedure

- 8.1 A batch consists of a group of samples of similar matrix treated and distilled at the same time. A batch can not exceed (N-4) samples, where N is the number of available spaces in the heating block, to allow for a blank, spiked sample, sample duplicate, and control sample (see section 10.0). The maximum number of samples that would constitute a batch when working with duplicated samples will be (N-3)/2, where N is the number of available spaces in the heating block.

8.2 Predistillation Preparation

- 8.2.1 Enough micro-distillation tubes are unpackaged to complete the batch. It should be verified that the sealed upper portion of each tube contains approximately 1.5 mL of vendor-supplied sodium-hydroxide trap solution.
- 8.2.2 The upper and lower halves of each micro-distillation tube should be labeled with the appropriate sample identification information. Every batch will consist of samples, a duplicate sample, spike, a control sample, and a method blank. For QC requirements, see Section 10. The required number of 15-mL glass vials used to transfer the distillates out of the hot cell should be labeled. A disposable-glass stir bar should be placed in each vial. The vials are labeled and placed in secondary containment to keep them externally free of radioactive contamination.
- 8.2.3 The joint where the upper and lower portions of each tube join should be smeared lightly with silicone grease.
- 8.2.4 The power to the heat block is turned on. At least 30 min should be allowed for the unit to warm up. It should be verified that the temperature of the heating block is $128 \pm 3^{\circ}\text{C}$, using a calibrated thermometer or thermocouple. The actual temperature should be recorded on a bench sheet.
- 8.2.5 A balance performance check should be performed.
- 8.2.6 The delivery of all pipets that will be used both in-cell and out should be checked and documented. The checks on the bench sheet should be documented.
- 8.2.7 The appropriate amount of spike solutions is pipeted or weighed into the lower parts of the appropriate micro-distillation tubes before introducing them into the hot cells. The appropriate amounts should contain an amount of cyanide approximately equal to that expected in the samples. The lower tube sections should be placed into an ice cream carton to keep them upright while they are being transferred into the cells.
- 8.2.8 An approximately 0.5-g sample (nearest 0.01 g) is weighed into a tared scintillation vial. Approximately 5 g pretreatment solution (nearest 0.1 mg) are added to the vial along with a magnetic stir bar. Weights of sample and pretreatment solution should be recorded. The sample and pretreatment solution mixture are stirred in the capped vial vigorously for at least 30 min to dissolve the alkali-nickel-ferrocyanide compounds present in the tank material and in the spiked samples.

8.3 Distillation

- 8.3.1 The still separated micro-distillation tube sections are transferred into the hot cell.
- 8.3.2 The upper tube sections should be placed in the large holding block in a logical sequential order.
- 8.3.3 The bottom tube sections should be placed in the small holding block in logical order.
- 8.3.4 Approximately 1 g of sample pretreatment solution mixture (section 8.2.8) is weighed into the appropriate lower tube section and the weight recorded on the bench sheet. The weight of mixture taken should be measured to the nearest mg or better.
- 8.3.5 The lower tube section should be filled to the flange with sample pretreatment solution.
- 8.3.6 Using the MDTA/D, 0.6 mL of the $\text{H}_2\text{SO}_4/\text{MgSO}_4$ releasing solution is added to the lower tube section. The upper and lower tube sections should be sealed together. **Note:** This sealing operation must be done as quickly as possible to minimize the potential loss of HCN. The sealed tubes are placed in the heating block.
- 8.3.7 The heating/distillation process is allowed to proceed for at least 25 min, but no longer than 35 min.
- 8.3.8 Using the MDTA/D, the lower portions of the tubes are disconnected from the upper section, and the lower section is discarded. The elapsed time between removing a tube from the heat block and parting the upper and lower sections should be minimized to prevent the potential backflow of distillate into the lower tube sections. Failure to minimize the time interval may result in low recoveries.
- 8.3.9 Each upper tube section should be held horizontally and rotated slowly to rinse the walls with the distillate. The tube section should be tapped on a firm hard surface (e.g., the hot cell floor) to ensure that all of the trap solution is in the lower portion just above the semipermeable membrane. The upper tube section is broken in the location pre-scored by the manufacturer. The distillate is transferred into a prelabeled 15-mL glass vial. Each half of the upper tube section should be rinsed with approximately 5 mL of 0.25 M NaOH (squeeze bottle), and the rinses are added to the glass vial.

8.3.10 The glass vials containing the distillates and rinses should be transferred out of the hot cell to the fume hood where the titrations are to be done.

8.4 Titrations

For each sample:

8.4.1 A clean 10-mL buret is filled with 0.0192 N AgNO₃.

8.4.2 While stirring the sample by means of magnetic stirrer and stirbar, three drops of Rhodanine indicator are added to the vial.

8.4.3 The sample is stirred and titrated to the first permanent appearance of a "salmon" color. The volume of AgNO₃ used should be recorded on the bench sheet.

9.0 Calculations

9.1 Since the titer of 0.0192 N AgNO₃ is 1.00 mg CN⁻/mL, the volume of the titrant used (in mL) is numerically equal to the mg CN⁻ in the distillate. Therefore,

$$\text{mg CN}^- \text{ found} = \text{mL AgNO}_3 \text{ used to titrate distillate} - \text{mL AgNO}_3 \text{ used to titrate distillation blank}$$

9.2 Let

W_1 = weight (g) sample taken (section 8.2.8)

W_2 = weight (g) pretreatment solution taken (section 8.2.8)

The weight fraction of the sample in the mixture = $W_1 / (W_1 + W_2) = C$

For samples and blank spikes,

$$\% \text{ CN}^- = \frac{\text{mg CN}^- \text{ found} \cdot 100}{(W_s)(X) \cdot 1000}$$

W_s = weight (g) mixture taken (section 8.3.4)

9.3 Spiked Samples

$$\text{Spike recovery (\%)} = \frac{\left[V_{SP} - V_B - \frac{(W_s)(X)}{1000} \cdot \frac{A}{100} \right]}{W_{SP}} \cdot 100$$

where

V_{SP}	=	mL AgNO_3 used to titrate spiked sample distillates
V_B	=	mL AgNO_3 used to titrate blank distillate
W_{SP}	=	weight (mg) of CN^- in added spike
W_s	=	weight (g) mixture (Section 8.3.4) taken
A	=	% CN^- found for unspiked sample

10.0 Quality Control

- 10.1** Each analytical session (distillation + titration) shall include, as a minimum, one blank, one spiked sample, one sample duplicate, and one spiked blank a.k.a. control sample. Duplicates of all samples may be required by analytical protocol for single-shell tank wastes.
- 10.2** The preparation/method blank and control sample represent known performance indicators for this procedure and are used to evaluate the analytical session. Evidence of contamination in the blank and/or control sample recovery falling outside 80 to 120% warrant immediate corrective action.
- 10.3** Sample spike recoveries should fall within 80 to 120%.
- 10.4** The relative percent difference (RPD) for duplicate samples shall not exceed 15% if the cyanide content of the sample is >10 times the method detection limit.
- 10.5** Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) a tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:
- 10.5.1** Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within $\pm 10\%$ of the stated value.

- 10.5.2 When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

11.0 Method Performance

Method performance was established with a well characterized standard reference of sodium nickel ferrocyanide $\{\text{Na}_2\text{NiFe}(\text{CN})_6\}$ prepared by the laboratory. Extensive work with ion chromatography, FTIR, CHN analysis, and independent total cyanide analysis established this material as containing 34.5% CN^- . A secondary standard material, denoted as a "ferrocyanide waste simulant IF2R21," was also characterized by the method and used in the hot cell as a control sample.

- 11.1 Sodium nickel ferrocyanide determined by the method on three samples yielded $34.4\% \pm 0.2\%$ (1 σ) found (34.5% expected) as cyanide.
- 11.2 Simulant IF2R21 yielded the following data (expressed as % CN^-) in six separate test runs: 6.12%, 6.17%, 6.05%, 6.12%, 6.07%, 6.05%. The average recovery was 6.10%, and the standard deviation was 0.05%.
- 11.3 Spike recovery using $\text{Na}_2\text{NiFe}(\text{CN})_6$ as the spiking material and IF2R21 as the sample afforded an average recovery of 96% on four samples; the range was 93 to 99% of the expected value. The samples were spiked with an amount of cyanide equivalent to that expected from the IF2R21 simulant so that the spiked samples contained approximately twice that found in the normal samples.
- 11.4 For hot-cell performance evaluation, IF2R21 was used as the control sample, and $\text{Na}_2\text{NiFe}(\text{CN})_6$ was used as spike material. For the ferrocyanide tank core waste analyzed, the cyanide content was found to range from 0.3 to 1.0% CN^- by weight. Relative percent differences of duplicated runs were between 0.9% and 8.0% of the value obtained for the first run. Spike recovery from blank matrix yielded values of 89 to 103% of the expected value. Control samples were found to contain 88 to 99% of the expected added CN^- .

12.0 Further Reading

Lachat Instruments. 1989. *Micro-Dist Distillation System Reference and Methods Manual*. 6645 West Mill Road, Milwaukee, Wisconsin 53218.

Winters, W. I. 1987. *Analytical Methods for Determining Cyanide in Hanford Nuclear Waste*, RHO-SD-WM-TI-315, Rockwell Hanford Operations, Richland, Washington.

MM100^(a)

Inductively Coupled Plasma-Mass Spectrometry for Radionuclide Analyses

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

Inductively coupled plasma-mass spectrometry (ICP-MS) is an experimental technique generally used for trace analysis ($\mu\text{g/L}$) of elemental species in aqueous solutions. Instrument detection limits (IDLs) are typically in the pG/L to $\mu\text{g/L}$ range, depending on elemental sensitivity and potential matrix effects. Sample preparation, such as acid or microwave digestions, can be performed to accommodate analysis of nonaqueous sample matrices, such as soils, oils, sludges, glasses, and sediments. The ICP-MS technique is not conducive to concentrations of dissolved solids that exceed 0.2%, as these solids can saturate the detector and produce solid deposition on the system sampling interface components, thereby reducing instrument performance.

The intention of this method is to serve as a guidance document for generating laboratory specific ICP-MS standard operating procedures (SOPs). For some procedures, additional documentation, such as data quality objectives (DQOs) and statements of work (SOWs) may be required. Each laboratory SOP should be specific to site requirements and regulations and instrument types. Primarily, this method is intended to provide analytical protocols for environmental regulatory support. Secondly, because of the large potential analytical capability of ICP-MS, this method provides the latitude necessary for research and development projects.

This method supplements the U.S. Environmental Protection Agency (EPA) SW-846 Method 6020 (EPA 1992), and addresses the application of ICP-MS to radioactive elements that are not covered in 6020. Method 6020 should be used as the basis for this method. Table 1 provides a list of potential radionuclides for analysis.

(a) Method was submitted by Steven B. Wyrick (Science Applications International Corporation, Gaithersburg, Maryland), Gary M. Mong and Eric J. Wyse (Pacific Northwest Laboratory, Richland, Washington).

Determination of radionuclides by ICP-MS is a complementary technique to radiochemical counting. The major considerations when selecting ICP-MS versus radiochemical counting techniques are the limiting factors of detection. Generally, ICP-MS performs better for lower activity isotopes, as radiochemical counting methods may require several days to complete, while radiochemical counting methods are more accurate for higher activity isotopes. For samples with intermediate activities, the method of choice may depend on factors such as interferences or radiation handling requirements. Potentially, both methods could be used to complement and corroborate results.

2.0 Summary of Method

The aqueous sample is aspirated into an argon plasma to atomize, ionize, and entrain sample constituents in an argon gas stream. The ionized elements then pass through a sampling interface to reduce the pressure from 760 torr to 1×10^{-5} torr and then into a quadrupole mass spectrometer. The ionized elements are then separated, detected, and quantified according to their respective mass-to-charge ratios. The raw data are examined to correct for potential interference and matrix effects before characterizing the sample components.

This method is meant to be very basic; it will analyze low activity aqueous samples, using the basic instrument configuration (i.e., no instrument upgrades or any special sample preparation, separation or preconcentration). Also, this method is limited to low radioactivity levels, so that minimal special shielding is required. Any instrument upgrades or requirements beyond the scope of this method should be written as separate, element-specific procedures.

3.0 Interferences

Table 1 gives some potential interferences for radioisotopes to be analyzed. In addition, some isobaric interferences are described and accounted for in Method 6020. However, some of the equations used in Method 6020 for corrected interferences assume natural abundance for elemental isotopes; one must consider that samples covered in this method may not always have natural isotopic ratios.

Method 6020, Table 2 (EPA 1992) defines an interference check sample (ICS) to determine potential isobaric interferences. The high concentrations of the components seem to cause some concern to ICP-MS users as to the deleterious effect they may have on instrument performance^(a). Thus, an appropriate level of ICS material is to be determined by the instrumentation. In addition to the components listed in 6020, Ru should be added as a check for its potential contribution to ⁹⁹Tc. See Table 1 of this procedure for additional interferent information.

(a) R. Henry, personal written communication, Fisons Instrument (1993).

Certain techniques, such as dilution, preconcentration, and chemical and physical separation, are occasionally used to reduce or eliminate potential interferences. But the same techniques that minimize interference effects may inadvertently degrade the method detection limit and dilution-corrected concentration accuracy. Any sample modification should be fully described in a separate element-specific procedure.

4.0 Safety

Department of Energy wastes submitted for analysis by ICP-MS may contain various fission products in addition to the long-lived analytes to be determined by the technique. Laboratory protocols for radioactivity screening, handling radioactive samples, and surface decontamination should be in place before sample analysis. Two possible methods for screening are liquid scintillation counting and hand-held radiation monitor counting.

Laboratory and/or site radiation safety procedures should be closely followed. Additionally, laboratory and vendor manual safety procedures, involving the operation of the ICP-MS instrument should be used.

5.0 Apparatus and Materials

Some applications might require specialized modifications to the conventional ICP-MS instrument. These variations can improve sample input efficiency (and thus reduce the total amount of sample required), separate or preconcentrate sample analytes, reduce memory effects, and/or allow for analysis of solid or organic samples. These procedural changes should be covered in element-specific procedures. Some sample system variations are

- dynamic range enhancement
- ultrasonic nebulizer
- direct injection nebulizer
- chromatographic column
- electro-thermal vaporization
- laser ablation
- flow injection analysis.

6.0 Reagents

Isotopic standards must have elemental isotopic abundance well documented and traceable to appropriate national standards. One should not assume natural abundances for elemental isotopes (e.g., the natural abundance of ^{235}U is approximately 0.7%, but some U used for reference standards is depleted, and the ^{235}U isotopic abundance is closer to 0.3%). Calibration standards and quality control standards requirements, as they apply to DQOs should be addressed in appropriate SOPs, if required.

7.0 Sample Collection, Preservation, and Handling

7.1 Sample Collection. The initial sample collection and handling should be addressed in the SOP or in a project SOW, if applicable.

7.2 Sample Dissolution. The kind of dissolution required will depend on what type of analysis is required. Leachable analytes may be required for some applications, while total analytes may be required for other applications. If the samples to be analyzed were received as a solid, sludge, or slurry, they must be dissolved for conventional ICP-MS analysis. Dissolution procedures vary greatly between sample types, but the chosen procedure should be fully described in a separate element-specific procedure. Some dissolution methods are

- microwave digestion
- hot acid digestion
- cold acid digestion
- alkali fusion
- sodium fusion

7.3 Sample Dilution. If the elements of concern are of sufficiently high concentration ($\geq 500 \mu\text{g/L}$) sample dilution is usually necessary. Dilutions are usually made by volume (rather than by weight) with calibrated pipets. The solvent used for dilution is usually a dilute acid.

7.4 Sample Preconcentration. Sample preconcentration may be necessary if the concentration of an analyte is below the IDL, or if a separation is required, as described in section 3.0. Any sample preconcentration should be fully described in a separate element-specific procedure.

8.0 Procedure

- 8.1 Methods.** Several types of methods (with associated calibration protocols) are used to obtain various types of information, with each having its own level of uncertainty. Some of the more commonly used methods are quantitative (QA), semi-quantitative (SQA), standard addition (SA), isotope ratio (IR) and isotope dilution (ID) (Adams et al. 1988).

A qualitative or semi-quantitative scan can be run before other methods to gain a better understanding of the sample composition. These preliminary scans can be useful to determine if radioactive, hazardous, or undesirable analytes, which may produce significant memory or interference effects to the instrument, exist in the sample. If these analytes are not present, or if high accuracy is not required, then these elemental standards do not need to be introduced into the system.

Any prescreening methods should be included in the SOP, element-specific procedure, or project SOW, when required.

- 8.2 System Parameters.** Commercial ICP-MS instruments are provided with software that can automate data acquisition, calibration, and quantification. To take advantage of these capabilities, the analyst must specify the elements and isotopes to be determined, the mode of data acquisition, the calibration technique, standard concentrations, and the sequence in which samples and standards are to be measured. Analysts should refer directly to their instrument manuals for specific instructions on how to enter these parameters.
- 8.3 Data Acquisition.** The three methods of sample acquisition generally available are scanning, peakjumping, and single ion monitoring (Jarvis et al. 1992).
- 8.4 Tuning.** Instrument tuning should be specific to the laboratory SOP, but should meet, as a minimum, the requirements set in Method 6020. Tuning should be specific to the mass range to be analyzed. If specific shorter mass ranges are to be tuned for high resolution, then the associated tuning method should be addressed in the element-specific procedure or project SOW.

9.0 Calculations

Results are ordinarily calculated by the vendor supplied software; however, with some date, the results must be calculated manually or on a spreadsheet because the elemental isotopic abundances are not natural (e.g., samples that contain fission products). If the unnatural isotopic abundances are known, some vendors' software allows the user to modify the isotopic abundances.

For the radioisotopes, activity levels should be reported in addition to concentrations. Given the concentration, atomic weight, and half-life of a radioisotope, the activity can be determined as follows:

$$\frac{(X_i)(\ln 2)(N_o)(10^{12} \text{ pCi/Ci})}{(AW)(t_{1/2})(3.7 \times 10^{10})} = A_i$$

where

- A_i = the activity of species i in pCi/L
 X_i = the concentration of species i in g/L
 N_o = Avogadro's number (6.02×10^{23} atoms per mole)
 $t_{1/2}$ = half life of species i
 AW = atomic weight of species i
 $\ln 2$ = natural log of 2

Note: 3.7×10^{10} is the conversion factor for atomic disintegrations per sec to curies; other values are conversion factors to get desired activity units.

For example, if the concentration of ^{235}U were measured to be 0.28 $\mu\text{g/L}$, and given the half-life and atomic weight of ^{235}U are 7.1×10^8 years and 235 g/mole, respectively, the corresponding activity, A_i , in pCi/L would be calculated as follows:

$$\frac{0.28 \mu\text{g/L} \cdot 10^{-6} \text{ g}/\mu\text{g} \cdot 0.693 \cdot 6.02 \times 10^{23} \text{ atoms/mole} \cdot 10^{12} \text{ pCi/Ci}}{235 \text{ g/mole} \cdot 7.1 \times 10^8 \text{ yr} \cdot 3.1536 \times 10^7 \text{ sec/yr} \cdot 3.7 \times 10^{10} \text{ atoms/sec/Ci}} = 0.60 \text{ pCi/L}$$

10.0 Quality Control

- 10.1 Instrument Detection Limit.** Although Method 6020 defines the instrument detection limit (IDL), it is not being used consistently among ICP-MS users. The IDL defined below may be used; it differs from Method 6020, in principle, but retains the same intent. However, the user may still use the IDL method in Method 6020. The method used should be well documented in the SOP or project work plan.

On three nonconsecutive days, the analyst should calibrate the instrument with standards prepared per Method 6020. The analyst shall determine the concentration equivalent of the blank intensity for each analyte on each day. The standard deviations of the blank equivalent concentrations shall be pooled (Miller and Miller 1993) and multiplied by three; this number shall be defined as the instrument detection limit. In general, this figure of merit, once established, need not be re-evaluated unless: 1) a significant change in instrument sensitivity occurs, or 2) a significant change in instrument background occurs.

10.2 Control Charts

Long-term instrument stability should be monitored to maintain assurance the instrument is functioning properly, or to detect early signs of performance deterioration. Control charting is becoming a popular indicator of instrument performance. Control limits for the control charts should be stated in the SOP, according to the requirements set forth in relevant SOPs and DQOs. One possible plan for control charting is as follows:

Data for the control chart are obtained through a specific analysis on the control standard only; however, if an independent check standard containing the elements of interest is analyzed on a regular sample analysis, these data may also be used. A standard counting the appropriate elements {preferably a multi-element standard reference material (SRM), e.g., National Institute for Standards and Technology (NIST) 1643c} is analyzed against prepared calibration standards that originate from a different stock than does the control standard. Results obtained for each element are plotted against time on the control chart. At a minimum, the chart should display historic data from the current month, as well as the entire previous month. Data for the control chart should be obtained no less frequently than once a week, when the instrument is performing analyses, and no less than once a month, when the instrument is assumed to be functioning properly, but is not processing samples.

11.0 References

- Adams, F., et al., eds. 1988. *Inorganic Mass Spectrometry*. Ch. 6 and 7. J. Wiley and Sons, New York.
- Jarvis, K. E., A. L. Gray, and R. S. Houk. 1992. *Handbook of Inductively Coupled Plasma Mass Spectrometry*. Chapman and Hall, New York.
- Miller, J. C., and J. N. Miller. 1993. *Statistics in Analytical Chemistry: Third Edition*. P. 55, Ellis Horwood PTR, Prentice Hall, Chichester, United Kingdom.

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U. S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Wastes. Physical/Chemical Methods*, 3rd Edition, Proposed Update II, SW-846. Office of Solid Waste and Emergency Response. Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

Table 1. Potential Elements and Characteristics

Element	Isotope	Internal Standard	Interferant	Sample Prep	Analysis Method ^(a)	Comments
Tc	97	¹¹⁵ In	⁹⁷ Mo	TRU•Spec®	IR, ID	Sample preconcentration
	99	¹¹⁵ In	⁹⁹ R	Ion Exchange	QA, ID	
I	127	¹¹⁵ In	¹²⁹ Xe	IC ^(b)	QA	Memory effects
	129	¹¹⁵ In			IR, ID	Preconcentration
Ra	226	²³² Th			SQA	Use ²³⁸ U
	228	²³² Th			SQA	
Th	230	²³² Th			IR, ID	
	232	²⁰⁹ Bi			QA	
U	233	²³² Th	²³⁸ Pu	TRU•Spec®	IR	Use ²³⁸ U
	234	²³² Th			IR	Use ²³⁸ U
	235	²³² Th			IR	Use ²³⁸ U
	236	²³² Th			IR	Use ²³⁸ U
	238	²³² Th			QA	Use ²³⁸ U
Np	237	²³² Th			SQA	Use ²³⁸ U
Pu	239	²³² Th	UH	TRU•Spec®	SQA	Use ²³⁸ U
	240	²³² Th			SQA	Use ²³⁸ U
	241	²³² Th			SQA	Use ²³⁸ U
	242	²³² Th			SQA	Use ²³⁸ U
Am	243	²³² Th			SQA	Use ²³⁸ U

(a) Analysis methods are defined in section 8.1.

(b) Ion chromatography

MM210^(a)ICP-MS of ⁹⁹Tc, ²³⁰Th, and ²³⁴U Using Flow Injection Preconcentration

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method consists of a procedure for measuring ⁹⁹Tc and a procedure for measuring ²³⁰Th and ²³⁴U in soil samples. It is intended as an alternative to radiochemical methods because it is faster, requires less labor, and produces less waste than many radiochemical methods.

The method contains quality control (QC) procedures that are derived from U.S. Environmental Protection Agency (EPA) procedures for inorganic analysis and are provided as guidance. The required level of QC may vary between laboratories and projects. Each laboratory must adopt QC procedures that are adequate for the projects being supported.

The techniques used in this method can also be used to measure other radionuclides, including ²³⁷Np, ²³⁹Pu, and ²⁴⁰Pu. This method will be revised to include other analytes when the procedures are developed.

2.0 Summary of Method

Soil samples are dried, ground, and blended to achieve homogeneity. For ⁹⁹Tc analysis, samples are fused with sodium peroxide and dissolved in nitric acid. For ²³⁰Th and ²³⁴U analysis, samples are fused with lithium metaborate and dissolved in nitric acid.

Sample solutions are analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). A flow injection (FI) analysis system attached to the nebulizer of the ICP-MS system is used to concentrate the analytes by solid-phase extraction and, in the case of ⁹⁹Tc, to provide separation from interferences. Rhenium, ²²⁹Th, and ²³³U are used as internal standards for ⁹⁹Tc, ²³⁰Th, and ²³⁴U, respectively, to correct for varying chemical recovery and instrument drift.

EICrom Industries TEVA•Spec[®] resin is the extraction medium for ⁹⁹Tc. Rhenium and Tc are loaded onto the resin from dilute nitric acid and eluted with 8 M nitric acid. EICrom Industries

(a) This method was submitted by Mark Hollenbach (RUST Geotech Inc., Grand Junction, Colorado).

TRU•Spec[®] resin is used for ²³⁰Th and ²³⁴U. Thorium and U are loaded onto the resin from 4 M HNO₃ and eluted with 0.1 M ammonium oxalate.

The FI concentration step reduces detection limits by approximately a factor of 10 compared to ICP-MS with conventional sample introduction. The instrument detection limits are approximately 0.8 pCi/L for ⁹⁹Tc, 1 pCi/L for ²³⁰Th, and 0.2 pCi/L for ²³⁴U. These correspond to 0.3 pCi/g for ⁹⁹Tc, 0.1 pCi/g for ²³⁰Th, and 0.02 pCi/g for ²³⁴U in soil samples. The analysis time for a sample solution is 4 min.

3.0 Interferences

This method contains mechanisms to identify and control all interferences that are normally encountered. A discussion of interference management is provided below for each analyte.

3.1 Technetium-99

The measurement method could be subject to interferences from ⁹⁹Ru because ⁹⁹Tc cannot be distinguished from ⁹⁹Ru. Ruthenium is a very rare element with an abundance in the earth's crust on the order of 1 ng/g-1 (Cotton and Wilkinson 1972) of which ⁹⁹Ru makes up 12.7%. Naturally occurring Ru is not expected to present a serious problem because it is so scarce. Ruthenium-99 is also a fission product produced from the beta-decay of ⁹⁹Tc. However, ⁹⁹Ru resulting from ⁹⁹Tc decay is also expected to be scarce because the half-life of ⁹⁹Tc is 212,000 years and ⁹⁹Tc has only been produced from fission for approximately 50 years.

High concentrations of Mo could cause an interference if the ¹⁰⁰Mo peak is large enough to overlap with mass 99. The magnitude of the interference depends on the concentration of Mo and the abundance sensitivity of the ICP-MS in use. Newer instruments generally have better abundance sensitivities than older systems.

The TEVA•Spec[®] resin is effective at separating Tc from Ru and Mo. The separation efficiency varies slightly between extraction columns from 97% to greater than 99.5%. The interference check standards described in section 10, Quality Control, are analyzed at the beginning and end of each analytical run to verify that separations from Mo and Ru are effective. Molybdenum-100 and ¹⁰¹Ru are monitored in each analysis to verify the absence of interferences.

3.2 Thorium-230 and Uranium-234

High concentrations of ²³²Th in samples could interfere with both ²³⁰Th and ²³⁴U determinations. Natural thorium is essentially 100% ²³²Th. Any ²³²Th present in the samples is also concentrated by the FL process.

Thorium-232 could interfere with ^{230}Th if the peak at mass 232 is large enough to have a tailing overlap at mass 230. If uncorrected, this would result in a positive interference on ^{230}Th determinations. The magnitude of the interference depends on the concentration of ^{232}Th and the abundance sensitivity and resolution of the ICP-MS in use.

Thorium-232 could interfere with ^{234}U determinations by producing a peak at mass 233 from ThH^+ that overlaps with ^{233}U , which is used as the internal standard. This would result in a negative interference. The amount of ThH^+ observed relative to Th^+ is approximately 0.01% or less, but it will vary with different instruments and operating conditions. Instrument operating conditions should be set to minimize the formation of polyatomic ions.

The magnitude of the interferences should be determined by measuring the count rate at masses 230 and 233 produced by a series of ^{232}Th standards covering the concentration range of ^{232}Th anticipated in samples. When analyzing samples, mass 231 should be monitored to indicate the amount of ^{232}Th present in the sample. Monitoring the tail of ^{232}Th at mass 231 is preferable to actually monitoring mass 232 because ^{232}Th present in samples even at the average crustal abundance {~10 mg/kg (Siegel 1974)} gives an intensity of several million ions per sec at mass 232.

If the potential for interference is significant enough to require correction, the ^{230}Th and ^{233}U counts could be corrected based on the counts observed at mass 231. The correction factor is determined by measuring the ratio of 230 and 233 counts to 231 counts in a ^{232}Th standard at a high enough concentration to produce an interference.

The interference check standards described in section 10, Quality Control, should be analyzed at the beginning and end of each analytical run to demonstrate that ^{232}Th can be tolerated up to the level present in the check standards.

4.0 Safety

The laboratory must have safety and environmental-protection procedures in place to address the following safety issues:

- Handling samples from U.S. Department of Energy (DOE) sites that could contain radioactive material and/or hazardous components
- Handling radioactive material used to prepare standards for this method
- Handling chemicals and operating equipment used for sample preparation and fusion

- Operating ICP-MS and FI analysis systems
- Minimizing and controlling laboratory waste

5.0 Apparatus and Materials

If an apparatus or material is used with only one procedure, the procedure is indicated in parentheses after the description of the apparatus or material.

5.1 Sample Preparation

The following apparatus should be in place before sample preparation.

- Oven that can be maintained at 103°C used for drying samples.
- Pulverizer equipped with ceramic plates for grinding samples, Bico-Braun International model 242-67 or equivalent.
- Sample blender, Patterson-Kelly cross-flow type or equivalent.
- Hotplate with temperature range up to at least 300°C.
- Zirconium crucibles with 55-mL capacity for sodium peroxide fusions (^{99}Tc).
- Oven, with removable hearth plate, for sodium peroxide fusions that can be maintained at 470°C (^{99}Tc).
- Vacuum filtration apparatus and 0.45- μm filter membranes.
- Platinum dishes with 5-mL capacity for lithium metaborate fusions (^{230}Th and ^{234}U).
- Gas burner for lithium metaborate fusions (^{230}Th and ^{234}U).
- Pyrex beakers, 250-mL size (^{230}Th and ^{234}U).
- Shaking hotplate with temperature range up to at least 150°C (^{230}Th and ^{234}U). Can be made by mounting a hotplate onto a platform shaker.

5.2 Flow Injection Analysis System

The following items are elements of the FI analysis system.

- 5.2.1 Perkin-Elmer model FIAS-400MS FI analysis system or equivalent that can be interfaced to an ICP-MS. The system should have a 5-port valve, two multi-channel pumps, an autosampler, and the capability to control a peristaltic pump remotely.
- 5.2.2 Figure 1 is a schematic of the FI manifold showing the tubing arrangement. The following materials and brands or their equivalent should be used. All tubing used to construct the manifold is made of polytetrafluoroethylene (PTFE) with an outer diameter of 0.062 in. such as is available from Upchurch Scientific. The tubing from the valve to the nebulizer is 0.01 in. inner diameter (ID) and the remaining tubing is 0.03 in. ID. The tubing connections are made with Upchurch Scientific Super Flangeless brand or flangeless-style fittings because they do not use O-rings, which are attacked by strong acid, and because tubing connections can be made quickly and easily without a flanging tool. Super Flangeless fittings made of poly ether ether ketone (PEEK) are used to connect the tubing to the column because the fittings are designed for connections that need to be made and broken often. The rest of the tubing connections are made with Tefzel flangeless-style fittings. The tee connectors are made of Tefzel.
- 5.2.3 Pump tubing, Perkin-Elmer 1.52-mm ID, or equivalent, for pumping sample and column rinse solution and 1.14-mm ID, or equivalent, for pumping eluent.
- 5.2.4 Perkin-Elmer flow-injection analysis system (FIAS) columns or equivalent with a volume of approximately 50 μL . Pack columns with EICrom Industries TEVA•Spec[®] resin for ⁹⁹Tc analysis or TRU•Spec[®] resin for ²³⁰Th and ²³⁴U analysis.
- 5.2.5 Peristaltic pump that can be controlled by the FI system and tubing to rinse the nebulizer and spray chamber (see Figure 1).

5.3 ICP-MS Instrument System

The following ICP-MS instrument was used. An equivalent instrument should suffice for general ICP-MS work.

- Perkin-Elmer model ELAN 5000 or equivalent with software and interface to control the FI analysis system.

- Meinhard type C nebulizer and quartz spray chamber or equivalent that are compatible with 8 M HNO₃ (⁹⁹Tc).

6.0 Reagents

All references to water in this method refer to deionized or distilled water that is free of detectable concentrations of the analytes.

6.1 Technetium-99

- 6.1.1 Sodium peroxide, Na₂O₂, powder, 98%.
- 6.1.2 Nitric acid, HNO₃, 16 M (concentrated), Fisher Scientific trace metal grade or equivalent, used for sample dissolution and standards preparation.
- 6.1.3 Nitric acid, 8 M, used for eluent, and 0.5 M, used for the column rinse solution, prepared from Seastar Chemicals double sub-boiling distilled in quartz or equivalent because the molybdenum content is lower than in the trace metal grade.
- 6.1.4 Prepare Re, Mo, and Ru standards from vendor-supplied stock standards.
- 6.1.5 Calibration, QC, and spiking standards should be prepared by diluting National Institute for Standards and Technology (NIST) standard reference material (SRM) 4288 ⁹⁹Tc standard or another suitable stock solution in 0.5 M HNO₃. The following standards are recommended:
 - Calibration standard: 200 pCi/L ⁹⁹Tc in 0.5 M HNO₃
 - Low-concentration check standard (CRI): ⁹⁹Tc at twice the laboratory-determined reporting limit or 5 pCi/L in 0.5 M HNO₃
 - Interference check standard part A (ICSA): 100 µg/L Mo and 25 ng/L Ru in 0.5 M HNO₃
 - Interference check standard part AB (ICSAB): 100 µg/L Mo, 25 ng/L Ru, and 100 pCi/L ⁹⁹Tc in 0.5 M HNO₃
 - Continuing calibration verification standard (CCV): 100 pCi/L ⁹⁹Tc in 0.5 M HNO₃
 - Spiking standard: 200 pCi/mL ⁹⁹Tc in 0.5 M HNO₃

- 6.1.5 The independent-source standard used for initial calibration verification (ICV) should be prepared in 0.5 M HNO_3 from a stock standard obtained from a source other than that of the calibration standard. The concentration of the ICV should be within the linear range, but different from that of any calibration standard.

6.2 Thorium-230 and Uranium-234

- 6.2.1 Hydrofluoric acid, 29 M (concentrated), reagent grade.
- 6.2.2 Nitric acid, 16 M (concentrated) and 4 M, Fisher Scientific trace metal grade or equivalent.
- 6.2.3 Lithium metaborate, LiBO_2 , anhydrous, powder, reagent grade.
- 6.2.4 Thorium-232 standards should be prepared from vendor-supplied thorium standards.
- 6.2.5 Ammonium oxalate, 0.1 M solution in water, should be prepared from reagent grade material used for the eluent.
- 6.2.6 Calibration, QC, and spiking standards for ^{230}Th should be prepared from a vendor-supplied standard. Calibration, QC, and spiking standards for ^{234}U should be prepared by dissolving and diluting New Brunswick Laboratory (NBL) can this be defined (CRM) U500 uranium isotopic standard or from another suitable standard. The following standards are recommended:
- Calibration standard: 800 pCi/L ^{230}Th and 300 pCi/L ^{234}U in 4 M HNO_3
 - CRI: ^{230}Th and ^{234}U at twice the laboratory-determined reporting limit or 8 pCi/L ^{230}Th and 6 pCi/L ^{234}U in 4 M HNO_3
 - ICSA: 1 mg/L Th in 4 M HNO_3
 - ICSAB: 1 mg/L Th, 400 pCi/L ^{230}Th , and 150 pCi/L ^{234}U in 4 M HNO_3
 - CCV: 400 pCi/L ^{230}Th and 150 pCi/L ^{234}U in 4 M HNO_3
 - Spiking standards: 80 pCi/mL ^{230}Th in 0.5 M HNO_3 and 30 pCi/mL ^{234}U in 0.5-M HNO_3 .

- 6.2.7 The ICV standard for ^{230}Th and ^{234}U should be prepared by dissolving and diluting NBL Reference Material 101-A pitchblende ore-silica mixture or from another suitable standard obtained from a source other than that of the calibration standard. The standard is prepared in 4 M HNO_3 . The concentration of the ICV should be within the linear range, but different from that of any calibration standard.
- 6.2.8 The ^{229}Th and ^{233}U standards used as internal standards for ^{230}Th and ^{234}U , respectively, should be prepared from vendor-supplied stock standards.

7.0 Sample Collection, Preservation, and Handling

7.1 Sample Collection and Preservation

Sample collection should be addressed in other standard operating procedures, work plans, or work statements. No special sample preservation techniques are required for the analytes discussed in this method.

8.0 Procedures

8.1 Initial Sample Preparation

Soil samples should be dried in an oven at 103°C for 12 to 24 h, ground to pass through a 200-mesh screen, and blended. This results in a homogeneous sample with a particle size that is readily attacked by the fusions.

8.2 Sodium Peroxide Fusion for ^{99}Tc

- 8.2.1 A 0.250 ± 0.002 g quantity of sample is weighed into a zirconium crucible.
- 8.2.2 For the spiked sample, a small volume of spiking standard is pipetted onto the sample and dried on a hotplate at 90°C . The sample lump is broken up with a small metal spatula. Use of 50 μL of a 200-pCi/mL standard is recommended for spiking.
- 8.2.3 A 2.25 g quantity of sodium peroxide is added to the crucible and mixed with the small metal spatula.
- 8.2.4 The crucible is placed on a hearth plate and heated in an oven at 470°C for 30 min.

- 8.2.5 The crucible is removed from the oven and allowed to cool to room temperature.
- 8.2.6 Approximately 40 mL of water are added to the crucible, and the fusion mixture is allowed to dissolve for approximately 1 h until the effervescence stops.
- 8.2.7 A 4 mL quantity of concentrated HNO_3 is added to the crucible.
- 8.2.8 The mixture is diluted to 100 mL with water.
- 8.2.9 The sample solution is filtered through a 0.45- μm membrane filter to remove turbidity that could plug the extraction column.
- 8.3 Lithium Metaborate Fusion for ^{230}Th and ^{234}U**
- 8.3.1 A 1.00 ± 0.01 g quantity of sample is weighed into a platinum dish, and the sample is moistened with approximately 1 mL of water.
- 8.3.2 For the spiked sample, a small volume of spiking solution is pipetted into the dish. Use of 0.5 mL of an 80 pCi/mL ^{230}Th standard and 0.5 mL of a 30 pCi/L ^{234}U standard is recommended.
- 8.3.3 Approximately 3 mL of concentrated HF are added and heated on a hotplate at approximately 100°C until dry.
- 8.3.4 Step 8.3.3 is repeated two more times for a total of three treatments with HF.
- 8.3.5 A 1.5 g quantity of LiBO_2 is added.
- 8.3.6 The dish is heated over a gas burner to melt the flux. The dish is held with tongs and rocked from side-to-side to contact the entire sample with molten flux. The sample is heated for approximately 8 min until it is completely attacked.
- 8.3.7 The hot dish is dropped into a Pyrex beaker containing approximately 50 mL of water and 5 mL of concentrated HNO_3 .
- 8.3.8 The beaker is heated on a shaking hotplate at approximately 100°C and 100 rpm until the fused sample dissolves. (Note: the fused samples dissolve much faster with a shaking hotplate than with a stationary hotplate.)

- 8.3.9 A 20 mL quantity of concentrated HNO_3 is added, and the sample solution is diluted to 100 mL with water.
- 8.3.10 The sample solution is filtered through a 0.45- μm membrane filter to remove the gelatinous material that forms in some samples and could plug the extraction column.

8.4 Instrument Configuration

- 8.4.1 The FI manifold is assembled as shown in Figure 1 and described in section 5.2. A column packed with the appropriate resin is used for the analysis.
- 8.4.2 The reservoirs are filled with the required eluent and column rinse solution.
- 8.4.3 The FI system is programmed. An example program and a description of the program steps are given in Table 1.
- 8.4.4 The ICP-MS instrument operating conditions and data acquisition parameters should be set. Examples are given in Table 2.

8.5 Instrumental Analysis

- 8.5.1 The ICP-MS system is turned on, and adequate warm-up time is allowed.
- 8.5.2 All daily performance checks required by laboratory procedures should be conducted, such as tuning, sensitivity, resolution, mass calibration, oxide levels, and doubly-charged species levels.
- 8.5.3 The FI system is attached to the nebulizer of the ICP-MS, and a standard, such as the calibration standard, is analyzed in the graphics mode to verify proper system performance. It should be verified by visual inspection that the peak's appearance time, shape, and size are normal. It should be verified that the selected integration time is adequate to measure the peak from baseline to baseline. Figure 2 gives an example of elution profiles for ^{99}Tc and Re standards. Figure 3 gives an example of elution profiles obtained for ^{229}Th , ^{230}Th , ^{233}U , and ^{234}U standards.
- 8.5.4 If ^{230}Th or ^{234}U analyses are being done using correction factors to compensate for ^{232}Th interferences, a Th standard should be analyzed at least in duplicate to determine the correction factors. Use of the ICSA standard is recommended. The correction factor for ^{230}Th is the ratio of blank-corrected counts at mass 230 to blank-corrected counts at mass 231. The correction factor for ^{233}U is the ratio

of blank-corrected counts at mass 233 to blank-corrected counts at mass 231. The correction factors should be entered into the elemental equations for ^{230}Th and ^{233}U .

- 8.5.5 Standards and samples should be loaded into the autosampler, and the required internal standard(s) should be added. Adding 0.05 ng/mL of Re is recommended for ^{99}Tc analysis and approximately 5 pCi/mL of ^{229}Th and 4 pCi/mL ^{233}U are recommended for ^{230}Th and ^{234}U analyses, respectively.
- 8.5.6 The instrument is calibrated with a blank and at least one calibration standard.
- 8.5.7 The calibration is verified by analyzing the ICV standard and a calibration blank (ICB).
- 8.5.8 The CRI, ICSA, ICSAB, CCV standards, and a calibration blank (CCB) should be analyzed in that order.
- 8.5.9 All prepared samples are analyzed followed by the CRI, ICSA, and ICSAB standards with a CCV standard and CCB after every 10 analytical samples and at the end of the analysis run. The CCV and CCB do not count as analytical samples.
- 8.5.10 If ^{230}Th or ^{234}U analyses are being done using correction factors to compensate for ^{232}Th interferences, analyze the Th standard at least in duplicate that was used to determine the correction factors to verify that the correction factors did not change significantly during the run.
- 8.5.11 Any performance checks required by laboratory procedures, such as tuning, are performed at the end of an analytical run.
- 8.5.12 The FI manifold is rinsed thoroughly with water.

9.0 Calculations

The ICP-MS system can be calibrated to report results for sample solutions as pCi/L. Results are converted from pCi/L to pCi/g by correcting for the dilution that results from the digestion. For ^{99}Tc , pCi/L in the sample solution is multiplied by 0.4 to convert the result to pCi/g. For ^{230}Th and ^{234}U , pCi/L is multiplied by 0.1 to get pCi/g. The results are corrected for any additional dilutions done at the time of analysis. The dilution factors could also be programmed into the ICP-MS system software.

The specific activities and the half-lives used to derive them are given in Table 3 for the radionuclides mentioned in this procedure. The specific activities can be used to convert units of radioactivity to units of weight.

10.0 Quality Control

- 10.1 Each laboratory should establish QC procedures that fulfill the requirements of the projects being supported. The QC procedures in this method are derived from U.S. EPA procedures for inorganic analysis and are provided as guidance.
- 10.2 The instrument detection limit (IDL) or MDL should be determined periodically as required by laboratory procedures and whenever the instrument is adjusted in any way that affects the detection limit. The IDL is defined as the concentration equivalent to a signal due to the analyte, which is equal to three times the standard deviation of a series of seven replicate measurements of a reagent blank's signal (EPA 1992). The MDL is defined in Chapter 2 of this manual.
- 10.3 The linear range should be determined periodically as required by laboratory procedures. The linear range is determined by analyzing a check standard during a routine analytical run. The result obtained should be within 5% of the true value. The concentration of the standard is the upper limit of the linear range. If the result for any sample exceeds the linear range, the sample must be diluted and reanalyzed.
- 10.4 Method blanks, matrix duplicates, matrix spikes, and matrix spike duplicates (defined in Chapter 2) should be analyzed at the frequency required by laboratory procedures. Analysis of one of each of these for every preparation batch and for every 20 samples is recommended. Control limits and corrective actions should be established. Generally, the result for the method blank should be no more than the laboratory-determined reporting limit, the relative percent difference for matrix duplicates should be no more than 20% for results greater than 5 times the detection limit, and matrix spike recovery should be within 80% to 120% if the analyte concentration in the sample is less than four times the spike amount.
- 10.5 A laboratory control sample (LCS), defined as a soil sample containing known concentrations of the analytes, should be analyzed with each digestion batch. Control limits should be established for the LCS based on historical method performance.
- 10.6 One serial dilution analysis should be done for each batch of samples. A sample is diluted five fold and analyzed. If the analyte concentration is greater than 10 times the detection limit, the result for the serial dilution should agree within 10% of the original sample result after correction for dilution.

- 10.7** Control limits and corrective actions should be established for the ICV, ICB and CCBs, CRI, ICSA, ICSAB, and CCVs. A control limit of 90% to 110% of the true value is recommended for the ICV and CCVs. A control limit of $0 \pm$ the laboratory-determined reporting limit is recommended for the ICB and CCBs. A control limit of 80% to 120% of the true value is recommended for the ICSAB. No recommendations are made for control limits for the CRI or ICSA.

11.0 Method Performance

11.1 Technetium-99

The IDL is approximately 0.8 pCi/L, which corresponds to 0.3 pCi/g in soil samples.

No soil reference materials with known amounts of ^{99}Tc are available to verify the accuracy of the method. Therefore, samples of two soils contaminated with ^{99}Tc were obtained from the Portsmouth Gaseous Diffusion Plant site and prepared for use as reference materials. The samples, designated PORT11 and PORT13, were dried and ground as described above under section 8.1 "Initial Sample Preparation," blended for overnight, and packaged in 100-g bottles.

Ten bottles of each sample were shipped to the Portsmouth Plant laboratory for ^{99}Tc analysis by the following radiochemical method. Five g of sample were leached with a mixture of sulfuric acid and potassium persulfate. Technetium was extracted from the leachate with tri-n-butyl phosphate (TBP) that was previously equilibrated with sulfuric acid. The TBP was mixed with a scintillation cocktail, and the ^{99}Tc activity was measured by liquid scintillation counting (personal communication with B. W. Short of Martin Marietta Utilities Services, Inc., Radiochemistry Division, Piketon, Ohio, in 1993).

The samples were also analyzed by the FI-ICP-MS method. The results are given in Tables 4 and 5. The 95% confidence intervals were calculated as described by Natrella (1966) based on the t-distribution by multiplying the appropriate t value times the estimated sample standard deviation and dividing by the square root of the number of measurements. The mean result obtained by the FI-ICP-MS method for ^{99}Tc in PORT11 agrees well with the mean result obtained by the radiochemical method considering the proximity of the results to detection limits for both methods. The mean result obtained by FI-ICP-MS for ^{99}Tc in PORT13 is within 2% of the mean radiochemical result, and the relative standard deviation (RSD) of the results is 4.1%.

11.2 Thorium-230 and Uranium-234

The instrument detection limits are approximately 1 pCi/L for ^{230}Th and 0.2 pCi/L for ^{234}U . These correspond to 0.1 pCi/g for ^{230}Th and 0.02 pCi/g for ^{234}U in soil samples.

Accuracy and precision of the method for ^{230}Th and ^{234}U were assessed by analyzing three soil reference materials, designated TRM-4, NRM-4, and NRM-5, that were prepared and characterized by the U.S. Department of Energy (DOE) Grand Junction Projects Office laboratory (Donivan and Chessmore 1987; Donivan and Chessmore 1988). The recommended values were established for the reference soils by alpha-energy spectrometry. Results of FI-ICP-MS are given in Tables 6, 7, and 8. The 95% confidence intervals were calculated as described for ^{99}Tc .

The reference sample TRM-4 contains approximately 8 mg/kg ^{232}Th . This is low enough that correction for interferences caused by ^{232}Th was not required. The mean results obtained were within 1% of the reference values and the relative standard deviations were less than 3% for both analytes. The matrix spike recoveries were all in the range of 90% to 110%.

The reference samples NRM-4 and NRM-5 contain 87 and 165 mg/kg ^{232}Th , respectively. This is approximately 9 and 16 times, respectively, of the average crustal abundance of ^{232}Th . The correction factors described in section 3.2 and step 8.5.4 were used to obtain the results for NRM-4 and NRM-5 listed in Tables 7 and 8. The mean results obtained were within 10% of the reference values, and the RSDs were less than 6% for both analytes in both samples. The matrix spike recoveries were all in the range of 90% to 110%.

12.0 References

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Program Step	Description of Step
1	Sample is pumped at 8 mL/min through the valve to waste to prepare for loading. Analytes are loaded onto the column.
2	Column rinse solution is pumped through the column to waste at 3.5 mL/min to remove residual sample. This step also improves separation from Ru and Mo for ⁹⁹ Tc analysis.
3	Eluent is pumped through the column to the nebulizer at 2 mL/min. This step is used to delay the start of the read cycle until the analytes approach the nebulizer.
4	This is the same as step 3 except that the ICP-MS read cycle is initiated.
5	Eluent is pumped through the column at 3.3 mL/min to rinse any remaining analyte.
6	Column rinse solution is pumped through the column to waste at 3.5 mL/min to rinse residual eluent and prepare the column for loading of the next sample.
7	Pump speed and valve position are set for the autosampler rinse cycle. The autosampler returns to the rinse position for 30 sec to rinse the sample inlet line.

Program Step	Start	Time (sec)	Pump 1 Speed (rpm)	Pump 2 (rpm)	Valve Position	Remote Pump
7	1	15	120	0	2	On
6	1	60	75	0	1	On
5	2	15	0	40	1	Off
4	3	6	0	30	2	Off
3	4	18	0	30	2	Off
2	5	60	0	50	2	Off
1	6	20	0	40	1	Off
Pre-Sample	7	1	120	0	2	On

Table 1. Example FI Program and Description of Program Steps

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Table 2. Example of Instrumental Operating Conditions**ICP-MS**

Forward Power	1000 W
Plasma gas flow rate	15 L/min
Auxiliary gas flow rate	0.8 L/min
Nebulizer gas flow rate	0.8-1.0 L/min

Acquisition parameters (all analyses)

Dwell time	50 ms
Integration time	17 sec
Scan mode	Peak-hop transient
Sweeps per reading	1
Resolution	0.8 amu at 10% peak maximum
Signal processing	Spectral peaks integrated; signal profile counted

Acquisition parameters (⁹⁹Tc analyses)

Readings per replicate	75
Isotopes measured	⁹⁹ Tc, ¹⁰⁰ Mo, ¹⁰¹ Ru, ¹⁸⁷ Re
Internal standard	¹⁸⁷ Re for ⁹⁹ Tc

Acquisition parameters (²³⁰Th and ²³⁴U analyses)

Readings per replicate	61
Isotopes and masses measured	²²⁹ Th, ²³⁰ Th, ²³³ U, ²³⁴ U, Mass 231
Internal standards	²²⁹ Th for ²³⁰ Th and ²³³ U for ²³⁴ U

Table 3. Specific Activities and Half-Lives of Radionuclides Mentioned in this Method

Radionuclide	Specific Activity	Half-Life ^(a) (years)
Technetium-99	17.0 pCi/ng	2.12×10^5
Thorium-229	213 pCi/ng	7340
Thorium-230	19.4 pCi/ng	8.0×10^4
Thorium-232	0.109 pCi/μg	1.41×10^{10}
Uranium-233	9.48 pCi/ng	1.62×10^5
Uranium-234	6.19 pCi/ng	2.47×10^5

(a) From *CRC Handbook of Chemistry and Physics*, 62nd Edition, 1981-1982.

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Table 4. Comparison of ^{99}Tc Results Obtained by FI-ICP-MS and Radiochemical Methods for PORT11 Soil Sample

	<u>FI-ICP-MS (pCi/g)</u>	<u>Radiochemical Method (pCi/g)</u>
	0.9	1.0
	0.8	1.0
	1.1	0.8
	1.0	1.6
	0.9	0.9
	1.0	1.0
	1.1	0.9
	0.9	1.0
	1.2	1.0
	0.9	1.2
Mean Result $\pm$ 95% Confidence Interval	1.0 $\pm$ 0.1	1.2 $\pm$ 0.1
Relative Standard Deviation	18%	12%
Matrix Spike Recovery	93%	

Table 5. Comparison of ^{99}Tc Results Obtained by FI-ICP-MS and Radiochemical Methods for PORT13 Soil Sample

	<u>FI-ICP-MS (pCi/g)</u>	<u>Radiochemical Method (pCi/g)</u>
	12.3	11.5
	11.0	11.5
	11.9	12.4
	12.1	10.7
	11.3	11.4
	11.4	11.4
	11.7	11.6
	11.2	11.5
	10.7	11.9
		11.7
Mean Result $\pm$ 95% Confidence Interval	11.5 $\pm$ 0.2	11.7 $\pm$ 0.2
Relative Standard Deviation	4.1%	2.6%
Matrix Spike Recovery	100%	

Table 6. FI-ICP-MS Results and Matrix Spike Recoveries for ^{230}Th and ^{234}U in the Reference Soil TRM-4

	Thorium-230 Results (pCi/g)	Uranium-234 Results (pCi/g)
	43.8	43.5
	43.8	44.1
	43.4	44.9
	46.6	44.5
	44.6	45.7
Mean Result $\pm$ 95% Confidence Interval	44.4 ± 1.6	44.5 ± 1.0
Relative Standard Deviation	2.9%	1.9%
Reference Values	44.0 ± 1.6	44.6 ± 1.2
Mean Recovery	101%	100%
	Matrix Spike Recovery	Matrix Spike Recovery
	91%	100%
	105%	106%
	99%	101%
	101%	104%
Mean Matrix Spike Recovery	99%	103%

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Table 7. FI-ICP-MS Results and Matrix Spike Recoveries for ^{230}Th and ^{234}U in the Reference Soil NRM-4

	Thorium-230 Results (pCi/g)	Uranium-234 Results (pCi/g)
	12.0	11.6
	13.1	11.8
	11.4	11.1
	12.7	11.5
	12.4	11.3
Mean Result $\pm$ 95% Confidence Interval	12.3 ± 0.8	11.5 ± 0.3
Relative Standard Deviation	5.3%	2.4%
Reference Values	13.5 ± 1.1	11.4 ± 0.6
Mean Recovery	91%	101%
	Matrix Spike Recovery	Matrix Spike Recovery
	90%	97%
	95%	95%
Mean Matrix Spike Recovery	92%	96%

Table 8. FI-ICP-MS Results and Matrix Spike Recoveries for ^{230}Th and ^{234}U in the Reference Soil NRM-5

	Thorium-230 Results (pCi/g)	Uranium-234 Results (pCi/g)
	21.9	21.5
	23.5	21.5
	23.3	21.2
	23.1	20.1
	23.4	21.0
Mean Result $\pm$ 95% Confidence Interval	23.0 ± 0.8	21.1 ± 0.7
Relative Standard Deviation	2.8%	2.7%
Reference Values	25.5 ± 1.8	22.2 ± 1.7
Mean Recovery	90%	95%
	Matrix Spike Recovery	Matrix Spike Recovery
	96%	96%
	105%	95%
Mean Matrix Spike Recovery	100%	96%

MM800^(a)**Ion Chromatography and Inductively Coupled-Mass Spectrometry
Determination of Uranium Concentration Isotopic Abundance in
Groundwater and Drinking Water**

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This procedure can be used to determine U concentration or isotopic ratio composition in groundwater and drinking water, using ion chromatography (IC) and inductively coupled plasma-mass spectrometry (ICP-MS) techniques, at concentrations >10 pg/mL. The information provided by this procedure will allow for evaluation and determination of ²³⁵U enrichment or depletion.

2.0 Summary of Method

The IC and ICP-MS determination of U concentration and isotopic abundance was obtained by adding a ²³³U spike solution with known isotopic and elemental concentration to the sample before sample preparation. Using a 10-mL, 1-bed volume (BV) column of Dowex-1X8 anion exchange resin in the chloride form and a solution chemistry of 2 M HCl as the mobile phase provides for a U chloro-complex having a distribution coefficient (K_d) of 10² (Kraus and Nelson 1956). This allows for 10 BV of a 1% sample solution to be processed. Standard operating procedures for ICP-MS are outlined in (section 8.3).

3.0 Interferences

Spectral interferences include isobaric elemental, molecular, and doubly charged ion interferences. Unless an element is monoisotopic, an interference-free isotope can usually be used. When an interference-free isotope does not exist, the contribution from the interferant can usually be determined and subtracted; the method used in doing so shall be properly documented.

(a) This method was supplied by O. T. Farmer, G. M. Mong, A. Sharma, and C. J. Cementson (Pacific Northwest Laboratory, Richland, Washington).

Only those interferences >0.1% for elements common at higher concentrations and >1% for less common elements should be reported in the final results summary. Isobaric interferences for U isotopes may be observed for U.S. Department of Energy (DOE) wastes due to the presence of Pu, Pa, and Np. However, these elements may be considered as an analog to the lanthanide elements, which do not produce anion chloro-complexes in HCl solutions. This should be confirmed using a Pu, Pa, and Np spike. Other interferences, such as mass loading, may also be observed due the presence of elements such as Zn and Fe. However these elements do not produce isobaric interferences for the determination of U using ICP-MS. Table 1 lists possible isobaric interferences for uranium isotopic determination. For more details on interpreting interferences, refer to the Fisons PlasmaQuad Software Manual, or U.S. Environmental Protection Agency (EPA) Method 6020 CLP-M v. 8.0.

Table 1. Isobaric Interferences for Uranium								
Name: Plutonium Element Nuclides:			Name: Protactinium Element Nuclides:			Name: Neptunium Element Nuclides:		
Nuclide	Weight	Half-Life	Nuclide	Weight	Half-Life	Nuclide	Weight	Half-Life
²³⁶ Pu	236.046	2.87 y	²³⁴ Pa	234	6.69 h	²³⁵ Np	235	1.085 y
²³⁷ Pu	237.048	45.2 d	^{234m} Pa	234	1.17 m	²³⁶ Np	236	1.6E05 y
²³⁸ Pu	238.049	87.7 y				^{236m} Np	236.05	22.5 h
						²³⁸ Np	238	2.117 d

4.0 Safety

Ordinary laboratory safety procedures are assumed. DOE waste, either as leachates or as specific chemical separation process material, may contain significant amounts of fission products or actinides. Shielding and radiochemical safe-handling practices are assumed for those instances where radioactivity is present.

5.0 Apparatus and Materials

5.1 Sample Preparation

- 250 mL nalgene beaker
- Nalgene cover glass
- adjustable hot plate
- 0.1, 1.0, and 10.0-mL pipettes

- Four place balance
- 0.45- μm Filtration system

5.2 Ion Exchange

- 10-mL column with zero head space
- Dowex 1 X 8 anion resin
- Gradient pump
- Sample pump
- Eluent delivery module
- Fraction collector

5.3 ICP/MS

- Ultrasonic Nebulizer (USN)
- Auto sampler

6.0 Reagents

- American Society for Testing and Materials (ASTM) Type II water (ASTM D1193)
- Concentrated HCl
- 30% H_2O_2
- Concentrated HNO_3
- Natural isotopic U standard
- ^{233}U standard

7.0 Sample Collection, Preservation, and Handling

This procedure implements processes specified in Method 6020 CLP-M Version 8.0 whenever applicable. Special care should be taken to avoid contamination while collecting samples. All samples should be placed in a sealed container. Proper shielding should be provided to handle the sample safely.

8.0 Procedure

8.1 Acid Digestion Procedure for IC and ICP-MS Analysis

- 8.1.1 The sample should be shaken, and 10 mL of the sample should be transferred to a 20-mL plastic sample bottle. Then 0.1 mL of (1:1) $\text{HNO}_3\text{:H}_2\text{O}_2$ are added to the sample.
- 8.1.2 The ICP-MS is optimized using a 10-ng/mL solution of natural U for a maximum ^{238}U count rate. Each sample solution should be compared to this standard for relative concentration. This procedure will determine the amount of ^{233}U spike that will be added in the actual sample preparation. The ratio of $^{233}\text{U}/^{238}\text{U}$ in the final sample solution should be between 0.5 to 1.5. The amount of ^{233}U spike is determined by the cognizant scientist and should be near the value expected for the sample U concentration or at a minimum at a detectable amount (5 to 10 times the instrument detection limit). If the ^{238}U is above 0.1 $\mu\text{g/mL}$ in this solution, the sample should be diluted before it is prepared.
- 8.1.3 The sample should be shaken, and 100 mL of well-mixed sample should be transferred to a 250-mL Nalgene beaker.
- 8.1.4 Then 1 mL of (1:1) $\text{HNO}_3\text{:H}_2\text{O}_2$ and 2 mL of 30% H_2O_2 are added to the sample to oxidize U(IV) to U(VI) and break down any organic material.
- 8.1.5 An appropriate amount of a spike solution of ^{233}U (as defined by the above procedure) is added to the samples being prepared. The sample should be labeled with the sample identification.
- 8.1.6 The sample is covered with a watch glass or similar cover and heated on a steam bath of hotplate for 2 h at 95°C or until the sample volume is reduced to between 25 and 35 mL.
- 8.1.7 The sample is cooled and filtered with a 0.45- μm filter to remove insoluble material.

- 8.1.8 Then 17 mL of 12 M HCl are added to the digestion vessel, and the sample volume is adjusted to 100 mL, which will provide an ~2 M HCl sample solution. The sample is now ready for IC separation.

8.2 Ion Exchange

8.2.1 Column Characteristics

Before any column separation of U can be preformed, the column characteristics must be established. This is accomplished by loading a zero head space column with prewashed Dowex 1X8 anion resin (100-200 mesh), strong base resin that has all inert material removed.

The next step is to condition the resin to the chloride form using 2 to 4 BV of 2 M HCl. A solution of 100 ng/mL of natural uranium having a solution matrix of 2 M HCl is processed through the column and directly into the ICP-MS to determine the number of BV required for U breakthrough (BT). The determination of BT will establish the number of mL of sample in 2 M HCl that can be processed with this column. This procedure will only require that 15 BV be obtainable before U BT.

The next step is to determine the number of mL of H₂O necessary to elute a 100-mL (10 BV) U solution off the column. First, the column is conditioned with 2 to 4 BV of 2 M HCl. Second, 100 mL (10 BV) of a 2 M HCl U solution is loaded. Third, 2 BV of 2 M HCl are processed; these fractions are diverted to waste. Fourth, the U is eluted using H₂O directly into the ICP-MS, and the BV of H₂O required to remove U is determined. These characteristics will now be used to separate and collect U in groundwater and drinking-water samples. (Note: If the ²³³U spike solutions are contaminated with Pu, Np, or Pa or the 2 M HCl eluent is contaminated with U, then an IC separation or clean up can be performed using this procedure. If this is done, then an analysis of the solution is required to determine the U concentration and isotopic abundance of this solution using ICP-MS. The need for any spike cleanup will be displayed in the blank solution if there is shown to be any alteration in the U isotopic ratios after IC separation.) (Kunin 1956; Marcus 1968).

8.2.2 Sample Processing

System configuration for separating and eluting U is defined in Figures 1 through 4. In Figure 1, the anion column is equilibrated with 20 mL of 2 M HCl to convert the resin to the Cl⁻ form, with this solution being diverted to waste. In Figure 2, the gradient pump is turned off and valve 5 is switched to the off

<u>Time</u>	<u>Gradient</u>		<u>% E2</u>	<u>V5</u>	<u>V6</u>	<u>Fraction Collector</u>	<u>Sample Pump</u>
	<u>Flow</u>	<u>% E1</u>					<u>Flow</u>
0.0	5.0	0.0	100	On	Off	Waste 2	0.0
4.0	5.0	0.0	100	On	Off	Waste 2	0.0

Figure 1. Column Conditioning with 2 M HCl

<u>Time</u>	<u>Gradient Flow</u>	<u>% E1</u>	<u>% E2</u>	<u>V5</u>	<u>V6</u>	<u>Fraction Collector</u>	<u>Sample Pump Flow</u>
4.0	0.0	0.0	0.0	Off	Off	Off	5.0
24.0	0.0	0.0	0.0	Off	Off	Off	5.0

Figure 2. 100-mL Sample Loading on Column

position; the sample pump is put inline to the column, and 100 mL of sample are loaded. The output from the column is also diverted to waste. This solution will contain lanthanide elements, actinides, alkali, alkaline earth elements, and most transition elements (Kraus and Nelson 1956; Hudgen 1956). In Figure 3, the gradient pump is turned on, valve 5 is switched to the on position, and the column is washed with 20 mL of 2 M HCl. This is to remove all elements that have little or no Kd values for anion chemistry in 2 M HCl. This solution is also diverted to waste. In Figure 4, the eluent is changed to H₂O, and U is eluted with 20 mL of H₂O. This solution is collected by the fraction collector and is ready for analysis by ICP-MS.

8.3 ICP-MS

8.3.1 Instrument Detection Limit

The instrument detection limit (IDL) is determined by multiplying by three the average of the standard deviations obtained from the analysis of a standard solution (each analyte in reagent water) at a concentration 3 to 5 times the expected IDL, with seven consecutive measurements. For general purposes, once an IDL has been established, it is valid until either 1) a significant change in instrument response occurs, or 2) there is a major change or repair to the instrument (e.g., a new sample interface or quadrupole); certain projects may have more stringent requirements regarding the frequency and/or protocol of determining the IDL (March 1968).

9.0 Instrument Operation and Analysis

The following procedures are to be used in conjunction with the VG Plasmaquad operating and user's manuals. The procedures below assume that the instrument is operating and functioning normally.

9.1 Normal Operating Conditions

Operating conditions typically change on a daily basis. The following parameters are guidelines for proper instrument performance:

Plasma Gas	~13 liters/min (Lpm)
Auxiliary Gas	~0.8 Lpm
Nebulizer Gas	~0.9 Lpm
Forward Power	1250 W
Reflected Power	<5 W
Nebulizer	USN

<u>Time</u>	<u>Gradient</u>		<u>% E1</u>	<u>% E2</u>	<u>V5</u>	<u>V6</u>	<u>Fraction Collector</u>	<u>Sample Pump Flow</u>
	<u>Flow</u>							
24.0	5.0		0.0	100	On	Off	Waste 2	0.0
28.0	5.0		0.0	100	On	Off	Waste 2	0.0

Figure 3. Wash Column with 2 M HCl

Time	Gradient		% E1	% E2	V5	V6	Fraction Collector	Sample Pump Flow
	Flow							
28.0	5.0		100	0.0	On	Off	On	0.0
32.0	5.0		100	0.0	On	Off	On	0.0

Figure 4. Elution of Uranium with H₂O

Sampling Height
(mm above load coil) 12 mm

9.2 Tuning the Instrument

At least 30 min should be allowed for the instrument to equilibrate before analyzing any samples. The ICP-MS is then tuned by aspirating the tune solution and adjusting the lens voltages for optimal sensitivity. The element in the tune solution having the middle mass (e.g., In at 115 amu) is typically tuned first, with the low and high masses being tuned subsequently only if their resulting sensitivities are determined to be insufficient.

9.2.1 Instrument Response and Precision Check

The instrument response is determined using the tune solution, and shall be at least 1×10^6 counts per second per ppm at 115.0 amu by pneumatic nebulization (assuming the tune solution contains In) to be considered acceptable for analysis. Because it enhances instrument response by 10 to 50 times, tuning using the USN (Cetac Model U-5000) is typically performed using a tune solution with element concentrations approximately 1 to 10% that of the pneumatic nebulizer tune solution, and requires optimization of both the instrument and the nebulizer. The "level" and "tuning" settings on the USN are adjusted to maximize output (indicated on the output meter); output may be slightly compromised, however, to optimize the aerosol density and/or instrument response. The ICP-MS is tuned in the same manner with the USN as with the pneumatic nebulizer. Instrument response using the USN must be at least 5×10^7 cps/ppm at middle mass to be acceptable for analysis. The USN chiller must be running for at least 30 min before data acquisition using the USN, and preferably before USN operation.

10.0 Calculations

10.1 Mass Bias Correction

A natural uranium standard is run to evaluate ^{235}U and ^{238}U isotopic abundance. The system background is subtracted from each isotope. This gives the known abundance. This step is repeated three times. The following equations are used to calculate the mass bias correction:

$$\text{Avg} \left[\left(\frac{{}^{235}\text{U} - \text{Bkg}}{({}^{235}\text{U} - \text{Bkg}) + ({}^{238}\text{U} - \text{Bkg})} \right) \right] = \text{Measured } {}^{235}\text{U}$$

$$\text{Avg} \left[\left(\frac{(^{238}\text{U} - \text{Bkg})}{(^{235}\text{U} - \text{Bkg}) + (^{238}\text{U} - \text{Bkg})} \right) \right] = \text{Measured } ^{238}\text{U}$$

$$\frac{X_{\text{measured}}}{X_{\text{true}}} = \text{Mass Bias Correction (MBC)}$$

where, X_{Measured} represents the actual value obtained from the mass spectrometer in counts per second, and X_{True} represents the true value of the standard used in counts per second.

10.2 Isotopic Concentration

Isotopic concentration can be determined by introducing a known amount of ^{233}U as the spike. The isotopic concentration of ^{235}U and ^{238}U can be determined relative to ^{233}U by the following equation:

$$\frac{\text{CPS of } ^{235}\text{U} \times \text{MBC} \times \frac{\text{Conc. of } ^{233}\text{U}}{\text{CPS of } ^{233}\text{U}}}{\text{Sample Volume (mL)}} = \frac{\text{gm } ^{235}\text{U}}{\text{mL}}$$

$$\frac{\text{CPS of } ^{238}\text{U} \times \frac{\text{Conc. of } ^{233}\text{U}}{\text{CPS of } ^{233}\text{U}}}{\text{Sample Volume (mL)}} = \frac{\text{gm } ^{238}\text{U}}{\text{mL}}$$

where CPS = counts per second

10.3 Total Uranium Concentration

Total U concentration is the sum of all observed U isotopes. Since ^{234}U and ^{236}U are relatively low in natural abundance, these isotopes can be neglected in total U concentration determinations. The following equation should be used:

$$\text{Total U} = ^{235}\text{U (gm)} + ^{238}\text{U (gm)}$$

10.4 Isotopic Abundance

Once total U is determined, the isotopic abundance of ^{235}U and ^{238}U can be obtained by taking their concentration respective to the total U. This is shown in the following equation:

$$\frac{^{235}\text{U}}{\text{Total U}} = ^{235}\text{U Abundance}$$
$$\frac{^{238}\text{U}}{\text{Total U}} = ^{238}\text{U Abundance}$$

Once isotopic abundance is known, depletion or enrichment can be determined by comparing the ratio with 0.715, which is the naturally occurring ratio. If the ratio is less than 0.715, U is depleted, and if it is greater than 0.715, it is enriched.

11.0 Quality Control

11.1. Sample Preparation Check Sample

11.1.1 A matrix sample solution is used having a known concentration and isotopic abundance of U spiked with ^{233}U and processed through all steps of the sample-preparation procedure. This solution validates the sample preparation.

11.2 Instrument Check Sample

11.2.1 To evaluate the instrument response, a known natural U standard is spiked with a known amount of ^{233}U .

12.0 Method Performance

To be provided.

13.0 References

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Chapter 10

Radiochemistry

Scope and Application

This chapter summarizes guidance pertinent to U.S. Department of Energy (DOE) sites for successfully characterizing radionuclides in environmental and waste management (EM) samples. This chapter and the corresponding methods are intended to supplement other standard methods available through such organizations and/or publications as the American Society for Testing and Materials (ASTM 11.01, 11.02, 12.01, 1993), U.S. Environmental Protection Agency (Kreiger and Whittaker 1980), the Environmental Measurements Laboratory (Chieco et al. 1990), and *Standard Methods for the Examination of Water and Wastewater* by the American Public Health Association (Greenberg et al. 1992). The guidance in this section includes limitations of radiochemical analyses, definitions of minimum detectable activity (MDA), quality control (QC), sub-sampling considerations, data reporting, and a brief summary of radiochemistry methods included in this chapter.

For the purposes of this chapter, radiochemistry methods refer to the preparations and chemical separations where final measurements are based on detection of alpha, beta, X-ray, neutron, and/or gamma emissions. Sample matrices covered by this chapter include, but are not limited to, soil, water, high-level radioactive tank waste, and surfaces (e.g., surface contamination). Methods in this chapter include those with significant adaptations of standard methods, new technologies, and consolidated procedures from the *DOE Procedures Database* at Los Alamos National Laboratory. Field and laboratory screening techniques are also included.

Limitations

It is important to understand the purpose for the analytical data; often what is initially requested is not what is actually needed. The data quality objectives planning process (see Chapter 1) is generally used to resolve such issues. As a part of the planning process, it is important to clarify the inherent limitations of methods and detection systems used for radiochemical analyses. For a chosen method, it is recommended that the client also be made aware of any associated limitations as they pertain to the analytical samples.

The radioactive nature of the sample often imposes limits on analytical choices. Examples of these limitations include sample aliquot size and sample handling options (e.g., hot cells). Other sample-matrix considerations also may influence analytical operations. For example, samples with extremely high levels of U contamination will probably need a special U cleanup before chemical separation for Pu and Am. Known analytical limitations specific to each radiochemistry method are listed with the method.

Large samples are usually obtained in the field so that many different types of analyses can be conducted on the sample. Laboratory sub-sampling is often difficult due to the heterogeneous nature of many samples. The samples should be sub-sampled in the laboratory for one or more particular analyses such that they are representative of the original sample. Standards established for sub-sampling (e.g., grinding, coning, and quartering soils) may not be practical for use with high-level radioactive samples. Laboratory

protocols should be developed to ensure that representative sub-samples are taken. The protocols should incorporate limitations imposed by the radioactive nature of the samples as well as specific project needs.

Facility-design considerations, with their potential impact on the quality of radioanalytical results, have been thoroughly evaluated with respect to radioanalytical laboratories and nuclear instrumentation rooms (ANSI standard N42.2).^(a)

General laboratory-safety considerations are discussed in Chapter 4, Safety. Specific and unusual safety concerns associated with a particular method are called out in the safety section of the method.

Definitions

Various terms are defined in this section because they relate specifically to radiochemistry applications. More general usage terms can be found in Chapter 2, Quality Control.

Decision Level Count Rate (DLR). The DLR {also referred to as L_c (Currie 1968)} at which a signal is designated as being statistically different than background {with a 5% probability of a Type I (false positive) error} should be calculated using the formula:

$$DLR = 1.645 S_o \quad (1)$$

where

S_o = the standard deviation in the net count rate of a sample that has no added analyte, but

may have interfering nuclides equal in concentration to the sample in question

and

$$S_o = (S_{B1}^2 + S_{B0}^2)^{1/2} \quad (2)$$

where

S_{B1} = the standard deviation in the count rate of the sample (B1), by the routine measurement procedure, where the sample contains no actual analyte activity above that of the appropriate blank, but may contain typical contaminating radionuclides. When applicable, this term should include the propagated uncertainty in making any radioactivity interference corrections to the net sample count rate if not included in S_{B0}

S_{B0} = the standard deviation in the count rate of an appropriate blank (B0).

If the background of the detection system is very stable and reproducible (as determined through a statistical test), and no radioactivity interferences are present in the sample, then S_{B0} may be minimized using a very long counting time.

For applications where the number of background counts accumulated in a typical counting interval of a blank is less than 10, the net count rate distribution will not be Gaussian. Under this circumstance, the number of false-positive results observed will be greater than 5%. The actual distribution of the S parameter obtained from repetitive blank (or background) measurements should be evaluated to determine the net count rate corresponding to the upper 5%. The net count-rate value corresponding to the upper five percentile of this measured distribution will be the DLR.

(a) American National Standards Institute (ANSI) N42.2. "Measurement Quality Assurance of Radioassay Laboratories," February 9, 1994, Draft.

The DLR concept is a statistical evaluation of the radiation measurement system's capability to measure a true signal above its background. As such, the DLR-calculated value is independent of other radioactivity or concentration parameters and is referenced to the time of the measurement and not to any sample collection date.

Decision Level Concentration (DLC). The DLC is used to express the DLR term in units of radioactivity concentration.

$$\text{DLC} = \text{DLR}/(K \cdot Q \cdot Y \cdot I) \quad (3)$$

where, for the individual sample,

K = calibration factor or efficiency (e.g., cps/Bq, cpm/dpm)

Q = sample quantity, mass or volume

Y = chemical yield

I = decay or in-growth factor.

Minimum Detectable Count Rate (MDR). The MDR {equivalent to L_D (Currie 1968)} is the mean expected count rate of samples having a 5% probability of not being detected where activity is present. The MDR may be calculated from the formula:

$$\text{MDR} = \frac{2.71}{T_B} + 2 \cdot \text{DLR} = \frac{2.71}{T_B} + 3.29 S_0$$

where

2.71 = adjustment for low-level background count rate

T_B = counting time of the appropriate blank.

Using different sample and background count times, the following equation may be applied to calculate the MDR:

$$\text{MDR} = \left[3.29 \cdot \sqrt{\frac{\text{CR}_B}{T_B} \cdot \left(1 + \frac{T_B}{T_S} \right)} \right] + \frac{2.71}{T_B}$$

where

CR_B = background or blank count rate

T_B = background or blank count time

T_S = sample count time.

In the more specific case, where the sample count time is equal to the background or blank count time ($T_B = T_S$) and the standard deviation of the blank is equal to the standard deviation of the sample ($S_{B1} = S_{B0}$), the following simplified equation may be used:

$$\text{MDR} = \frac{4.65 \sqrt{C_B}}{T_B} + \frac{2.71}{T_B}$$

where

C_B = the background or blank counts.

Minimum Detectable Concentration (MDC). The MDC is calculated from the MDR as follows:

$$\text{MDC} = \frac{\text{MDR}}{Q \cdot Y \cdot I \cdot K}$$

where

Q = sample quantity, mass or volume

Y = chemical yield

I = decay or in-growth factor

K = calibration factor or efficiency (e.g., cps/Bq, cpm/dpm)

This simplified equation is typically used for calculating the nominal MDC parameter for simple applications (single nuclide, no interferences, constant background, etc.) and should be used only for estimating a detection system's capability under typical conditions. Further information on appropriate calculations to determine MDC is given by EPA 520 (1980) and the Nuclear Regulatory Commission (NRC 1986, NRC 1984).

Primary Radionuclide Standard. This is a standard directly traceable to the National Institute of Standards and Technology (NIST) or other certified vendor.

Secondary Radionuclide Standard. This is a standard calibrated relative to a primary standard.

Quality Control

Quality control for radioisotopic measurements in the laboratory is implemented at two stages, sample preparation and nuclear instrumentation. General QC considerations of these two steps are discussed below.

Sample Preparation

General issues regarding QC for sample preparation and analysis are discussed in Chapter 3, Quality Control. Qualification guidelines for modified methods are discussed in Appendix B. Method-specific QC parameters are identified in the specific method under the Quality Control heading. Some common QC parameters for radiochemistry applications include criteria for chemical yield and purity of the separated fraction. Use of sample duplicates, method blanks, and blank spikes are usually indicated to aid in evaluating the batch data. Quality control applied to screening techniques is expected to be much less restrictive. Screening applications may employ the

use of a method blank and the means of evaluating (or normalizing to) the chemical recovery (e.g., tracers or carriers).

Nuclear Instrumentation

All measurements in a radioanalytical laboratory eventually require the use of counting equipment to measure alpha, beta, X-ray, gamma, or neutron radiation. General considerations of instrument calibration and control are discussed below.

Initial Calibration

Instrument calibrations should be performed as needed using primary or secondary radionuclide standards traceable to the NIST or other recognized vendors. Re-calibration is recommended in the event that the instrument/system has malfunctioned, and the response of repaired equipment to a QC test exceeds the QC chart's control limit. Calibration standards should be prepared homogeneously and in accurately defined geometries having exact (or within correctable parameters) radiometric characteristics of the sample matrix/geometry. Instrument reliability tests {e.g., plateau curves for gross alpha and beta detectors, and peak locations and peak widths for pulse height analyzer (PHA) systems} should be performed at the time of calibration and periodically as appropriate for the instrument. The scope and frequency of these tests may need to be adjusted to meet other analytical requirements.

Verification of Instrument Response

To ensure that an instrument responds in the same manner after its calibration, an instrument-response check source should be used in conjunction with an instrument QC chart (see Chapter 3). The QC chart and the response of an instrument QC check source are directly linked to the calibration of the instru-

ment. Check sources for instrument response should provide adequate counting statistics (a minimum of a 1% Poisson statistical uncertainty) over the time period for which the source is to be counted. However, the source should not be so radioactive as to cause pulse pileups, dead time that is significantly different from that to be expected from routine samples, or gain shift in the case of PHA systems. For example, a check source for a PHA system, equipped with a modern analog to digital converter (ADC), should not count a total rate exceeding 1000 counts per second (c/s). The check source-to-detector geometry should be known and reproducible.

Tolerance limits for the associated control chart should be commensurate with the performance criteria for sample analysis. For example, the control limits could be set at a percent deviation from the mean response value, which ensures instrument performance at an acceptable level.

Data Reporting

Unless otherwise required, the report of radioanalytical results should provide the following items:

- sample identifying code or information
 - reference date for the reported results (e.g., collection date)
 - quantification and identity of radionuclides
 - estimate of total propagated uncertainty (includes contributions from all parts of the analytical process)
 - detection limit (DLC and/or MDC) for each nuclide analyzed if the analyte value is below the DLC or MDC
 - identification of specific measurement processes
 - identification of person responsible for the report
- The following information should be available and reported upon request:
- total volume or weight of the sample submitted and analyzed
 - estimate of the counting uncertainty
 - QC data demonstrating the quality of the measurement process
 - identification of radioisotope standards
 - specific analytical parameters; i.e., chemical yields, count times, decay factors, counter efficiency, etc.
 - primary data (e.g., laboratory notebook, preparation logs, instrument printouts, etc.)
 - date, time, mode, and place of sub-sampling
 - receipt or chain-of-custody information
 - definition of reporting conventions, such as "detection limit"
 - references to equipment, calibrations, and other QC-related documents
 - procedural deviations

- performance-evaluation results

The following conventions are used in data reporting:

- uncertainty estimates should be rounded to two significant figures
- concentration should be rounded to the same decimal place as the uncertainty estimate
- detection limits should be rounded to no more than two significant figures.

For data retained in electronic storage media, negative values should not be rounded or truncated. For data to be averaged, negative values should not be truncated or zeroed.

Summary of Methods

A brief description of factors used in choosing the most appropriate method is provided in Chapter 6, Choosing the Correct Method. The method numbering system was briefly described in the Introduction. Table 10.1 identifies methods available in this chapter and elsewhere (ASTM, Chieco et al, Greenberg et al., Kreiger et al.). They are listed as they apply to specific analytes and matrices. Table 10.2 includes a brief summary of each of the methods available in this chapter.

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Table 10.1* Available Standard Radiochemistry Methods

Field	Laboratory			
	Soil	Soil	Aqueous	Tank/ High Level
Sample Preparation		C 999 ^(a)		
Screens				
Alpha		RP710 ^(b)	900.0 ^(c) , 7110 ^(d) , D 1943 ^(a) , RP710 ^(b)	RP710 ^(b)
Beta		RP710 ^(b)	900.0 ^(c) , 7110 ^(d) , D 1890 ^(a) , RP710 ^(b) , RP720 ^(b)	RP710 ^(b)
Tritium			RP720 ^(b)	
Actinides		RP735 ^(b)	RP725 ^(b) , RP735 ^(b)	RP725 ^(b)
Gamma Spectrometry				
Ge(Li) or HPG	RS100 ^(b)	RI010 ^(b)	D 3649 ^(a) , RI010 ^(b) , 901.1 ^(c)	
Nal(Tl)		RP730 ^(b)	D 4962 ^(a) , 901.1 ^(c) , RP730 ^(b)	
Chemical Separations				
For Alpha Analysis				
Pu		C 1001 ^(a) , Pu-02 ^(c) , Pu-03 ^(c)	D 3865 ^(a) , RP800 ^(b)	RP800 ^(b)
U		C 1000 ^(a) , U-02 ^(c)	908.0 ^(c) , 7500-U ^(d)	
Am/Cm		Am-01 ^(c) , Am-02 ^(c)	D 3972 ^(a) , U-02 ^(c)	
Ra		Ra-02 ^(c) , Ra-04 ^(c)	Am-03 ^(c) , RP800 ^(b)	RP800 ^(b)
			903.0 ^(c) , Ra-03 ^(c) , 903.1 ^(c) , Ra-05 ^(c)	
			7500-Ra ^(d) , D 2460 ^(a)	
For Beta Analysis				
Tritium		RP580 ^(b)	906.0 ^(c) , 7500- ³ H ^(d)	RP580 ^(b)
			D 4107 ^(a) , RP580 ^(b) , ³ H-01 ^(c)	
			³ H-02 ^(c)	
			RP300 ^(b)	RP300 ^(b)
			RP530 ^(b)	RP530 ^(b)
⁵⁹ Ni, ⁶³ Ni			905.0 ^(c) , Sr-01 ^(c) , RP501 ^(b)	
⁷⁹ Se			RP500 ^(b) , RP510 ^(b) , RP501 ^(b)	
⁸⁹ Sr, ⁹⁰ Sr		RP510 ^(b) , RP520 ^(b)	7500-Sr ^(d) , Sr-02 ^(c) , RP520 ^(b)	RP501 ^(b)
⁹⁰ Sr		Sr-02 ^(c)	RP550 ^(b) , Tc-01 ^(c) , RS551 ^(b)	
			Pb-01 ^(c) , RP280 ^(b)	
			904.0 ^(c)	
⁹⁹ Tc	RS551			
²¹⁰ Pb				
²²⁸ Ra				
For LEPS/Gamma Analysis				
⁹⁴ Nb, ^{95m} Nb			RP330 ^(b)	RP330 ^(b)
¹²⁹ I			RP230 ^(b)	RP230 ^(b)
¹³¹ I			D 4785 ^(a) , 7500-I ^(d) , 902.0 ^(c)	
Non-Specific Methods				
Electrodeposition			G-01 ^(c) , G-02 ^(c)	
Co-precipitation			G-03 ^(c)	
Instrumental Analysis				
Gamma Spectroscopy			D 3649 ^(a)	
Alpha Spectroscopy				
Gross Beta Analysis			RP710 ^(b)	
Gross Alpha Analysis			RP710 ^(b)	
Beta Spectroscopy (LSC)			RI100 ^(b)	
Miscellaneous				
Surface Analysis				
Alpha Emission Rate	RA010 ^(b) , RA020 ^(b)			

(a) From the 1993 Annual Book of ASTM Standards, Water (I), Vol. 11.01, Water (II), Vol. 11.02, and Nuclear Energy, Vol. 12.01.

(b) Included in this document.

(c) From EPA's Prescribed Procedures for Measurement of Radioactivity in Drinking Water.

(d) From Standard Methods for the Examination of Water and Wastewater.

(e) From EML Procedures Manual (HASL-300).

Table 10.2. Radiochemistry Methods

Method Number	Title	Summary
RS100	<i>In Situ</i> Analysis of Gamma-Ray-Emitting Radionuclides by Borehole Logging	A calibrated gamma spectrometer is used to measure and map the gamma-emitting isotope distribution as a function of depth from the surface.
RS551	Rapid Isolation and Measurement of Technetium-99 Using Anion-Exchange Filter Membranes	Anion-exchange filter membranes are used to selectively adsorb pertechnetate from aqueous solutions. The membranes are counted by LSC or by gas-flow proportional counting. Matrix-specific adsorption efficiency is determined as a function of the activity on the two membrane filters.
RP230	Iodine-129 Analysis in Aqueous Solutions	Iodine is isolated by repeat extractions and ion exchange. Determination proceeds by gamma counting ^{129}I and gravimetric yield determination, or by neutron activation analysis followed by counting ^{130}I where yield is determined by ^{131}I tracer.
RP280	Determination of Lead-210 in Water Using Extraction Chromatography	Lead is selectively extracted onto Sr-Spec [®] resin from an aqueous matrix; then eluted with ammonium oxalate and set aside for ^{210}Bi ingrowth. The solution is then prepared for gas-flow proportional counting, and the ^{210}Pb is determined based on the ^{210}Bi ingrowth.
RP300	Nickel-59 and Nickel-63 Determination in Aqueous Samples	Nickel is isolated using a dimethylglyoxime precipitation column. Nickel-59 is determined by LEPS, ^{63}Ni is determined by LSC, and the yield is determined by stable Ni recovery.
RP330	Separation of Niobium for Niobium-93m and Niobium-94 Determination	Niobium is isolated from a complex matrix by precipitation of hydrated niobium pentoxide. The ^{94}Nb and $^{93\text{m}}\text{Nb}$ are determined by gamma counting and X-ray counting, respectively; yield is determined by the radiochemical tracer recover of ^{95}Nb .
RP500	Purification of Strontium in Water Before Strontium-89/Strontium-90 Measurement	Strontium is purified by use of an Eichrom Sr-Spec [®] column. Chemical yield is traced radiochemically or gravimetrically. Several initial volume reduction and follow-on counting options are presented.
RP501 Rev. 1	Determination of Total Radioactive Strontium in High-Level Samples Using Extraction Chromatography	Strontium is purified by use of an Eichrom Sr-Spec [®] column. Chemical yield is determined with ^{85}Sr tracer. Counting is performed with gas proportional counters or by LSC. Purification options are presented if high amounts of ^{137}Cs or Pu are expected.

Table 10.2 (contd)

Method Number	Title	Summary
RP510	Determination of Strontium-90 in Dissolved Environmental Samples Using a Chelating Resin	Strontium is purified in an aqueous sample by carbonate precipitation followed by an $\text{Fe}(\text{OH})_3$ scavenge. After ^{90}Y in-growth, the Y fraction is purified using a Chelex-100 column. Yttrium is eluted and mounted as the oxalate for subsequent gas-flow proportional counting. Yield is determined by ^{85}Sr and stable Y.
RP520	Determination of Strontium-90 in Soil, Water, and Filter Samples	Complete sample dissolution is accomplished by fusion. Strontium is precipitated as the sulfate. After suitable ^{90}Y in-growth, Y is purified by a series of hydroxide and oxalate precipitations. Yttrium oxalate is counted on a gas-flow proportional counter. Yield is determined by ^{85}Sr and stable Y.
RP530	Determination of Selenium-79 in Aqueous Samples	Selenium is isolated using ion exchange and precipitation techniques. The activity of ^{79}Se is determined by liquid scintillation counting relative to a ^{14}C calibration. Yield is determined by the chemical recovery of stable Se.
RP550	Technetium-99 Analysis using Extraction Chromatography	Pertechnetate is purified on a TEVA-Spec [®] column. The resin may be mixed with LSC cocktail and counted by LSC or the Tc may be eluted and measured by ICP/MS.
RP580	Water Distillation from Soil and Aqueous Matrices Using a Micro-Distillation System for Tritium Determination	Water from soil and aqueous matrices is distilled using a Lachat microdistillation tube. A sample of the distillate is analyzed by LSC.
RP710	Laboratory Method for Gross Alpha and Beta Activity Determination	Samples are leached and oxidized if necessary, and an appropriate aliquot is dried onto a counting planchet. Samples are counted on a gas-flow proportional counter. A discussion of calibration curve generation and cross-talk correction is provided.
RP720	Rapid Determination of Gross Alpha, Gross Beta, and Gross Tritium in Water Using a Liquid Scintillation Counter	Spectral ranges for alpha, beta, and tritium are established on a liquid scintillation counter. Counting efficiencies are determined as a function of quenching. Sample aliquots are added directly to LSC cocktail and counted.
RP725	Group Actinide Screening Using Extraction Chromatography	A semi-quantitative screening for actinides (including Am, Cm, Pu, Np, U, and Th) is accomplished using extraction chromatography on a TRU-Spec [®] column. The separated sample is then plated and counted by alpha-energy analysis. Yield may be determined using a tracer.

Table 10.2 (contd)

Method Number	Title	Summary
RP730	Gross Gamma Screening for Environmental Matrices	Soils and waters are counted on a gamma detector in a calibrated geometry. An average efficiency is applied to the gross count rate to determine the gross-gamma activity.
RP735	Determination of Total Fissile Content by Neutron Activation Followed by Delayed Neutron Counting	The total fissile element (e.g., U, Pu, Np, etc.) concentration in matrices that do not activate to form long-lived radionuclides is determined after neutron bombardment by counting delayed neutrons. The fissile material in a sample is quantified as equivalents of fissile material based on the delayed neutron counts for the comparative standard.
RP800	Sequential Separation of Americium and Plutonium by Extraction Chromatography	Americium and Pu are separated from complex matrices and from each other on a TRU-Spec [®] extraction column. The Am and Pu fractions are prepared for alpha-energy analysis. Yields are based on radiochemical tracer recoveries.
RI010	Gamma-Ray Spectrometry	Gamma-emitting radionuclides are qualitatively or quantitatively determined in aqueous, geological, and vegetation samples with a gamma spectrometer.
RI100	Liquid Scintillation Instrumentation Method	General operating principals of liquid scintillation counters are discussed, including steps to construct a quench curve (efficiency calibration).
RA010	Method for Utilization of Electret Ionization Chambers for Characterization of Gross-Alpha Emission from Indoor Surfaces	A simple, inexpensive alpha-track detector is placed on an indoor surface for a set amount of time. The resulting damage track density on the detector surface, using a suitable calibration, is a measure of the alpha activity on the sample surface.
RA020	Method for Utilization of Alpha Track Detectors for Characterization of Gross Alpha Emission from Indoor Surfaces	A simple, inexpensive electret ionization chamber is placed in contact with a sample surface. The rate of change of the electret surface charge is converted to alpha activity using an appropriate calibration factor.

RS100^(a)***In Situ* Analysis of Gamma-Ray-Emitting Radionuclides by Borehole Logging****1.0 Scope and Application**

A detector lowered into boreholes or wells measures gamma-ray-emitting contaminants in the subsurface. This high-purity germanium detector identifies specific radionuclides by the energies of their gamma rays. The concentrations of source radionuclides located in the soil out to a radius of 20 to 30 cm from the borehole can be calculated from the detected count rates. Moving the detector along the length of the borehole yields a concentration profile with depth from the surface in a process called "logging." Borehole logging is an accurate and economical way to identify contaminants and determine their locations and movements in the subsurface. It can also serve as a screening method for selecting locations where samples should be collected for conventional laboratory analyses. Gamma-ray logging provides concentrations (activity per gram of earth material) of the following elements: ^{40}K , ^{226}Ra (via ^{214}Bi), ^{238}U (via $^{234\text{m}}\text{Pa}$), ^{235}U , ^{232}Th (via ^{208}Tl), ^{60}Co , ^{125}Sb , ^{137}Cs , ^{152}Eu , ^{154}Eu , ^{237}Np (via ^{233}Pa), ^{239}Pu , ^{240}Pu , and ^{241}Am .

2.0 Summary of Method

Borehole logging is a field technique in which electronic equipment, often including radiation detectors, is lowered into boreholes (or wells) in the ground to gather information on the earth formation adjacent to the boreholes. Of specific interest in environmental applications is the detection of radioactive contaminants present in the subsurface. High-resolution gamma-ray detectors identify and quantify radionuclides that emit gamma rays. Examples of these radionuclides include ^{137}Cs and ^{60}Co , both of which originate from man-made sources, and ^{40}K , ^{238}U , and ^{232}Th , which are naturally present in earth formations. Logging allows subsequent revisiting of boreholes for a more detailed assay or for contaminant movement monitoring.

The radiation detectors and electronics that are lowered into wells are contained in special "logging tools" that provide protection from liquids, such as water, in the borehole and from abrasion with the borehole wall or casing. The gamma-ray logging tool used in the present equipment is 9.3 cm in diameter and 2.3 m long. It is lowered into the borehole by a cable connected to a winch on a special truck that also contains a computer to collect data transmitted from the logging tool over the cable. An odometer measures cable movement to provide the

(a) This method was submitted by D. C. Stromswold (Pacific Northwest Laboratory, Richland, Washington) and R. K. Price (Westinghouse Hanford Company, Richland, Washington).

computer with the depth of the logging tool in the borehole. During data collection, the logging tool is usually stationary at a given depth, but dynamic logging while the tool moves up or down the hole is also possible. Typical operation at the U.S. Department of Energy's Hanford site uses 80-sec data collection periods in a move-stop-acquire mode of operation that obtains data at 15.2-cm (6-in) intervals. The interval spacing can be decreased (minimum 2.4-cm spacing) or increased for special applications.

3.0 Interferences

Field logging conditions that differ from those present during calibration generally require that corrections be made to the calculated radionuclide concentrations. Steel casing in the wells necessitates a significant correction, especially for low-energy gamma rays and thick casings. However, the amount of this correction is readily known from experiments in which steel casings are placed around the logging tool, and changes in the number of gamma rays reaching the detector are observed in calibration models. Casing correction is implemented for logging data by multiplying the counts in the observed gamma-ray peak by the correction factor appropriate for the casing thickness and gamma-ray energy.

Hole diameter can also affect the observed count rates. For air-filled holes, the diameter of the hole has a negligible effect because air does not significantly attenuate the gamma rays. Because most of the logging at Hanford occurs in the unsaturated zone where the holes are filled with air and maximum hole diameter is 30 cm, no correction for hole diameter is generally required. However, when water is present in the holes, corrections are necessary. Measurements made in calibration models with various hole sizes provide data for determining the effects of water-filled hole size. As with steel casings, the corrections are applied to the observed count rates as multiplicative factors.

Additional interference to the gamma-ray method can arise from cement or grout located between the casing and the formation. If the thickness of the material is known, corrections can be made for its effects on the measurement. Frequently, however, the thickness of this material is not known, and corrections for it are then not made.

4.0 Safety

Borehole logging necessitates the conventional safety precautions used in working with vehicles and mechanical equipment, such as the winch to move the logging tool along the borehole. The slow movement of the winch and logging tool, maximum speed 9 m/min (30 ft/min), makes their associated safety risks low.

Although the logging tool does not emit radiation, its surface must be checked for contamination when logging through potentially contaminated zones. For logging at Hanford, the tool is typically wrapped in plastic, which can easily be discarded if it becomes contaminated. Radiation

surveys of the cable, the plastic covering the tool, and the tool itself are made upon removal from boreholes where contamination could occur.

Liquid nitrogen used to cool the germanium detector in the logging tool requires care to avoid "burns" to skin and oxygen deficiency when breathing in enclosed areas. Liquid nitrogen handling procedures have shown no such problems in this logging application.

5.0 Apparatus and Materials

5.1 Subsurface

The logging tool contains a detector made of germanium to detect gamma rays and measure their energy (Koizumi et al. 1992; in press). The detector is approximately 5 cm in diameter and 5 cm long. Liquid nitrogen in an internal flask cools the detector and allows logging for periods of about 16 h before refilling is necessary. Temperature-monitoring circuitry in the tool warns of detector warming. Nitrogen gas vents to the surface through a special tube in the logging cable. Monitoring the gas flow rate provides an additional means of detecting depletion of liquid nitrogen in the tool. Venting the nitrogen through the cable allows logging in water-filled wells, although most logging actually occurs in air-filled holes through the unsaturated zone.

The logging tool has a diameter of 9.3 cm and a length of 2.3 m. The pressure vessel of the tool is made of stainless steel that is 0.13 cm thick at the detector locations. A spring centralizes the tool within the well. Signals from the tool travel to the surface on a special logging cable that is about 2.5 cm in diameter and 180 m long. It has six coaxial conductors plus eight non-coaxial ones for power supply. These electrical conductors surround the central vent tube made of flexible steel. Kevlar filaments in the cable provide strength, and a neoprene covering facilitates decontamination after logging.

5.2 Surface

A computer in the logging truck controls data acquisition and tool movement. A multichannel analyzer in the truck accepts signals sent from the logging tool via the cable and digitizes them into 4000 channels covering the gamma-ray energy of 0 to 3 MeV. Tool movement is under computer control, based on operator-selected counting times, for collection either as the winch in the truck moves the tool continuously along the borehole or stops it at specific locations for data collection.

Logging data are recorded on the computer's magnetic hard disk during the logging process. To archive the data permanently, an optical disk on the truck records the information, together with well identification and calibration checks, in a mode such that the data can be read, but not altered (WORM - write-once read-many format). This

archival method has the advantages of data integrity and long storage life, which can be important for contamination assessment and remediation operations. The data are transferred to a different computer, not located in the truck, for analysis.

6.0 Reagents

Liquid nitrogen, which cools the germanium gamma-ray detector, is the only consumable material used, other than fuel needed to operate the truck.

7.0 Sample Collection, Preservation, and Handling

Samples are not collected because this is an *in situ* method.

8.0 Procedure

8.1 Calibration

Large borehole models (1.2 m diameter) containing known amounts of K, U, and Th mixed with concrete to simulate the geometry of earth formations are used to calibrate the detection system (Brodeur et al. 1991; Koizumi et al. 1992). A central hole in these models allows insertion of the logging tool. These models are located at Hanford and Grand Junction, Colorado. The concentrations of K, U, and Th are in units of pCi of the radioelements per gram of model mass, and they are directly traceable to gamma-ray counting standards certified by the U.S. Department of Energy's New Brunswick Laboratory, Argonne, Illinois (Trahey et al. 1982; Steele and George 1986). Table 1 gives the concentrations of the Hanford models.

Table 1. Concentrations of K, U, and Th in Hanford Spectral Gamma-Ray Models.

Model	Potassium	Concentration (pCi/g) Uranium	Thorium	Dry Bulk Density (g/cm ³)	Partial Density H ₂ O (g/cm ³)
K	53.5 ± 1.7 ^(a)	1.16 ± 0.11	0.11 ± 0.02	1.82	0.25
U	10.7 ± 0.8	191 ± 6.0	0.66 ± 0.06	1.90	0.24
Th	10.6 ± 1.3	10.0 ± 0.5	58.1 ± 1.4	1.92	0.23
Mix	41.8 ± 1.8	126 ± 4	39.1 ± 1.1	1.87	0.25

(a) Uncertainties are 95% confidence levels.

Data collected with the tool in these models provide an energy-dependent detector-efficiency calibration for converting observed count rates in field logging to concentrations (pCi/g or Bq/g) of radionuclides. The detector efficiency calibration is also valid for man-made radionuclides that are not actually present in the models. Observation of the characteristic energies of the gamma rays allows identification of their source radionuclide, and knowledge of the gamma-ray production coefficients of the radionuclides provides the number of gamma rays emitted per decay (Koizumi et al., 1992; in press). Section 9.0 below describes the use of this method to determine concentrations of both natural and man-made radionuclides.

8.2 Field Data Collection

Data collection for field sites proceeds as follows:

- Pre-logging check using a radioactive source to assure consistency of operation since calibration
- Borehole logging with the tool either moving or at fixed depths
- Post-logging check using a radioactive source to assure consistency of operation

Under typical operating conditions, the system logs 35 m per 8-h day using the move-stop-acquire mode of data collection.

8.3 Data Analysis

Data that have been collected on the logging truck are transferred to a laboratory computer for analysis. A special program performs the following functions:

- Reads spectral data into system
- Analyzes spectrum
- Locates peaks in spectrum
- Determines peak centroid
- Determines peak areas (counts/s in peaks), including statistical uncertainty
- Determines energy calibration (channel number to energy relationship)
- Identifies radionuclides based on gamma-ray energy

- Performs calibration conversion (Koizumi et al. 1992)
- Adjusts peak areas based on known
 - attenuation of gamma rays by steel casing in hole
 - effects of liquid-filled boreholes of various diameters
- Calculates radionuclide concentrations using
 - peak areas
 - gamma-ray emission properties (e.g., branching ratios)
- For nuclides with multiple peaks, determines “best” concentration based on statistical uncertainties
- Sums all channels to give gross value for entire energy spectrum and divides by counting time
- Generates report
 - graphical display (borehole log) using commercial program “Sigma Plot”
 - analyst’s findings and comments

9.0 Calculations

Use of the calibration models described in section 8.1 allows determination of a detector efficiency for various energy gamma rays. An example of an efficiency equation for one particular detector is

$$I(E) = (3.2 \pm 0.1) \times 10^{-2} + (8.8 \pm 0.6) \times 10^{-6}E + (-0.57 \pm 0.06)\ln(E)/E$$

where

$I(E)$ = efficiency (in (gamma rays/s/g)/(c/s))

E = energy (keV)

Indicated uncertainties are one standard deviation values.

Field data are analyzed as described below to determine concentrations of gamma-emitting radionuclides. The energy of a detected gamma ray identifies its source radionuclide, and the concentration of the radionuclide is calculated by

$$C_x \text{ (Bq/g)} = [I(E)/N_x] A_x$$

where

E = gamma-ray energy

N_x = number of gamma rays of energy E emitted per nuclear decay of element "x"

A_x = detected net gamma-ray count rate in the peak at energy E

Since 1 decay/sec (1 Bq) is equal to 27.0 pCi, the concentration can also be written in terms of pCi/g of formation mass:

$$C_x \text{ (pCi/g)} = 27.0 [I(E)/N_x] A_x$$

The number of gamma rays emitted per decay, N_x , is readily determined once the gamma-emitting radionuclide is known. The high-resolution detector makes it easy to identify specific radionuclides in most cases because it allows gamma-ray peaks to be identified at characteristic energies. For example, detection of a 0.662 MeV gamma-ray indicates the presence of ^{137}Cs , which emits this gamma ray in 85% of its decays; hence $N_{\text{Cs}} = 0.85$. Table 2 shows the characteristic energies and N_x for some gamma-ray emitting isotopes of interest.

10.0 Quality Control

A small, radioactive source containing ^{60}Co , ^{133}Ba , ^{137}Cs , and ^{152}Eu provides the means for checking the logging system's consistency of operation between calibrations. Data collected with the logging tool above ground and the check source near the detector must fall within expected limits, after background subtraction, for the logging system to pass its quality control requirement.

Dead-time corrections made by the multichannel analyzer system in the truck adjust the observed counts for losses in high counting-rate conditions. Monitoring peak positions of known gamma rays in the spectrum provides information on any gain shifts that could affect identification of contaminant radionuclides and calculation of their concentrations.

Table 2. Gamma-Ray Energies and Number of Gamma Rays per Decay, N_γ , for Radionuclides.

Nuclide	Energy (MeV)	Gamma rays per decay (N_γ)
^{40}K	1.461	0.1070
^{238}U (via $^{234\text{m}}\text{Pa}$)	1.001	0.0083
^{235}U	0.186	0.54
^{232}Th (via ^{208}Tl)	0.583	0.310
^{232}Th (via ^{208}Tl)	2.614	0.360
^{60}Co	1.173; 1.332	1.00
^{137}Cs (via $^{137\text{m}}\text{Ba}$)	0.662	0.846
^{152}Eu	0.344	0.270
^{154}Eu	0.123	0.405
^{154}Eu	1.275	0.355
^{237}Np (via ^{233}Pa)	0.312	0.337
^{125}Sb	0.428	0.296
^{239}Pu	0.129	0.620×10^{-4}
^{239}Pu	0.414	0.151×10^{-4}
^{240}Pu	0.104	0.70×10^{-4}
^{240}Pu	0.160	0.42×10^{-5}
^{241}Am	0.060	0.363

Ref. Moss (1986) for $^{234\text{m}}\text{Pa}$; Erdtmann and Soyka (1979) for other nuclides.

11.0 Method Performance

The variabilities of conditions under which field data are collected make it difficult to specify the measurement accuracy of the technique. For example, cement or grout thickness between the casing and formation are often unknown, and this affects the observed count rates and calculated concentrations.

For screening the length of the borehole to aid in choosing sample collection locations for laboratory analysis and for monitoring contaminant movement over time, precision is an important measure of logging performance. The estimated precision for measurements of contaminants such as ^{137}Cs and ^{60}Co is ± 0.07 Bq/g (2 pCi/g) or $\pm 5\%$, whichever is less stringent, for concentrations of 0.04 to 200 Bq/g (1 to 5,000 pCi/g). Above about 200 Bq/g for these two radionuclides, the counting rate can become too high for proper analysis. The precisions and concentration levels at which other contaminants can be measured vary according to the radioactive-decay properties of the individual radionuclides.

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RS551(a)

Rapid Isolation and Measurement of Technetium-99 Using Anion-Exchange Filter Membranes

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method describes the rapid isolation of TcO_4^- from aqueous samples using anion-exchange membranes and the subsequent membrane preparation for measuring the ^{99}Tc beta activity^(b). The method has been applied to groundwater and surface water samples. Its applicability could be extended to other aqueous samples. The method requires minimal operator involvement and chemical manipulations, and it produces virtually no chemical waste. Because the sample preparation is so simple, it can readily be applied to field analysis.

2.0 Summary of Method

A sample is passed through two positively charged anion-exchange membrane filters set up in sequence. The TcO_4^- exchanges onto the membrane filters as the water is passed through them. The membrane filters are dried and then counted for beta activity. The extraction efficiency is determined as a function of the activity on the two membrane filters.

3.0 Interferences

Ruthenium is taken up by the anion-exchange membrane; therefore, ^{103}Ru and ^{106}Ru can positively interfere with the ^{99}Tc beta determination.

(a) This method was supplied by K. A. Orlandini, J. G. King, and M. D. Erickson (Argonne National Laboratory, Argonne, Illinois)

(b) The article "The Rapid Separation and Measurement of Technetium-99" by K. A. Orlandini, J. G. King, and M. D. Erickson, is in the review process with *Radiochimica Acta*.

Both NO_3^- and I^- will result in lowered TcO_4^- uptake efficiency on the filters. When the total anion content becomes extreme at any pH, some reduction in uptake efficiency for Tc occurs. The reduced uptake efficiency influences chemical yield and thus increases detection limits.

The anion-exchange membrane operates efficiently from pH 1 to pH 10.

4.0 Safety

No special safety precautions are indicated for this method.

5.0 Apparatus and Materials

- Anion-exchange membrane filters (e.g., Acropor SB-6407 or HP-200 from Gelman Sciences, Ann Arbor, Michigan)
- Paper divider (e.g., Whatman #41 paper disc, 47 mm diameter)
- Membrane-support filter apparatus (e.g., Sterifil Aseptic System, 47 mm, catalog number XX11-047-00, Millipore Corporation, Bedford, Massachusetts)
- Vacuum system
- Beta counter

6.0 Reagents

None.

7.0 Sample Collection, Preservation, and Handling

Nitrates interfere with the TcO_4^- uptake on the membrane. Therefore, samples should not be preserved with HNO_3 .

8.0 Procedure

- 8.1 If visible solids are present in the sample, the sample should be prefiltered through a 0.45- μm filter. This can be done with the membrane-support filter apparatus.
- 8.2 The two membrane filters are pre-wetted with deionized water, then mounted in series in the membrane-support apparatus. One anion-exchange membrane filter is placed on the filter support (provided with the filter apparatus), a pre-wetted paper disc is placed on top of this filter, and then another anion-exchange membrane filter is placed on the paper disc.

- 8.3 The reservoir is tightened to the collection vessel. The whole apparatus is leak tested with deionized water.
- 8.4 A known volume of aqueous sample is passed through the membrane filters at an approximate flow rate of 2 mL/min.
- 8.5 The filters are rinsed with a few milliliters of deionized water.
- 8.6 The membrane filters are dried in a drying oven at 50 to 60°C for about 15 min; then they are allowed to cool.
- 8.7 The membrane filters are counted by gas-flow proportional or liquid scintillation counting.
- 8.8 The ^{99}Tc counting efficiency may be determined as follows:
- 8.8.1 Filters are prepared in sequence in the filtration apparatus as described.
- 8.8.2 A small volume (e.g., 5 to 10 mL) of dilute ammonium hydroxide solution containing a known amount of ^{99}Tc is passed through a membrane sequence in the same manner as a sample solution.
- 8.8.3 The two filters are dried and counted by gas-flow proportional counting. Alternatively (or additionally), the filters are placed in two liquid scintillation counting (LSC) vials and scintillation cocktail is added. These samples are counted by LSC.

The counting efficiency can be assessed from the count rate of the Tc standard spike absorbed to the membrane. The counting efficiency from a small volume of ammonium hydroxide solution has been found to be 99+%. Virtually all Tc will be on the first membrane.

9.0 Calculations

- 9.1 The collection efficiency of TcO_4^- onto the anion-exchange filter is derived as follows:

$$\begin{aligned}\text{CR}_1 &= \text{CR}_0 \cdot P \\ \text{CR}_2 &= (\text{CR}_0 - \text{CR}_1) \cdot P\end{aligned}$$

$$P = 1 - \left(\frac{CR_2}{CR_1} \right)$$

where

CR_0 = ^{99}Tc net count rate in the aqueous sample

CR_1 = ^{99}Tc net count rate on the first (top) membrane filter

CR_2 = ^{99}Tc net count rate on the second (bottom) membrane filter

P = ^{99}Tc collection efficiency parameter.

9.2 The ^{99}Tc -filter geometry counting efficiency is calculated as follows:

$$E_{\text{Tc}} = \frac{CR_1}{A_{\text{Tc}} \cdot V_{\text{Tc}} \cdot \left(1 - \frac{CR_2}{CR_1} \right)}$$

where

E_{Tc} = ^{99}Tc counting efficiency

A_{Tc} = activity concentration of ^{99}Tc standard

V_{Tc} = volume of ^{99}Tc standard.

CR_1 and CR_2 are the first and second filter net count rates of the standard preparation.

9.3 The ^{99}Tc activity in a sample is calculated as follows:

$$[^{99}\text{Tc}] = \frac{CR_1}{P \cdot Q \cdot E_{\text{Tc}}}$$

where

Q = sample quantity passed through the filters.

10.0 Quality Control

A blank should be run with each analytical batch. A blank spike and/or a matrix spike provide useful information on the successful application of the analysis; however, their application does not work well in field applications.

11.0 Method Performance

Various ions were evaluated for their effect on the Tc uptake on the membrane filter. Test sample compositions, as indicated in Table 1, were prepared, and a known quantity (5000 to 8000 dpm) of ^{95m}Tc was added to each. The samples were then passed through Acropor SB-6407 filters, which were then dried and counted on a Na(I) gamma counter. The percent uptake results are presented below.

Table 1. Percent Uptake of ^{99}Tc in the Presence of Potential Interferences			
Potential Matrix Interference	Acidic Solution pH = 4.5 to 6.5	Neutral Solution pH = 7.0	Basic Solution pH = 7.5 to 9.5
none (DI water)		>99	
PO_4^{3-} (1000 $\mu\text{g/mL}$)	>99	>99	>99
SO_4^{2-} (1000 $\mu\text{g/mL}$)	99	99	99
F^- (1000 $\mu\text{g/mL}$)	>99	99	99
B (H_3BO_3) ^(a)	>99	>99	99
B ($\text{Na}_2\text{B}_4\text{O}_7$) ^(a)	99	90	>99
CO_3^{2-} (1000 $\mu\text{g/mL}$)		>99	>99
I^- (1000 $\mu\text{g/mL}$)			28
OCl^- (as NaOCl) ^(b)			97
(a) 1000 $\mu\text{g B/mL}$			
(b) 25 $\mu\text{g OCl}^-/\text{mL}$			

Hydroxide solutions of pH 9, 10, 11, and 12 were prepared, and the uptake efficiency was evaluated to be $\geq 99\%$.

Various samples were analyzed by the this method and an alternate method. The sample volumes, pH, count rate from the first and second filters (A1 and A2, respectively), collection efficiency (P), calculated activity, and activity determined by the alternate analysis technique are presented in Table 2.

Table 3 compares analysis times, labor hours, and waste generation of several ^{99}Tc -analysis methods to this method. The " ^{99}Tc Assay" method entails a liquid-liquid extraction of pertechnetate ion with methyl ethyl ketone. The Holm method uses a liquid-liquid extraction of pertechnetate with tributyl phosphate (Holm 1984). The HASL-300 method uses precipitation and ion-exchange techniques (Chieco et al. 1992).

12.0 References

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Table 2. Comparison of Filter Membrane Extraction Analysis to Other Methods of ^{99}Tc Determination.

Sample	Volume (mL)	pH	A ₁ cpm	A ₂ cpm	E	A ₀ (measured) dmp/L	Tc dmp/L
Well water + ^{99}Tc	250	1 (HCl)	18.9	4.7	0.75	336 ± 16	347 ± 12
Deionized water + ^{99}Tc	20	1 (HCl)	3.0	0.18	0.94	532 ± 31	550 ± 31
Deionized water + ^{99}Tc	10	9	3.8	0.008	1.0	1,267 ± 65	1,267 ± 65
Mono Lake + ^{99}Tc	100	10	11.5	5.4	0.53	723 ± 21	723 ± 17
FSB 79 (SRS) ^a	10	3.3	0.45	0.18	0.6	234 ± 14	222 ± 22 ^d
FSB 79 (SRS) duplicate	10	3.3	0.39	0.19	0.51	238 ± 12	222 ± 22 ^d
Paducah ^b							
5920	100	1.5 (HNO ₃)	0.41	0.30	0.27	43 ± 2 ^c	71 ± 24 ^d
6275	25	1.5 (HNO ₃)	4.37	1.72	0.61	922 ± 120	950 ± 104 ^d
5598	25	1.5 (HNO ₃)	9.78	5.76	0.41	2,954 ± 100	2,682 ± 118 ^d

a. Ambient ^{99}Tc from seepage basin aquifer, Savannah River Site, Aiken, South Carolina

b. Ambient ^{99}Tc from Gaseous Diffusion Plant, Kentucky

c. Split sample analysis using method similar to RP550 resulted in 37 ± 1 dpm/L

d. reported values

Table 3. Comparison of Methods for ^{99}Tc Analysis

Method Name	Single Sample Time (h)	Average Sample Time (h)	Labor Hours per Sample	Secondary Waste
^{99}Tc assay (a)	3	0.75	0.20	20 mL mixed
HASL-300 (Chico et al. 1992)	24	1.4	0.25	500 mL mixed
Holm Method (Holm 1984)	216	26.4	3	97 mL mixed
RS551	2.7	0.50	0.20	membranes

(a) Personal communication with R. Williams of Martin Marietta Services, Inc., Paducah, Kentucky.

RP230^(a)**Iodine-129 Analysis in Aqueous Solutions****1.0 Scope and Application**

This method is used to separate and analyze ^{129}I in low- to high-level activity samples in an aqueous matrix (e.g., tank waste in solution, drinking water, well water, etc.). It is comprised of two "sub-methods," one ending with the precipitation of iodide and the other ending with neutron activation analysis of iodide. The former method is similar to the standard American Standard Testing and Materials (ASTM) method D 2334 Test Method C. This method provides for more analytical choices and an additional cleanup step by cation exchange.

2.0 Summary of Methods

This method is divided into two distinct sub-methods based on the final determination steps used: 1) precipitation of the iodide or 2) neutron activation analysis of the iodide. Analytical choices can be made in the use of extraction solvent and precipitating agent.

2.1 Iodine Precipitation. Iodine species in the sample are first oxidized, then reduced to iodide. The iodide is then oxidized to iodine. Iodine is separated from the matrix by using one or more solvent extraction steps. Iodine extraction results in a high degree of separation from other radioisotopes and elements, with the exception of Cl and Br. Extraction is followed by ion exchange chromatography. Iodide is eluted from a column and precipitated as PdI_2 or AgI . Recovery is determined by gravimetric yield of PdI_2 or AgI . Determination of ^{129}I is performed by gamma counting the ^{129}I in the iodide precipitate. The instrument detection limit is approximately 0.4 Bq (10 pCi).

2.2 Neutron Activation Analysis. The chemistry for use with the neutron activation analysis (NAA) method is similar to that used with the precipitation method. Recovery is determined by the radiochemical recovery of ^{131}I . The ^{129}I is collected on an anion exchange column followed by neutron activation to ^{130}I . The ^{130}I is determined by subsequent gamma counting.

(a) This method was compiled by S. K. Fadeff (Pacific Northwest Laboratory, Richland, Washington) from seven analytical procedures obtained from the *DOE Procedures Database*.

3.0 Interferences

- 3.1 Depending on the quantity present, non-radioactive iodine in the original sample may interfere by causing an overcorrection in the final gravimetric yield.
- 3.2 It is possible that some radioactive species, especially halides, may be carried through the separation process; the presence of these additional radionuclides may cause interferences in the final analysis. In such cases, additional extractions may be carried out before precipitation to further separate iodine from other radionuclides.
- 3.3 Bromide in solution will follow the iodide. Depending on the amount present, it may interfere with the gravimetric yield determination of iodine.

4.0 Safety

This analysis method uses carcinogens (CCl_4 or CHCl_3), corrosives, oxidizing agents, and reducing agents. This method does not address the safety problems associated with using these reagents. Appropriate health and safety protocols to be used when handling these reagents are the responsibility of the user of the method.

5.0 Apparatus and Materials

5.1 General

- Separatory funnels appropriate for sample size, or for small samples (e.g., less than 5 mL), glass vials (e.g., 35 mL)
- Heating block to fit vials, if vials are used
- Pasteur transfer pipets

5.2 Specific to Precipitation

- Filter apparatus for collecting PdI_2 or AgI
- Filter paper to fit filter apparatus, e.g., Whatman 934AH 1.5 μm pore size or equivalent. (Tuffryn™ would probably work well; a cellulose/acetate filter will not work well as it will change weight with an alcohol wash.)
- Cation exchange column - A small plug of glass wool should be placed in a 3-mL plastic dropper (approximately 0.5 cm cut off at top), 2 cc AG 50W-X8 (other options to include Dowex 50, AG MP-50, Amberlite IR and Zeolon

900) 100 to 200 mesh H^+ ion exchange resin are added, and the resin is allowed to settle. Another small tuft of glass wool is added to the top of the resin bed. The resin is washed with 3 mL 0.1 M $(\text{NH}_4)_2\text{SO}_3$.

5.3 Specific to NAA

- Anion exchange column - Approximately 0.8 mL AG 1-X8 resin, 100 to 200 mesh in nitrate form, is added to a 0.8-cm diameter x 3.2-cm long capsule (latex tube) fitted with a porous polyethylene disc over a perforated bottom. Then a porous polyethylene disc is placed on top of the resin. It may be best to convert the chloride form of AG 1-X8 to nitrate with ammonium nitrate to ensure a low-sodium content.

6.0 Reagents

6.1 General

- Phenolphthalein indicator
- Sodium hydroxide, 2 M
- Sodium hypochlorite (NaClO), 5 % — commercial bleach
- Carbon tetrachloride (CCl_4) or chloroform (CHCl_3)
- Nitric acid (HNO_3), 16 M and 1 M
- Ammonia (NH_4OH)
- Ammonium sulfite $((\text{NH}_4)_2\text{SO}_3)$, 1 M
- Ethanol, absolute

6.2 Specific to Precipitation

- Stable I carrier: potassium iodide (KI) — 10 mg/mL iodide, standardized
- Ammonium sulfite $((\text{NH}_4)_2\text{SO}_3)$, 0.1 M
- Sodium nitrite (NaNO_2), 3 M (7 day shelf life)
- Sodium bisulfite solution (NaHSO_3), 1 M

- Hydrochloric acid
- Sulfuric acid (H_2SO_4), 10%
- Palladium chloride (PdCl_2), 0.2 M, or silver nitrate (AgNO_3), 0.1 M.

6.3 Specific to NAA

- Stable I carrier: potassium iodide (KI) — 10 mg/mL iodide
- Hydroxylamine hydrochloride, 4 M ($\text{NH}_2\text{OH}\cdot\text{HCl}$)
- ^{131}I tracer, enough to provide appropriate counting statistics
- ^{129}I standard as neutron activation yield monitor for activation of ^{129}I to ^{130}I

7.0 Sample Collection, Preservation, and Handling

Samples for radioactive iodine analysis should be collected in glass and preserved with sulfite in an alkaline or neutral solution. The container should be sealed; refrigeration is not necessary. If short-lived radioactive iodine analysis is required, then sample analysis should commence as soon as practical; otherwise, holding times are not defined.

It may be advisable to use a laminar flow hood equipped with a charcoal trap as well as a HEPA filter to capture any radioiodine gas.

8.0 Procedure

8.1 Gravimetric Yield Determination

- 8.1.1 The volume of sample to be used is measured and added to an appropriately sized separation funnel. If very small sample sizes are to be analyzed, 35-mL glass vials may be appropriate to use as a sample preparation vessel.
- 8.1.2 An aliquot of stable I^- carrier (precisely known, e.g., 10 or 20 mg I) is added to each sample to be analyzed in the batch. The stable iodide will be used to determine the chemical recovery.
- 8.1.3 While stirring, two to four drops of phenolphthalein indicator are added. If the solution is not basic (pink), 2 M sodium hydroxide should be added until the pink color persists for at least 30 sec.

- 8.1.4 Five mL of 5% sodium hypochlorite solution are added for each 100-mL solution, or 1 mL of sodium hypochlorite for samples less than 20 mL to oxidize all iodine species to iodate. The sample is shaken well and allowed to stand for 10 to 30 min, or the sample is boiled gently for 10 min, then cooled.
- 8.1.5 Approximately 10 to 15 mL CCl_4 or CHCl_3 extractant are added to the separatory funnel or vial.
- 8.1.6 Two to four drops of phenolphthalein should be added and the mixture cautiously acidified with concentrated HNO_3 ; then 1 mL NaHSO_3 solution is added until an orange color appears and remains in the aqueous phase. This reduces the iodate to iodide. The solution is allowed to stand for 5 min.
- 8.1.7 One milliliter of 3 M NaNO_2 is added to the sample. This oxidizes iodide to I_2 ; the I_2 dissolves in the extractant, producing an intense purple color. The sample is shaken well to complete the extraction.
- 8.1.8 After phase separation, the bottom (organic) phase is drained out (if using separatory funnel), or the extractant is transferred with a disposable pipet into a clean vial.
- 8.1.9 Approximately 5 to 15 mL fresh CCl_4 or CHCl_3 extractant are added to the aqueous sample, which is then shaken. The extractant is transferred into the previously collected extractant. This step is repeated until no appreciable color appears in the extractant. The aqueous portion is discarded.
- 8.1.10 The combined CCl_4 or CHCl_3 is washed with 20 to 40 mL (8 to 12 mL for small samples) of 1 M HNO_3 . The aqueous phase is discarded.
- 8.1.11 Approximately 5 to 10 mL water are added to the extractant. The I_2 is reduced to iodide with one drop of aqueous ammonia and several drops of 1 M $(\text{NH}_4)_2\text{SO}_3$ or 1 M NaHSO_3 . The sample is shaken. If the organic phase is still pink or purple, another drop of 1 M $(\text{NH}_4)_2\text{SO}_3$ is added, and the sample is again shaken. This addition of 1 M $(\text{NH}_4)_2\text{SO}_3$ is continued until the extractant layer is colorless or slightly yellow. The organic phase is discarded to an appropriate waste container.

The sample may be checked for relative purity at this point by gamma counting or with a portable beta-gamma detector. If activity is low (close to background), the method is continued with step 8.1.12. If the sample activity is considerably greater than the blank, the sample is diluted (e.g., to about 50 mL) with 1 M HNO_3 , and steps 8.1.5 to 8.1.11 are repeated.

Cation Exchange and Sample Mounting

- 8.1.12 A 2-cc cation exchange column is prepared.
- 8.1.13 The sample is passed through the cation resin column, and the column is then rinsed with 2 mL 0.1 M $(\text{NH}_4)_2\text{SO}_3$. All effluent that contains the iodide is collected in a small beaker or glass vial. This step removes traces of ^{137}Cs .
- 8.1.14 The sample solution may be mounted in a calibrated geometry for gamma counting at this point, followed by precipitation for gravimetric yield determination, steps 8.1.15 through 8.1.20. If interferences are apparent, further separations by extraction or column chromatography may be performed.
- 8.1.15 Two options exist for producing a precipitate.
1. For PdI_2 precipitate, 3 to 5 drops conc HCl are added to the sample, which is then mixed; 15 to 25 drops PdCl_2 solution are added, and the sample is again mixed.
 2. For AgI precipitate, 2 mL 10% H_2SO_4 are added, and the solution is allowed to stand for 10 min; then 1 mL 0.1 M AgNO_3 solution is added, and the sample is mixed.
- 8.1.16 The sample is heated 5 to 15 min to coagulate the precipitate; then it is cooled.
- 8.1.17 A filter apparatus with a tared filter is assembled.
- 8.1.18 The PdI_2 or AgI precipitate is transferred onto the tared filter paper using water to rinse the container and wash the precipitate.
- 8.1.19 The precipitate is rinsed with 2 to 3 mL ethanol. Then air is drawn through the filter to dry the precipitate completely.
- 8.1.20 The precipitate and filter paper are weighed, and the net precipitate weight is determined.
- 8.1.21 If the sample was not already counted (step 8.1.14), the sample should be mounted in a calibrated geometry.
- 8.1.22 The sample is counted by gamma-ray spectroscopy using a low-energy photon detector, which accommodates the low energy (39.6 keV) of ^{129}I . The detector should have been or will be calibrated for the counting efficiency.

The gamma peak energy of ^{129}I is low at 39.6 keV. Because of this, the efficiency of detection may vary as a function of the precipitate weight. A calibration curve should be constructed to correct for self-absorption effects due to variations of sample mass.

8.2 Neutron Activation Analysis

A high background in the final gamma count following neutron activation can be caused by samples containing gamma-emitting neutron activation products that interfere with the detection of ^{130}I . Samples with Br, Cl, and Na are of particular concern because they have half-lives similar to ^{130}I . In this section, therefore, reagents containing these elements are minimized or replaced.

- 8.2.1 The volume of sample to be used is measured and added to an appropriately sized separation funnel. If very small sample sizes are to be analyzed, 35-mL glass vials may be appropriate to use as a sample prep vessel.
- 8.2.2 An aliquot of stable I carrier is added to each sample analyzed in the batch. A known amount of ^{131}I tracer is added for determination of chemical recovery. The same volume of ^{131}I tracer will need to be added to a prepared column (step 8.2.14) for use as a comparative yield standard.
- 8.2.3 Two to four drops of phenolphthalein indicator are added. If the solution is not basic (pink), NaOH is added until the pink color persists for at least 30 sec.
- 8.2.4 Five milliliters of 5% sodium hypochlorite solution are added for each 100-mL solution, or 1 mL of sodium hypochlorite is added for samples less than 20 mL to oxidize all iodine species to iodate. The solution is shaken well and allowed to stand for 10 to 30 min.
- 8.2.5 Approximately 10 to 15 mL CCl_4 or CHCl_3 extractant are added to the separatory funnel or vial.
- 8.2.6 Two to four drops of phenolphthalein are added, and the sample is cautiously acidified with concentrated HNO_3 ; then 4 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution is added until an orange color appears and remains in the aqueous phase. This reduces the iodate to iodine.
- 8.2.7 The sample is shaken well to complete the extraction. The I_2 dissolves in the extractant, producing an intense purple color.
- 8.2.8 After phase separation, the extractant is transferred into a clean separatory funnel or vial.

- 8.2.9 Approximately 5 to 15 mL fresh CCl_4 or CHCl_3 extractant are added to the aqueous sample, which is then shaken. The extractant is transferred into the previously collected extractant. This extraction step is repeated until no appreciable color appears in the extractant. The aqueous portion is then discarded.
- 8.2.10 The combined CCl_4 or CHCl_3 fractions are washed with 20 to 40 mL (8 to 12 mL for small samples) of 1 M HNO_3 . The aqueous phase is discarded.
- 8.2.11 Approximately 5 to 10 mL water are added to the CCl_4 or CHCl_3 . The I_2 is reduced to iodide with one drop of aqueous ammonia and several drops of 1 M $(\text{NH}_4)_2\text{SO}_3$. The sample is shaken. If the organic phase is still pink or purple, another drop of 1 M $(\text{NH}_4)_2\text{SO}_3$ is added and the mixture is shaken. Addition of the 1 M $(\text{NH}_4)_2\text{SO}_3$ is continued until the extractant layer is colorless or slightly yellow. The organic phase is discarded into an appropriate waste receptacle.

The sample may be checked for relative purity at this point by gamma counting or with a portable beta-gamma detector. If activity is low, or comparable with ^{131}I standard, the method is continued with step 8.2.12. If the sample activity is considerably greater than the standard, the sample should be diluted (to ~50 mL) with 1 M HNO_3 , and steps 8.2.5 to 8.2.11 should be repeated.

Anion Exchange and Sample Mount for NAA Applications

- 8.2.12 An anion exchange column is prepared with AG 1-X8 anion exchange resin in the nitrate form.
- 8.2.13 The aqueous sample is passed through the column. The separatory funnel or vial is washed with water (5 mL), and the wash is passed through the column. The column is washed with 10 to 20 mL water (to rinse away any cations). The column is dried by passing 1 mL of acetone or ethanol through it.
- 8.2.14 An ^{131}I tracer standard is prepared by placing an accurately measured volume into about 5 mL of water. This water solution is passed through an AG 1-X8 anion exchange resin column, as described in step 8.2.13.
- 8.2.15 Both ends of the columns are capped and sealed.
- 8.2.16 The sample (column) is counted on an intrinsic Ge or Ge (Li) gamma spectrometer (which has been or will be calibrated for counting efficiency) for ^{131}I (364.5 keV) determination.

- 8.2.17 The standard and sample activities are compared after appropriate decay corrections to obtain the chemical yield.
- 8.2.18 To lower the Na background, the exterior column is wiped free of handprints and soaked in deionized water before irradiation.
- 8.2.19 The analytical sample batch is packaged for irradiation. Each batch introduced into the reactor should have one ^{129}I standard with enough activity to provide appropriate counting statistics when counting for ^{130}I ; it should also have one blank (standard blank) and one method blank (from the particular sample preparation used).
- 8.2.20 The sealed resin column is placed in an appropriate neutron activation container.
- 8.2.21 The sample is irradiated to obtain adequate activation of the iodine (e.g., for 1 to 2 h at a thermal flux of 10^{12} to 10^{13} n/cm²/sec).
- 8.2.22 After being retrieved, the samples should be allowed ~6 to 9 h to decay; this allows short-lived irradiated (previously stable) I and Cl activation products to decay. Longer-lived activated Br and Na products will not decay away significantly in this time frame. The activated (previously stable) iodine will decay away in about 4 h ($t_{1/2}^{128}\text{I} = 25$ min). The ^{38}Cl will require about 6 h to decay away ($t_{1/2}^{38}\text{Cl} = 37$ min).
- 8.2.23 The columns are wiped free of any water soluble salts and soaked again in deionized water before the column is mounted on a gamma spectrometer counting holder.
- 8.2.24 Each column is gamma counted on an intrinsic Ge or Ge(Li) detector (^{130}I significant gamma energies are 536.1 keV, 668.6 keV, and 739.5 keV). For calculation purposes, the ^{130}I activity should be decay corrected ($t_{1/2}^{130}\text{I} = 12.36$ h) from end time of irradiation.

9.0 Calculations

9.1 Precipitation

9.1.1 Yield

$$Y = W_{\text{net}}/W_{100}$$

where

Y = yield

W_{net} = net precipitate mass

W_{100} = precipitate mass based on 100% chemical recovery.

9.1.2 Iodine-129 Concentration

$$^{129}\text{I concentration} = (^{129}\text{I}_{\text{gea}})/(Y \cdot Q)$$

where

Q = quantity (volume or mass) of sample analyzed

Y = chemical yield of iodine

$^{129}\text{I}_{\text{gea}}$ = activity determined by gamma energy analysis:
$$\frac{\text{net cpm}}{A \cdot E}$$

where

A = fractional abundance of the gamma ray, $\frac{\text{gamma ray}}{\text{disintegration}}$

E = photopeak detection efficiency

9.1.3 The uncertainty (σ) is determined as follows:

$$\sigma_{^{129}\text{I}} = ^{129}\text{I}_{\text{concentration}} \cdot \sqrt{\left(\frac{\sigma_{^{129}\text{I}_{\text{gea}}}}{^{129}\text{I}_{\text{gea}}}\right)^2 + \left(\frac{\sigma_{\text{net wt}}}{W_{\text{net}}}\right)^2 + \left(\frac{\sigma_{100 \text{ wt}}}{W_{100}}\right)^2 + \left(\frac{\sigma_Y}{Y}\right)^2}$$

where σ = error in the specified values.

9.2 Neutron Activation Analysis

9.2.1 Yield

$$^{131}\text{I tracer } Y = (^{131}\text{I cpm}_{\text{sample}}) / (^{131}\text{I cpm}_{\text{standard}})$$

9.2.2 Iodine-129 Concentration

$$^{129}\text{I concentration} = \frac{(^{130}\text{I}_{\text{sample}} - ^{130}\text{I}_{\text{blank}}) \cdot (^{129}\text{I}_{\text{std}} / ^{130}\text{I}_{\text{std}})}{V \cdot Y}$$

where

$^{130}\text{I}_{\text{sample}}$ = activity of ^{130}I , at end of sample irradiation

$^{129}\text{I}_{\text{std}}$ = activity of ^{129}I standard before irradiation

$^{130}\text{I}_{\text{std}}$ = activity of ^{130}I , at end of irradiation of ^{129}I standard

$^{130}\text{I}_{\text{blank}}$ = activity of ^{130}I in the neutron activation blank sample

V = volume or mass of sample analyzed

Y = chemical yield of iodine

9.2.3 The uncertainty (σ) is determined as follows:

$$\sigma_y = Y \cdot \sqrt{\left(\frac{\sqrt{^{131}\text{I}_{\text{count (sample)}}}}{\text{count time}_{\text{(sample)}}} \right)^2 + \left(\frac{\sqrt{^{131}\text{I}_{\text{counts (standard)}}}}{\text{count time}_{\text{(standard)}}} \right)^2}$$

$$\sigma_{^{129}\text{I}_{\text{(cpm)}}} = \sqrt{\left(\frac{\sqrt{^{130}\text{I}_{\text{counts (sample)}}}}{\text{count time}_{\text{(sample)}}} \right)^2 + \left(\frac{\sqrt{^{130}\text{I}_{\text{counts (blank)}}}}{\text{count time}_{\text{(blank)}}} \right)^2}$$

$$\sigma_{^{129}\text{I}(\text{conc})} = \sqrt{\left(\frac{\sigma_{^{129}\text{I}(\text{CR})}}{\text{CR } ^{130}\text{I}}\right)^2 + \left(\frac{\sigma_{\text{DR } ^{129}\text{I}_{\text{std}}}}{\text{DR } ^{129}\text{I}_{\text{std}}}\right)^2 + \left(\frac{\sigma_{\text{DR } ^{130}\text{I}_{\text{std}}}}{\text{DR } ^{130}\text{I}_{\text{std}}}\right)^2 + \left(\frac{\sigma_{\text{V}}}{\text{V}}\right)^2 + \left(\frac{\sigma_{\text{Y}}}{\text{Y}}\right)^2} \cdot ^{129}\text{I}_{\text{concentration}}$$

where

CR = net count rate

DR = disintegration rate

10.0 Quality Control

A quality control (QC) protocol sufficient for the needs of a particular sample request should be implemented to include duplicate samples so that standard deviation may be determined, as well as standard spikes to the samples for determining analytical bias.

One method blank per sample batch should be run to measure evidence of sample contamination.

One ^{129}I spike standard should be run with each sample batch.

11.0 Method Performance

The following method performance data were obtained from using the precipitation method of analysis. Sample analyses were performed using 35-mL vials as reaction vessels; CCl_4 was used as the extractant, and palladium was used to precipitate the I as PdI_2 .

Yield:	60 to 80%
Precision:	17.4% (one sigma)
Bias:	+0.2 %
Number of observations:	89
Detection limit:	0.4 Bq/sample (10 pCi/sample)

12.0 Further Reading

American Society for Testing and Materials (ASTM). 1992. "Standard Test Methods for Radioactive Iodine in Water." ASTM Method D 2334-88 (discontinued). *Annual Book of ASTM Standards*, vol. 11.02.

Clesceri, L. S., A. E. Greenberg, and R. R. Trussell, eds. 1989. *Standard Methods for the Examination of Water and Wastewater*, 17th Edition, American Public Health Association.

Kahn, M. and J. Kleinberg. 1977. *Radiochemistry of Iodine*. Technical Information Center, Energy Research and Development Administration.

Los Alamos National Laboratory (LANL). 1993. *DOE Procedures Database*. Electronic access through SEARCHmate (505-665-7409). Los Alamos, New Mexico.

13.0 Reviewers' Comments and Suggestions

It is very hard to keep PdI_2 from creeping up the sidewalls, and therefore the transferring process is difficult. The AgI works much easier.

It has been suggested xylene or toluene be used as the extractant, instead of chloroform or carbon tetrachloride, to reduce the hazardous nature of the waste.

It has been suggested cuprous chloride can be used as the precipitating agent for iodide (CuI). Follow-on procedure for the preparation and drying of the CuI should be followed according to ASTM Standard Test Method D4785.

It has been suggested that ^{125}I be used to trace the analysis instead of stable iodine. The gamma energy of ^{125}I is 35.5 keV, and if an appropriate amount is added, its peak should be resolvable from that of ^{129}I at 39.6 keV.

14.0 Acknowledgments

Idaho National Engineering Laboratory
Radiation Measurements Laboratory
Westinghouse Hanford Company
Argonne National Laboratory
Pacific Northwest Laboratory

15.0 Procedures Used as Sources

Determination of Iodine-129 in Air, Water, and Tissue by Neutron Activation Analysis, ESM 4922, Idaho National Engineering Laboratory, Idaho Falls, Idaho.

Determination of Iodine-129 in Water Samples, EG&G, Radiation Measurements Laboratory, 1987, Idaho National Engineering Laboratory, Idaho Falls, Idaho.

Determination of Iodine-129 in Waste Tank Samples, LA-378-103, 1992. Westinghouse Hanford Company, Richland, Washington.

Radionuclide Separation Analysis Procedure for Iodine-129, ESM 4921, Argonne National Laboratory, Argonne, Illinois.

Separation of Iodine-129 by Solvent Extraction and Distillation from Chloride Solutions Prior to Measurement by Gamma (X-Ray) Counting, 7-40.26, Pacific Northwest Laboratory, 1988, Richland, Washington.

Separation of Iodine-129 by Cation Exchange and Distillation Prior to Measurement by Gamma (X-ray) Counting, 7-40.17, Pacific Northwest Laboratory, 1988, Richland, Washington.

RP280^(a)

Determination of Lead-210 in Water Using Extraction Chromatography

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope

This method is used to determine the activity of ^{210}Pb in a water matrix. It describes the separation of Pb by extraction chromatography and preparation for gas-flow proportional counting (Horwitz, et al. 1992). This method is rapid and reliable and results in a small waste stream, primarily consisting of 1 M HNO_3 .

2.0 Summary of Method

Lead-210 is concentrated from a water sample by iron hydroxide scavenge. After dissolution, Pb is selectively extracted from the other coprecipitants on a Sr•Spec[®] column. The purified Pb fraction is mounted on a counting planchet. After allowing for ^{210}Bi ingrowth, the planchet is counted by gas-flow proportional counting.

3.0 Interferences

Any beta emitter can interfere when measuring the ^{210}Bi daughter of ^{210}Pb . Thoroughly washing the Sr•Spec[®] column effectively removes these interferences.

4.0 Safety

No significant safety problems are presented by this method other than the normal precautions for handling radioactive materials, acids, and bases.

5.0 Apparatus

- Aluminum foil
- Beta detector (gas-flow proportional counter)

(a) This method was provided by Eichrom Industries, Inc., Darien, Illinois.

- Centrifuge
- Centrifuge tubes (50 mL, plastic)
- Sr•Spec[®] pre-packed column (Eichrom Industries, Inc., 8205 Cass Avenue, Suite 107, Darien, Illinois 60559) or equivalent
- Column support rack
- Column reservoirs, 25 mL available from Eichrom
- Stainless steel planchets

6.0 Reagents

- Ammonium oxalate, 0.1 M
- Ammonium hydroxide, concentrated
- Iron carrier, 20 mg Fe/mL
- Nitric acid, concentrated HNO₃ (15.7 M), 1 M, and 0.1 M

7.0 Sample Collection, Preservation, and Handling

Aqueous samples should be acidified to pH <2 with HNO₃.

8.0 Procedure

- 8.1 An appropriately sized sample aliquot is measured into a beaker; then 2 mL of concentrated HNO₃ and 1 mL of Fe carrier are added. The beaker is covered with a watch glass and heated at near boiling for about 1 h.
- 8.2 The sample is cooled, and the watch glass is removed. Then 10 to 12 mL of concentrated NH₄OH are added to precipitate Fe as Fe(OH)₃. The solution is stirred with a glass rod if necessary.
- 8.3 If the sample is too large to transfer directly to a centrifuge tube, the precipitate is allowed to settle for at least 2 h, and the supernatant is discarded. The precipitate is transferred into a centrifuge tube using water to rinse the beaker.
- 8.4 The sample is centrifuged, and the supernatant is discarded.

- 8.5 The precipitate is washed with 10 mL of water and is again centrifuged, discarding the supernatant.
- 8.6 The precipitate is dissolved with 10 mL of 1 M HNO_3 .
- 8.7 A Sr•Spec[®] column is prepared by removing the bottom plug and cap and rinsing with 10 mL of 1 M HNO_3 .
- 8.8 The dissolved precipitate from step 8.6 is loaded onto the column. The eluent is discarded.
- 8.9 The column is washed with 10 mL of 1 M HNO_3 . The eluent is discarded.
- This will remove Bi, Fe, and ^{90}Y .*
- The time and date of this addition are recorded as they will be used to calculate the ingrowth of ^{210}Bi .
- 8.10 The column is washed with 10 mL of 0.1 M HNO_3 , and the eluent is discarded.
- This will remove any ^{210}Po and ^{90}Sr .*
- 8.11 A clean beaker is placed under the column; then 10 mL of 0.1 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is added to elute Pb.
- 8.12 The oxalate solution is evaporated to near dryness.
- 8.13 Five milliliters of concentrated HNO_3 are added, and the solution is evaporated to dryness. This is repeated once.
- The HNO_3 destroys the oxalate.*
- 8.14 The residue is dissolved in 2 to 3 mL of 0.1 M HNO_3 .
- 8.15 The solution is transferred to a planchet and evaporated to dryness. For quantitative transfer, 0.1 M HNO_3 is used to rinse the beaker.
- 8.16 After drying, the planchet is covered with aluminum foil and set aside for at least three days for ^{210}Bi ingrowth.
- 8.17 The planchet is counted on a gas-flow proportional counter.

9.0 Calculations

The ^{210}Pb activity is determined by counting the ^{210}Bi daughter, and is calculated as follows:

$$^{210}\text{Pb} = \frac{\text{CR}_s - \text{CR}_B}{E \cdot (1 - e^{-\lambda t}) \cdot Q} \cdot C$$

where:

CR_s = sample count rate

CR_B = background count rate

E = counter efficiency for ^{210}Bi

λ = 0.138 day^{-1} (decay constant for ^{210}Bi)

t = time from separation to counting (days)

Q = sample volume

C = conversion factor to convert to desired reporting units.

Chemical yields are assumed to be 100%.

10.0 Quality Control

It is recommended that one reagent blank and one blank spike be run with each analytical batch.

11.0 Method Performance

To be provided.

12.0 Reference

Horwitz, E. P., R. Chiarizia, M. L. Dietz. 1992. "A Novel Strontium-Selective Extraction Chromatographic Resin." *Solvent Extraction and Ion Exchange*, 10(2):313-336.

RP300^(a)**Nickel-59 and Nickel-63 Determination in Aqueous Samples****1.0 Scope and Application**

This method is used to determine the activity of ^{59}Ni and ^{63}Ni in a solution. It describes the separation and purification of Ni using column precipitation chromatography. It also describes the subsequent determination of ^{59}Ni and ^{63}Ni by low energy photon spectroscopy (LEPS) and liquid scintillation counting (LSC) methods, respectively. Stable Ni is used as a carrier, and yield is determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) (or equivalent) analysis of the Ni.

The method was developed for use with highly radioactive Hanford tank samples. It has also been applied to activated stainless steel samples. Variations in the radioactive isotopes present and the radioactive Ni activity will be factors used to determine aliquot size and amount of carrier added. Specific sample matrices {other than single-shell tanks (SST), double-shell tanks (DST), and activated stainless steel} may need to be tested with this procedure to ensure its applicability.

2.0 Summary of Method

A sample is equilibrated with stable Ni carrier and prepared for loading onto a dimethylglyoxime (DMG) precipitation column. The sample is loaded on the DMG column where the Ni forms a Ni-DMG complex. Other cations and anions are effectively eluted with the load and wash solutions. Nickel is stripped the column with 3 M HNO_3 . It is again precipitated as the Ni-DMG complex, filtered onto a 1-in. filter paper, and washed. The filter paper Ni-DMG complex is mounted for LEPS counting where ^{59}Ni activity is determined. The Ni-DMG complex is then oxidized in a muffle furnace leaving NiO, which is then dissolved. An aliquot of the Ni solution is then counted by LSC for ^{63}Ni activity, and another aliquot is analyzed for total Ni to determine yield.

3.0 Interferences

3.1 This method has been tested on Hanford waste tank matrices including drainable liquids and acid dissolved sludges. Validation testing of other matrices will need to be performed by the analytical laboratory.

(a) This method was supplied by Robert Strebin, Robert Orr, James Kaye, and Sandra Fadeff (Pacific Northwest Laboratory, Richland, Washington).

- 3.2 Careful attention needs to be paid to the separations of activated cobalt. The separation efficiency can be monitored with use of gamma energy analysis. If further separations are required, the Ni-DMG precipitate may be dissolved, re-precipitated, and washed.
- 3.3 Because stable Ni is used as a yield monitor, the amount of Ni in the original sample may need to be determined to calculate Ni recovery.
- 3.4 The method has not been tested for ratios of $^{59}\text{Ni}/^{63}\text{Ni}$ greater than 1/40. The ^{59}Ni activity is counted by liquid scintillation, and its peak energy is not resolvable from that of ^{63}Ni . A correction of the net LSC count rate may need to be performed for analyzing materials with greater relative ^{59}Ni activities.
- 3.5 The mass of Ni accommodated by this procedure is limited. The DMG precipitation column can only accommodate up to 3 mg Ni. Large amounts of Ni (e.g., >5 mg) may cause absorption and quenching problems with counting techniques. The absorption and quenching problems may be corrected with appropriate calibration curves.
- 3.6 This procedure uses ethanol, which will result in mixed waste; careful separation of the waste needs to be maintained such that the ethanol is not mixed with the HNO_3 .

4.0 Safety

This procedure uses ethanol in conjunction with an organic compound, dimethylglyoxime. Appropriate safety precautions need to be followed when storing and disposing of an organic with HNO_3 . Otherwise, no significant safety problems are presented by this procedure other than the normal precautions for handling radioactive materials, acids, and bases.

5.0 Apparatus and Materials

- Disposable column (Empty Quick-Snap Columns, Isolab or equivalent)
- Stopcock to fit disposable column
- Vortex stirrer
- Centrifuge
- Centrifuge tubes, plastic, 50 mL
- Transfer pipets, plastic and glass
- Plastic beakers, disposable, 5 mL

- Scintillation vial, low potassium glass, 20 mL
- Plastic screw cap bottles, 20 mL
- Filter holder, 50 mL polysulfone filter funnel with stainless steel support screen (Gelman 4203/4204) or equivalent
- Suction flask
- Tuffryn membrane filter, HT 200, 25 mm diameter or equivalent
- Petri dish

6.0 Reagents

All reagents are prepared from analytical reagent grade chemicals. Deionized water, with an electrical resistance of >16 megohms-cm, is used throughout this method. Except for the stable Ni carrier and radioisotope standards, concentrations are not critical and need only be within $\pm 10\%$ of stated values.

Holdback carrier: a suite of carriers may be used as deemed necessary to accommodate the nature of the sample. Suggested carriers for SST and DST samples include Sr, Co, La, Cs, and Y. The chemical form is not important as long as the compound is readily soluble. Carriers are usually prepared to make individual solutions of 1 to 10 mg/mL. A combined carrier mix can be made, which can then be added to each sample.

- Standardized Ni carrier solution of approximately 10 mg/mL in 1 to 2 M HNO_3 or HCl
- ^{63}Ni , certified ^{63}Ni standard from NIST or other certified vendor
- Sodium hydroxide, 5 M and 0.5 M
- Hydrochloric acid, 12 M (concentrated), 9 M and 0.1 M
- Ammonium hydroxide, 14.5 M (concentrated), and 0.7 M
- Ammonium citrate $\{(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7\}$, 1 M
- Ammonium citrate wash solution (15 mL 1 M ammonium citrate diluted to 100 mL adjusted to pH 8.5 to 9.0 with NH_4OH)

- Nitric acid, 16 M (concentrated), 3 M and 2 volume %
- Ultima-Gold™ LSC cocktail, liquid scintillation cocktail sold by Packard Instrument Company (or equivalent)
- Ethanol, absolute
- Basic buffer solution (water adjusted to pH 8.5 to 9.0 with NH_4OH ; one drop of concentrated NH_4OH in 100 mL of water will buffer to pH 8.5 to 9.0)
- Dimethylglyoxime (DMG)
- Dimethylglyoxime - Saturated Ethanol {Sufficient DMG (2 to 3 g) is added to 50 mL ethanol with mixing and allowed to stand overnight. The solution is saturated when solid DMG is still present.}
- Tartaric acid, 0.7 g/mL of water
- Microthene™, 50 mesh polyethylene powder

7.0 Sample Collection, Preservation, and Handling

Aqueous samples should be acidified to pH <2 with HCl or HNO_3 . No other preservation or storage requirements are indicated.

8.0 Procedure

8.1 DMG Column Preparation

- 8.1.1 To a beaker, 0.5 g DMG is added, followed by 50 mL ethanol. The mixture is stirred and heated as needed to aid dissolution. (This will be called the DMG-ETOH mix.)

This preparation is enough to fill 10 columns. If more than 10 columns are required, the reagent volumes will need to be proportionately increased.

- 8.1.2 To a beaker containing 4 g Microthene™, 5 to 10 mL of DMG-ETOH mix is added and evaporated with heating and stirring until the mix is a slurry. The addition of the DMG-ETOH mix and evaporation is repeated until all the DMG-ETOH mix from step 8.1.1 has been added, and the mix is a thick slurry.

- 8.1.3 Ten milliliters of basic buffer solution are added dropwise to the slurry with vigorous stirring. (This will be called DMG-MIC mix.)

If more buffer is added, the slurry will separate into phases.

- 8.1.4 A small disposable column is prepared by removing the bottom frit (if present), replacing it with a glass wool plug, and attaching a stopcock to the bottom of the column. The DMG-MIC is transferred to the column until the column has been filled to 3 mL. Excess liquid is drained off as the DMG-MIC is added.

When loading the column, a head of liquid should be kept over the microthene bed.

- 8.1.5 When the bed is filled to 3 mL, the liquid is carefully drained to just over the top of the bed (~1 mm). The frit that was removed from the bottom of the column is placed on the top of the bed, leaving a small gap between the frit bottom and the bed.

The headspace in the column is essential to allow for bed expansion as the Ni-DMG precipitates. Air pockets in the column should be avoided.

- 8.1.6 The prepared column is washed with 5 to 10 mL of basic buffering solution. The column is ready for use and can be allowed to stand wetted with the basic buffering solution. Just before use, the column is washed with 2 to 5 mL of basic buffering solution.

8.2 Separation Procedure

- 8.2.1 A known amount (e.g., 2 mg) of Ni carrier is added to each of the following:

- centrifuge tube (or appropriate size beaker) for each sample
- plastic LSC vial for a yield monitor (to be used to calibrate the stable Ni concentration)
- two glass LSC vials (for LSC blanks)
- two glass LSC vials (for LSC ^{63}Ni standards).

The yield monitor vial is capped and saved for step 8.3.8.

8.2.2 A known amount of ^{63}Ni (sufficient to give good counting statistics in a reasonable count time) is added to each of the following:

- blank spike
- matrix spike (if one is to be processed)
- two glass LSC vials identified above for LSC ^{63}Ni standards.

The LSC ^{63}Ni standards and blanks are saved for step 8.3.6; step 8.3.8 is unnecessary for the the LSC ^{63}Ni standards and blanks.

8.2.3 An appropriate sample aliquot is measured and placed in the 50-mL plastic centrifuge tube (or beaker) containing the Ni carrier. Holdback carriers may be added at this point.

8.2.4 Basic samples (such as tank drainable fluids) are acidified with conc HCl.

When basic tank fluids are acidified, a precipitate may form. The precipitate is centrifuged and washed twice with 6 M HCl, and the washes are combined with the sample. The washed precipitate is discarded.

8.2.5 Large samples (e.g., >5 mL) may be concentrated by evaporation or iron hydroxide precipitation. If concentration is not needed, the method is continued at step 8.2.6.

Iron Hydroxide Precipitation

8.2.5.1 A total of 0.1 to 0.2 mg Fe carrier is added to the sample.

8.2.5.2 Then 5 M NaOH is added dropwise, with stirring after each addition. The pH is tested when the first sign of precipitation occurs. Then 0.5 M NaOH and various concentrations of HCl are added to adjust the pH to 7 to 8.

Wide range pH paper (pH 2 to 10) and narrow range pH paper (pH 6 to 8) are used as appropriate to measure the pH. If the pH is exceeded, $\text{Ni}(\text{OH})_2$ will start to dissolve.

8.2.5.3 The sample is centrifuged 10 min on high setting, and the supernate is discarded.

- 8.2.5.4 The precipitate is washed with 5 to 10 mL of pH 7 water. The supernate is discarded.
- 8.2.5.5 The precipitate is dissolved in approximately 4 to 6 drops (or minimum amount needed) of 6 M HCl with swirling. The sample is diluted to 1 to 5 mL with water.
- 8.2.6 One milliliter of 1 M ammonium citrate is added to the sample, which is then stirred well. Concentrated NH_4OH is added to the sample dropwise to pH 8 to 9.
- The pH is not critical as long as it is at least pH 8 and < pH 10. The sample will turn from a green color to a blue color; the solution pH is checked with pH paper as the matrix color may mask the solution color change.*
- 8.2.7 The sample is loaded onto the DMG column in 1-mL aliquots. The column flow rate should be adjusted to approximately 1 drop per 2 sec.
- The Ni reaction with the DMG gives a red Ni-DMG complex precipitate band on the column.*
- The effluent is discarded.
- 8.2.8 The column is washed with 20 mL of ammonium citrate wash solution added in 1-mL aliquots for the first 5 mL, then in 1- to 3-mL aliquots. The wash volume may be increased. The effluent is discarded.
- A portion of the effluent may be counted to assess the separation.*
- 8.2.9 The Ni is stripped from the column with 15 mL of 3 M HNO_3 added in 1- to 5-mL aliquots.
- The red Ni-DMG dissolves, giving a colorless column and solution.*
- 8.2.10 A filter apparatus with a Tuffryn membrane filter is set up.
- 8.2.11 To the eluent from step 8.2.9, 0.1 mL of 0.7 g/mL tartaric acid is added and the solution stirred. Then 1 mL DMG saturated ethanol is added. Concentrated ammonium hydroxide is added dropwise with stirring to pH 8 to 9. The red Ni-DMG complex will precipitate. The solution is allowed to stand for about 1 h for complete precipitation.

8.3 Preparation for Counting

8.3.1 The solution is filtered (the filter will be removed for subsequent LEPS counting). The Ni-DMG complex precipitate is washed with 10 to 20 mL of hot water. The filter is removed, placed on a petri dish, and dried at 100 to 120° C for approximately 1 h.

8.3.2 The Ni-DMG complex filter is mounted for LEPS counting.

The mount may be performed as follows: Mylar film is sealed to the back of a cardboard planchet holder with a 1 in. diameter hole. The filter containing the Ni-DMG complex precipitate is placed in the opening, covered with mylar, and sealed.

8.3.3 The sample is counted on a LEP detector for ^{59}Ni activity.

If better separation is needed as determined from the LEP spectrum, then Ni-DMG may be dissolved in 3 M HNO_3 , reprecipitated, and re-washed as indicated in step 8.2.11 and 8.3.1.

8.3.4 After LEPS counting, the Ni-DMG complex/filter is placed in a glass LSC vial and muffled overnight (or until the oxidation is complete) at 500° C.

The Ni-DMG complex is converted to NiO .

8.3.5 The NiO is dissolved with a minimum of aqua regia (three parts conc HCl to one part conc HNO_3). The acid matrix is converted to the chloride form by evaporating the dissolved Ni to near dryness and adding one mL of concentrated HCl . The evaporation and HCl addition are repeated one to two times.

The $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has a boiling point of 137°C and can be lost if a nitrate solution goes to dryness; NiCl_2 is not volatile.

8.3.6 One mL of concentrated HCl is added, and the solution is evaporated to dryness under a heat lamp.

8.3.7 After cooling, exactly 1 mL of 0.1 M HCl is added to the LSC vial. The solution is allowed to stand about 30 min with occasional swirling to ensure dissolution and mixing of the Ni.

8.3.8 An aliquot (e.g., 0.05 or 0.1 mL) of the sample solution is transferred to an LSC vial and an exact volume (e.g., 10 mL of 2 volume % HNO_3) is added.

In the same manner, exactly 10 mL of 2 volume % HNO_3 are added to the yield monitor solution. The samples and yield monitor are ready for Ni analysis by ICP-OES (or equivalent) for yield determination.

- 8.3.9 Ultima-Gold™ LSC cocktail (e.g., 10 mL) is added to the LSC vial (from step 8.3.7), the vial is capped, and the solution is mixed well. The exterior of the LSC vial is wiped with ethanol or other suitable solvent to eliminate surface residues (e.g., fingerprints). The sample is now ready for scintillation counting.

8.4 LEPS Counter Calibration

The low-energy photon detector counting efficiency may be calibrated relative to ^{59}Ni or, if ^{59}Ni is not available, the counting efficiency may be interpolated relative to other X-ray emitters such as ^{55}Fe and ^{65}Zn . The K X-ray energies of ^{55}Fe (5.90 keV) and ^{65}Zn (8.05 keV) are close to that of ^{59}Ni (6.93 keV). The X-ray counting efficiencies can be determined after correction for the percentage of K X-rays produced per disintegration. The ^{59}Ni X-ray counting efficiency can then be interpolated, and after correction for the K X-ray abundance, the counting efficiency determined. The calibration source can be prepared by pipetting a known amount of ^{59}Ni uniformly on the filter paper geometry. Otherwise, two isotopes, ^{55}Fe and ^{65}Zn , are pipetted uniformly on separate filter papers. Geometry of the standards relative to the samples must be constant.

A calibrated ^{59}Ni standard has been prepared in the Ni-DMG complex geometry, and its counting efficiency was well within the error of the efficiency determined previously relative to an ^{55}Fe source (work performed at the Analytical Chemistry Laboratory, Pacific Northwest Laboratory, 1993).

8.5 LSC Counter Calibration

The LSC is calibrated relative to the ^{63}Ni standards and blanks prepared with the analytical batch (steps 8.2.1 and 8.2.2). The detector efficiency is determined based on the obtained count rate of the standard and the known ^{63}Ni activity. The calibration blank average containing added stable Ni is used for blank subtraction.

9.0 Calculations

9.1 Determination of ^{59}Ni Counting Efficiency

The 6.9 keV Co X-ray peak (from the electron capture decay of ^{59}Ni) counted on the LEP diode is used to calculate ^{59}Ni in the sample. The counting efficiency can be

determined directly if ^{59}Ni is used as a calibration source. The inverse of the counting efficiency (d/c) is determined for each LEP detector as follows:

$$\frac{d}{c} (^{59}\text{Ni}) = \frac{\text{DR}_{^{59}\text{Ni}}}{\text{net CR}_{^{59}\text{Ni}}}$$

where

$$\begin{aligned} \text{DR} &= \text{disintegration rate} \\ \text{CR} &= \text{count rate} \end{aligned}$$

The ^{59}Ni X-ray counting efficiency (E) may need to be interpolated between other X-ray emitters, ^{55}Fe and ^{65}Zn for example. The counting efficiencies of the X-rays produced as a result of the electron capture decay of ^{55}Fe and ^{65}Zn on the LEP diode are determined as follows:

$$\begin{aligned} E_{^{55}\text{Fe}} &= \frac{\text{net CR}_{^{55}\text{Fe}}}{\text{DR}_{^{55}\text{Fe}} \cdot \frac{\text{X-ray}_{^{55}\text{Fe}}}{d_{^{55}\text{Fe}}}} \\ E_{^{65}\text{Zn}} &= \frac{\text{net CR}_{^{65}\text{Zn}}}{\text{DR}_{^{65}\text{Zn}} \cdot \frac{\text{X-ray}_{^{65}\text{Zn}}}{d_{^{65}\text{Zn}}}} \end{aligned}$$

where (from Browne and Firestone 1986)

$$\frac{\text{X-ray}_{^{65}\text{Zn}}}{d_{^{65}\text{Zn}}} = 0.3828$$

$$\frac{\text{X-ray}_{^{55}\text{Fe}}}{d_{^{55}\text{Fe}}} = 0.2726$$

The X-ray counting efficiency for ^{59}Ni is then the average of the X-ray counting efficiencies for ^{55}Fe and ^{65}Zn . The inverse of the counting efficiency (d/c) for ^{59}Ni is then determined as follows:

$$\frac{d}{c}(^{59}\text{Ni}) = \frac{\left(\frac{\text{X-ray}_{^{59}\text{Ni}}}{d_{^{59}\text{Ni}}}\right)^{-1}}{\left[\left(E_{^{55}\text{Fe}}\right) + \left(E_{^{65}\text{Zn}}\right)\right] \cdot \frac{1}{2}}$$

where

$$\frac{\text{X-ray}_{^{59}\text{Ni}}}{d_{^{59}\text{Ni}}} = 0.3306$$

The values of (X-ray/d) are the sum of $K_{\alpha 1}$, $K_{\alpha 2}$, and $K_{\beta 1}$ X-ray absolute abundances per disintegration. Adding the value for $K_{\beta 1}$ to the ratio will depend on the users' LEP detector resolution, as the average energy difference between the $K_{\alpha 2}$ and $K_{\beta 1}$ is approximately 0.7 keV. Typically the resolution {full width half maximum (FWHM)} of a Ge detector is ~2 keV; therefore, a peak of 0.7 keV difference in energy would not be easily resolvable.

9.2 Determination of ^{59}Ni and ^{63}Ni Activity

The ^{59}Ni activity is calculated in the sample using the following equation:

$$A_{^{59}\text{Ni}} = \frac{(\text{net CR})(d/c_{^{59}\text{Ni}})(k)}{(Y)(Q)}$$

The ^{63}Ni activity is determined from the LSC spectra using the following equation:

$$A_{^{63}\text{Ni}} = \frac{(\text{net CR})(d/c_{^{63}\text{Ni}})(k)(v_{\text{corr}})}{(Y)(Q)}$$

where

A = analyte activity

net CR = the gross count rate minus the background count rate

k = factor to account for sample dilutions, and any other factors needed to produce the appropriate reporting units

Y = yield determined by the amount of stable Ni recovered relative to the amount added

- v_{corr} = sample volume correction at step 8.3.8 where a fraction of sample is taken for ICP analysis (volume total/volume for LSC analysis)
- d/c = disintegrations per count, inverse of efficiency (for LSC, this will include the quenching effects)
- Q = quantity (volume or mass) of sample analyzed.

The error (σ) in the activity is determined as follows:

$$\sigma_{59\text{Ni}} = A_{59\text{Ni}} \cdot \sqrt{\left(\frac{\sigma_{59\text{Ni}} \text{ CR}_{59\text{Ni}}}{\text{net CR}_{59\text{Ni}}}\right)^2 + \left(\frac{\sigma_{\text{eff}59\text{Ni}}}{\text{eff}_{59\text{Ni}}}\right)^2 + \left(\frac{\sigma_{\text{yield}}}{\text{yield}}\right)^2 + \left(\frac{\sigma_Q}{Q}\right)^2}$$

$$\sigma_{63\text{Ni}} = A_{63\text{Ni}} \cdot \sqrt{\left(\frac{\sigma \text{ CR}_{63\text{Ni}}}{\text{net CR}_{63\text{Ni}}}\right)^2 + \left(\frac{\sigma_{\text{eff}63\text{Ni}}}{\text{eff}_{63\text{Ni}}}\right)^2 + \left(\frac{\sigma_{v_{\text{corr}}}}{v_{\text{corr}}}\right)^2 + \left(\frac{\sigma_{\text{yield}}}{\text{yield}}\right)^2 + \left(\frac{\sigma_Q}{Q}\right)^2}$$

where

- σ = error in the specified value

The error tends to be driven by the errors in counting efficiency and yield. For low-level samples, the error in count rate (i.e., net cpm) also becomes significant.

10.0 Quality Control

- 10.1 It is recommended that one reagent blank, one sample duplicate, and one blank spike or matrix spike be run to provide an estimate of the analytical batch bias and precision.
- 10.2 Chemical yields should be over 50% and should not exceed 110%.
- 10.3 Chemical quench factors for liquid scintillation counting should be similar between the samples and the standards.

11.0 Method Performance

This method was performed by a single laboratory on single-shelled tank sludge waste matrix from Hanford samples A, B, and C. Previous studies indicated the waste contained little ^{59}Ni and ^{63}Ni ; therefore, triplicate samples could be spiked with an appropriate amount of ^{59}Ni and ^{63}Ni for a study of precision and bias. A 0.48-g sludge sample was digested in a hot cell with 50%

HNO₃, organics were then oxidized with 30% H₂O₂, and digestion was continued with 50% HCl. The sample was brought to 100 mL final volume. Triplicate 20-mL samples were taken and spiked with 0.77 Bq (46 dpm) ⁵⁹Ni and 31.7 Bq (1903 dpm) ⁶³Ni.

A second set of samples was prepared from activated stainless steel samples (Fadeff et al. 1994). These samples were sectioned from non-fuel bearing components of nuclear reactors. The samples were cleaned extensively, then separated according to this method. Two sets of cold stainless steel matrix spikes and blank spikes were run as well as three sets of duplicate samples (CRB6, BPRA5, and RCCA8).

A summary of the analytical bias is given in Table 1, and a summary of the analytical precision is given in Table 2. Typical chemical recoveries are equal to, or greater than, 90%. A summary of chemical recoveries obtained from a batch of 11 samples is given in Table 3.

Table 1 Bias and Precision of ⁵⁹Ni and ⁶³Ni

Sample ID	Bq ⁵⁹ Ni Added	Bq ⁵⁹ Ni Recovered	⁵⁹ Ni % Bias	Bq ⁶³ Ni Added	Bq ⁶³ Ni Recovered	⁶³ Ni % Bias
Tank Waste Matrix						
A	0.767 ± 0.093	0.730 ± 0.087	-5	31.72 ± 0.38	29.83 ± 1.83	-5.9
B	0.767 ± 0.093	0.802 ± 0.095	+5	31.72 ± 0.38	30.67 ± 2.00	-3.3
C	0.767 ± 0.093	0.777 ± 0.095	+1	31.72 ± 0.38	28.83 ± 1.83	-9.1
Activated Metals Blank Spike and Matrix Spike						
Matrix Blank Spike 1	1.52 ± 0.18	1.48 ± 0.17	-2.2	127.7 ± 1.6	127.7 ± 10.5	-0.04
Matrix Blank Spike 2	na			126.9 ± 1.6	128.8 ± 11.5	+1.5
Blank Spike 1	1.52 ± 0.18	1.50 ± 0.20	-1.1	127.7 ± 1.6	128.7 ± 10.8	+0.7
Blank Spike 2	na			126.9 ± 1.6	129.9 ± 11.5	+2.4

Table 2. Summary of Method Precision

Sample ID	^{59}Ni (Bq)	RPD/RSD ^(a) Tank Waste Matrix	^{63}Ni (Bq)	RPD/RSD
A	0.730 $\pm$ 0.087		29.83 $\pm$ 1.83	
B	0.802 $\pm$ 0.095	4.8%	30.67 $\pm$ 2.00	3.1%
C	0.777 $\pm$ 0.095		28.83 $\pm$ 1.83	
	(M Bq/g)	Activated Metals Matrix	(M Bq/g)	
CRB6	0.299 $\pm$ 0.037	4.2%	36.1 $\pm$ 3.0	0.20%
CRB6 duplicate	0.287 $\pm$ 0.037		36.0 $\pm$ 3.0	
BPRA3	0.077 $\pm$ 0.010	3.3%	8.21 $\pm$ 0.70	1.4%
BPRA3 duplicate	0.080 $\pm$ 0.010		8.10 $\pm$ 0.70	
RCCA8	3.05 $\pm$ 0.41	3.6%	377 $\pm$ 34	4.4%
RCCA8 duplicate	2.94 $\pm$ 0.37		361 $\pm$ 33	

(a) RPD - relative percent difference
RSD - relative standard deviation

Table 3. Chemical Recoveries

Sample No.	% Recovered
1	94
2	96
3	91
4	97
5	101
6	96
7	64
8	91
9	100
10	96
11	98
Average	93 $\pm$ 10

12.0 References

Browne, E., and R. B. Firestone. 1986. *Table of Radioactive Isotopes*. John Wiley and Sons, New York.

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13.0 Further Reading

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RP330(a)

Separation of Niobium for Niobium-93m and Niobium-94 Determination**Note:**

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method describes the separation of ^{93m}Nb ($t_{1/2} = 16.1$ yr) and ^{94}Nb ($t_{1/2} = 2.0 \times 10^4$ yr) from other radioisotopes in aqueous solution. The method is intended for samples that cannot be analyzed directly by gamma-ray spectrometry for ^{94}Nb and/or by low-energy photon (LEP) spectroscopy for ^{93m}Nb because of interferences from other gamma and X-ray emitters. For samples containing high levels of ^{94}Nb , no separation before analysis may be required as ^{94}Nb may be determined directly by gamma-ray spectrometry. Interferences are more common in the X-ray determination of ^{93m}Nb ; however, if a direct mount of the sample provides satisfactory resolution of the ^{93m}Nb X-ray peak(s), separation is not necessary for this isotope, either. The following separation method has been used to characterize Hanford waste-tank samples, activated stainless steel, and neutron activated metallic Zr/Nb buttons.

2.0 Summary of Method

Separation is accomplished by precipitating hydrated niobium pentoxide ("niobic acid"), which is collected by filtration and converted to Nb_2O_5 in air. Radiochemical yield is determined from the ^{95}Nb tracer recovery which is quantified by gamma-ray spectrometry. The ^{94}Nb and ^{93m}Nb activities are both determined by gamma-ray spectrometry. A low-energy photon detector is used to measure the X-rays produced from the isomeric transition decay from the 30.4 keV energy state of ^{93m}Nb .

(a) This method was submitted by S. K. Fadeff and N. L. Wynhoff (Pacific Northwest Laboratory, Richland, Washington).

3.0 Limitations and Interferences

Antimony is incompletely separated from Nb. Decay of ^{125}Sb produces Te K_{α} X-rays at 27.5 keV. These in turn may result in a Ge escape peak at 17.5 keV, which interferes with the $^{93\text{m}}\text{Nb}$ X-ray peak ($k_{\alpha} = 16.6$ keV). An evaluation will need to be made of the spectral results in terms of the amount of $^{93\text{m}}\text{Nb}$ and ^{125}Sb present and the required sensitivity for $^{93\text{m}}\text{Nb}$. Depending on the activities involved, a correction can be made for the ^{125}Sb interference, based on the 27.5 keV ^{125}Sb X-ray.

If a ^{95}Zr - ^{95}Nb tracer is used, then $^{95\text{m}}\text{Nb}$, the 3.6 day daughter of ^{95}Zr that also produces Nb X-rays, must be allowed to decay before counting for $^{93\text{m}}\text{Nb}$. The decay time allowed will depend on the detection limit and turn-around time required for the sample set.

4.0 Safety

Hydrofluoric acid is used in conjunction with this procedure. Handling this reagent properly, as well as others, is the responsibility of the user.

5.0 Apparatus and Materials

- Teflon[®] beaker, 250 mL or other appropriate size
- Plastic centrifuge tube, 50 or 100 mL
- pH paper, gross range, pH 2 to 10
- Teflon[®] stir bar
- Filter apparatus, to fit filter below
- Filters - glass microfiber (e.g., 4.7 or 5.5 cm diameter), 1.6 μm effective particle-size retention or better, or equivalent
- Mylar sheet {e.g., nominal thickness .0125 mm (.0005 in.)}
- Filter mounts that will result in a consistent counting geometry (e.g., cardboard support with a centered hole to accommodate filter)
- Filters - membrane, 4.7 cm diameter, any pore size, or other appropriate material that is stable with respect to the chemical matrix of the tracer solution—for use only in preparing the tracer standard (step 8.17)

6.0 Reagents

All chemicals used are reagent grade unless otherwise specified. The water used is deionized or distilled water.

- HCl, conc and 3 M
- HF, conc
- HNO₃, conc and 9 M
- Co (holdback) carrier, ~10 mg/mL
- Sb (holdback) carrier, ~20 mg/mL
- Nb carrier, 10 mg/mL - In a Teflon[®] beaker, 14.3 g Nb₂O₅ is dissolved in 50 mL conc HF. The solution is heated if necessary, then it is cooled to about room temperature and diluted to 1 L with water. The solution should be stored in Teflon[®] or polyethylene. (Note: Another Nb compound may be used or another concentration as long as the required mg of Nb⁺⁵ are added.)
- ⁹⁵Nb or ⁹⁵Zr-⁹⁵Nb tracer - An appropriate activity should be added to provide adequate counting statistics of the ⁹⁵Nb gamma-ray peak in a reasonable count time.
- NH₄OH, conc

7.0 Sample Collection, Preservation, and Handling

Niobium is most stable in HF and HNO₃ solutions. Aqueous samples should be preserved to pH <2 with HNO₃. A few drops of conc HF should be added before sampling to better solubilize any Nb which may have plated out.

8.0 Procedure

- 8.1 A sample aliquot is taken and then acidity is checked. If the sample is not highly acidic (i.e., pH ≤2), ≥9 M HNO₃ is added until the pH is ≤2. Large aqueous samples (that cannot fit in the centrifuge tube) may be evaporated to a low volume that is accommodated by the centrifuge tube.

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- 8.2 Three carriers are added to the sample: ~10 mg Co (holdback) carrier, ~20 mg Sb (holdback) carrier, and 200 mg Nb carrier.

The 20 mg of Sb holdback carrier substantially reduces the amount of any interfering ^{125}Sb present in the gamma and (low-energy photon) LEP spectra. Increasing the amount of Sb holdback carrier may further reduce the amount of ^{125}Sb present in the sample spectra.

- 8.3 An appropriate amount of tracer is added to the sample, which will provide adequate counting statistics in a reasonable count time.
- 8.4 The sample is made strongly basic ($\text{pH} \geq 9$) with conc NH_4OH with mixing. The pH is confirmed with pH paper.

A white precipitate, a hydrated niobium oxide, forms.

- 8.5 The sample is centrifuged, causing the precipitate to pack appropriately, and the supernate is discarded.
- 8.6 The precipitate is dissolved with 2 to 5 mL of conc HF (or with additional conc HF, if required). The holdback carriers are again added to the sample: ~10 mg of Co and ~20 mg of Sb.
- 8.7 Then 50 mL of concentrated HNO_3 are added to a 250-mL beaker (Pyrex or Kimax are satisfactory) and *then* the sample (HF solution) is quantitatively transferred to this beaker using HNO_3 as the rinse solution. Additional HNO_3 is added to make a total volume of at least 150 mL in the beaker.

If the sample solution in HF (from step 8.6) has a volume of >10 mL, the beaker size and volumes of conc HNO_3 should be scaled up proportionately. The large amounts of HNO_3 effectively dilute the HF such that its reaction with the silica from the beaker is inconsequential. Alternatively, Teflon[®] beakers could be used with 100 mL of added HNO_3 ; however, the Nb_2O_5 precipitate will be more difficult to see.

- 8.8 The solution is heated while stirring (to prevent popping) with a Teflon[®] stir bar, without boiling, until the solution has evaporated to half or less of its original volume, and the white niobic acid (i.e., $\text{Nb}_2\text{O}_5 \cdot x \text{H}_2\text{O}$) precipitate has formed. The beaker is cooled to about room temperature. The solution should not be evaporated to dryness.
- 8.9 The solution/precipitate is transferred to a plastic centrifuge tube with HNO_3 and centrifuged to produce a tight packing of the precipitate. The supernate is discarded. If

^{95}Zr (in equilibrium with ^{95}Nb) is used as the tracer, the date and time are recorded as the ^{95}Nb separation time.

The precipitate should not be left in contact with air for an extended time since NbO_x which is difficult to dissolve in HF, may form. Therefore, the supernate in step 8.9 or 8.10 should not be decanted until ready to immediately proceed with rinsing or dissolution.

- 8.10 The precipitate is rinsed three times with water, centrifuging and discarding the supernate after each wash.
- 8.11 Steps 8.6 through 8.8 are repeated one time.
- 8.12 The cooled solution (from repeat of step 8.8) is filtered, using a tared-glass microfiber filter. The filter is thoroughly rinsed with H_2O , and the filtrate is discarded.
- 8.13 The filter and precipitate are dried (a heat lamp may be used for low heat); then the dry filter and precipitate are weighed.
- 8.14 The filter with the precipitate is mounted for counting. This may be done as follows or with some other suitable technique for the laboratory.
 - 8.14.1 The filter is placed face down on a piece of Mylar that is supported by a clean (new) paper towel.
 - 8.14.2 The filter is taped to the mylar, completely covering and sealing the filter with tape.
 - 8.14.3 Excess tape/mylar are cut from around the filter, leaving sufficient material to overlap the edges of the hole in the cardboard holder.
 - 8.14.4 The filter is taped to the bottom of the cardboard filter holder such that the precipitate is centered in the hole and is visible from the top through the Mylar.
 - 8.14.5 The cardboard filter holder should be sealed into a plastic bag to provide secondary containment.
- 8.15 The sample is counted on a high-resolution Ge detector. The yield is determined from the ^{95}Nb peak at 766 keV, and the ^{94}Nb is determined from the 703-keV and/or 871-keV peaks.

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- 8.16** The sample is removed from the plastic bag and counted on an LEP detector. Niobium-^{93m} decays by isomeric transition from the 30.4-keV energy state, producing Nb X-rays at 17 keV.

Samples are counted in a standard geometry with the precipitate centered over the face of the detector. When counting on an LEP detector, the precipitate should be facing the detector face.

- 8.17** A 100% yield comparator tracer standard may be prepared.

8.17.1 An appropriate aliquot of tracer is stippled onto a filter over an area equal in size to the precipitate diameter of the samples. The drops should be distributed as uniformly and symmetrically as practical. The filter is air dried.

8.17.2 The tracer standard is mounted and counted identically to the samples.

- 8.18** A counting-efficiency curve should be generated for the count-rate losses due to absorption and scatter of the 17-keV X-rays within the Nb₂O₅ precipitate. This can be established as follows.

8.18.1 Various masses, in triplicate, of Nb carrier are added to test tubes, for example, 50 mg, 100 mg, 150 mg, and 200 mg. A ^{93m}Nb standard (enough to provide adequate counting statistics in a reasonable count time) is added to each test tube along with an appropriate volume of ⁹⁵Nb tracer (which again provides adequate counting statistics in a reasonable count time).

8.18.2 The solutions are processed according to steps 8.7, 8.8, and 8.12 (recording the ⁹⁵Zr/⁹⁵Nb separation at step 8.12, if appropriate) through 8.16.

9.0 Calculations

9.1 Niobium-95 Yield Calculation. The ^{95}Nb tracer yield is used to correct the ^{94}Nb and $^{93\text{m}}\text{Nb}$ for processing losses.

For counting the tracer standard, the net disintegration rate (dps of ^{95}Nb is calculated using the following equation. The ^{95}Nb is calculated from the net count rate (cps) of the 766-keV gamma ray and, if present, the ^{95}Zr must be calculated from the net count rate (cps) of the 724-keV and/or the 757-keV gamma rays.

$$\text{dps} = \frac{\text{net cps}}{E}$$

where

E = counter efficiency for the specific gamma-ray energy, branching ratio for ^{95}Nb or ^{95}Zr , and specific counting geometry

In the case where the $^{95}\text{Zr}/^{95}\text{Nb}$ (in transient equilibrium) tracer is used, the tracer standard count must be decay-corrected to the time of the separation of Nb from Zr (the Nb separation time from Step 8.9) {the ^{95}Nb ($t_{1/2} = 35$ d) is shorter-lived than its parent ^{95}Zr ($t_{1/2} = 64$ d)}. The decay-correction is performed according to the following equation:

$$A_{\text{Nb}} = \frac{A_{\text{Zr}}^{\circ} (\lambda_{\text{Nb}})}{(\lambda_{\text{Nb}} - \lambda_{\text{Zr}})} (e^{-\lambda_{\text{Zr}}t} - e^{-\lambda_{\text{Nb}}t}) + A_{\text{Nb}}^{\circ} e^{-\lambda_{\text{Nb}}t}$$

where

A_{Nb} = activity (e.g., dps) of ^{95}Nb in tracer standard at the time of the Nb separation

A_{Zr}° = the initial activity (e.g., dps) of ^{95}Zr in the tracer standard

λ_{Nb} = the decay constant for ^{95}Nb

λ_{Zr} = the decay constant for ^{95}Zr

t = the time from the tracer standard count (initial activity) to the Nb separation time

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A_{Nb}° = the initial activity (e.g., dps) of ^{95}Nb in the tracer standard.

Once the standard ^{95}Nb concentration is known, the fractional yield of ^{95}Nb may be calculated using the following equation:

$$Y = \frac{(DR_s) (e^{\lambda_{Nb}t}) (C)}{(DR_T)}$$

where

Y = chemical yield

$e^{\lambda_{Nb}t}$ = factor to decay correct the sample count rate to the sample separation time

C = a factor to account for any differences between the aliquot of tracer added to the sample and that evaporated as the tracer standard

DR_s = net disintegration rate (e.g., dps) of ^{95}Nb in sample at separation time

DR_T = net disintegration rate (e.g., dps) of ^{95}Nb in tracer at separation time.

If the pure ^{95}Nb tracer standard is used, then the yield is determined at a constant time relative to the standard, not necessarily the separation time.

$$Y = \frac{(CR_{S, t_i})}{(CR_{T, t_i})} \cdot C$$

where

CR_{S, t_i} = count rate of the sample at t_i

CR_{T, t_i} = count rate of the tracer at t_i

and t_i is a constant time, and C was defined above.

- 9.2 Niobium-94 Calculation.** The ^{94}Nb activity in the sample is calculated using the net count rate (i.e., the background-corrected count rate) of the 703-keV and/or the 872-keV gamma rays, using the following equation:

$$^{94}\text{Nb} = \frac{(\text{CR}_{\text{net}})(B)}{E \cdot Y \cdot Q}$$

where

^{94}Nb = the activity concentration of ^{94}Nb

CR_{net} = net count rate of the ^{94}Nb

E = counter efficiency for the specific gamma-ray energy, branching ratio for ^{94}Nb , and specific counting geometry

Q = quantity (mass or volume) of sample analyzed

B = a factor or factors to account for dilutions and any other factors needed to produce the appropriate reporting units.

9.3 Calibration of the LEP Detector for Niobium-93m Determination. The relationship between the Nb_2O_5 precipitate loading and the detection efficiency of the $^{93\text{m}}\text{Nb}$ needs to be established. This allows the correction for count rate losses due to absorption and scatter of the 17-keV X-rays within the Nb_2O_5 precipitate. The efficiency for each standard may be established as follows:

$$E_m = \frac{\text{CR}}{\text{DR} \cdot Y}$$

where

E_m = efficiency as a function of mass loading

CR = net count rate (e.g., cps) of the standard

DR = activity rate (e.g., dps) of added $^{93\text{m}}\text{Nb}$

The efficiency may be plotted as a function of the mass of precipitate loading, and an equation may be derived based on the best fit curve (e.g., $y = mx + b$).

9.4 Niobium-93m Calculation. The ^{93m}Nb activity in the sample is calculated using the net count rate (i.e., the background-corrected count rate) of the 17-keV X-ray, according to the following equation:

$$^{93m}\text{Nb} = \frac{(\text{CR}) (\text{B})}{(\text{Y}) \cdot (\text{E}_m) \cdot \text{Q}}$$

where

^{93m}Nb = activity concentration of ^{93m}Nb

CR = net count rate of the ^{93m}Nb

E_m = counting efficiency for the specific sample mass and specific counting geometry

Q = sample quantity (mass or volume)

B = a factor or factors to account for dilutions and any other factors needed to produce the appropriate reporting units.

10.0 Quality Control

It is recommended that a reagent blank, blank spike, and sample duplicate be analyzed with each analytical batch.

11.0 Method Performance

The performance of this method for the analysis of single-shelled tank samples from Hanford, activated stainless steel, and activated Zr/Nb buttons are summarized in Tables 1 and 2. Bias is determined relative to blank spikes and matrix spikes; precision is based on duplicate sample runs. The duplicate sample runs on the Hanford waste tank resulted in no detectable activity.

The detection limit for ^{93m}Nb is approximately 0.37 Bq (10 pCi or 22 dpm) per unit sample size, assuming a background count rate of 0.21 cpm, count time of 60 min, counting efficiency of 0.0245, and a yield of 0.60. The detection limit for ^{94}Nb is approximately 0.23 Bq (14 dpm or 6.4 pCi) per unit sample size, assuming a background count rate of 0.22 cpm, count time of 60 min, counting efficiency of 0.0385, and a yield of 0.60.

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Table 1. Summary of Performance Data for ⁹⁴ Nb Analysis			
Yield	Precision	Bias	
Single-Shell Tank 0.66 ± 0.23; n = 12	NA	-10% ± 1%; n = 2	
Activated Stainless Steel 0.85 ± 0.10; n = 27	12%; n = 1	-2% ± 10%; n = 4	

Table 2. Summary of Performance Data for ^{93m} Nb Analysis			
Yield	Precision	Bias	
Single-Shell Tank 0.66 ± 0.23; n = 12	NA	-1.5% ± 7.8%; n = 2	
Activated Zr/Nb Buttons 0.65 ± 0.08; n = 9	3.8%; n = 1	+1.0%; n = 1	

12.0 Further Reading

Wynhoff, N. L. 1991. *Determination of Niobium-93m and Niobium-94*. PNL-ALO-472. Pacific Northwest Laboratory, Richland, Washington.

13.0 Review Comments and Suggestion

Better chemical yields may be obtained if step 8.10 is altered to use a 2% ammonium nitrate precipitate rinse instead of a water rinse. The ammonium nitrate rinse solution minimizes suspension of niobic acid in the water rinse.

RP500^(a)**Purification of Strontium in Water Before Strontium-89/Strontium-90 Measurement****1.0 Scope and Application**

This method forms the basis for analyzing radioactive Sr (isotopes 89 and/or 90) in surface and groundwaters (including, but not limited to, drinking water). It applies to any sample volume that can be preconcentrated and redissolved in less than 20 mL of column feed solution. The detection limit depends on sample volume and counting protocol. After preconcentration, the chemistry takes about 4 h and is amenable to being batched (i.e., one person can process many samples simultaneously). Chemical waste per sample is approximately 30 mL 8 M HNO₃ plus a spent column, a dramatic reduction compared to traditional radiostrontium analytical methods.

2.0 Summary of Method

A yield monitor (normally stable Sr or ⁸⁵Sr) is added to the sample. Large samples are reduced in volume by evaporation, by cation exchange, or by coprecipitation (e.g., calcium carbonate or calcium phosphate). The sample is re-dissolved in column feed solution and passed through a Sr•Spec[®] column where Sr is selectively extracted into the column packing (crown ether supported on an inert substrate). Virtually all other elements (with the notable exceptions of Pb, Pu, and Np) are washed through the column. Strontium is then eluted with 0.05 M HNO₃, leaving Pb on the column. A Sr counting source is produced and counted using any of several options.

3.0 Interferences and Limitations

- 3.1 Stable Sr present in the sample will interfere with the gravimetric yield determination. If the Sr content in the sample is unknown, it should be determined {e.g., by atomic absorption (AA), inductively coupled plasma (ICP), or by a duplicate sample run with no added Sr carrier} so that appropriate adjustment can be made to the amount of Sr recovered.
- 3.2 Stable Sr will consume column capacity. The maximum Sr that can be accommodated by the Sr•Spec[®] column is approximately 10 mg Sr or 24 mg Sr(NO₃)₂. An appropriate working level is half that amount. Samples containing more than a few mg of Sr may need to use smaller sample volumes or larger columns to avoid lowered Sr recoveries.

(a) This method was supplied by D. M. Nelson (Argonne National Laboratory, Argonne, Illinois).

- 3.3 Lead and ^{210}Pb are potentially serious interferences. Since Pb is more strongly bound to the crown ether than is Sr, it will consume column capacity and displace Sr. More than a few mg of Pb present in a sample will begin to decrease Sr recovery. Lead-210 itself is well separated (by virtue of remaining on the column while Sr is eluted) and is not a direct interference. Ingrowth of its daughter ^{210}Bi during elution of Sr can be a problem in samples that are high in ^{210}Pb and low in radioactive Sr if a correction is not made for the ^{210}Bi .
- 3.4 Small amounts of the crown-ether extractant in the Sr eluent (due to column bleed) have been observed and could cause interferences in the gravimetric yield calculation for direct evaporation. The weight is reproducible (0.3 ± 0.1 mg per 10 mL of column eluate), and the presence of the crown ether acts as a binder for the $\text{Sr}(\text{NO}_3)_2$. It causes no problem so long as its mass is subtracted from the $\text{Sr}(\text{NO}_3)_2$ mass.
- 3.5 The Pu(IV) and Np(IV) are retained on the Sr•Spec[®] column under high-acid conditions and are eluted with Sr. This may cause interferences in subsequent beta counting if no alpha/beta discrimination is employed. This interference can be removed by passing the sample solution through an anion exchange column (to remove the Pu and/or Np) before the solution is applied to the Sr•Spec[®] column.
- 3.6 This procedure has not been tested with all possible matrices and interferences. Before use, it should be thoroughly tested for suitability on the specific waters of interest.

4.0 Safety

No significant safety problems are presented by this method other than the normal precautions for handling radioactive materials, acids, and bases.

5.0 Apparatus and Materials

- Beta detector - proportional counter, liquid scintillation counter, or Cerenkov counter
- Sr•Spec[®] column - 2 mL (0.7 g) of resin, available prepacked from Eichrom Industries, Inc., 8205 S. Cass Ave., Suite 107, Darien, IL, 60561 (800) 422-6693
- Counting containers - scintillation vials for liquid scintillation or Cerenkov counting, or stainless steel dishes for proportional counting (A dish with tapered sides is essential for maintaining a reproducible counting geometry.)

6.0 Reagents (purification procedure only)

- Nitric acid, 8 M
- Nitric acid, 0.05 M
- Column feed solution - 0.5 M $\text{Al}(\text{NO}_3)_3$ in 8 M HNO_3 (Pure 8 M HNO_3 is an acceptable alternative; $\text{Al}(\text{NO}_3)_3$ enhances the affinity for Sr and improves the separation from Ba.)
- Strontium carrier - 10.0 mg/mL $\text{Sr}(\text{NO}_3)_2$ in 0.1 M HNO_3

7.0 Sample Collection, Preservation, and Handling

Samples may be acidified to pH 1 with HNO_3 before sub-sampling.

8.0 Procedure

This procedure consists of

- several optional pre-concentration methods (A choice can be made based on sample characteristics, or another appropriate pre-concentration method can be used.)
- a method to isolate and purify the Sr fraction
- several detection methods (A choice can be made based on data quality needs, or another appropriate counting method can be used.)

Two options for determining chemical recovery are suggested, by measuring stable Sr {either by weighing the $\text{Sr}(\text{NO}_3)_2$ residue or by instrumental analyses of Sr, e.g., by AA or ICP} or by gamma counting of ^{85}Sr (added as a tracer). Either may be chosen, but using stable Sr introduces no counting interferences and is generally more appropriate for proportional or liquid scintillation counting. Strontium-85, on the other hand, is suitable for Cerenkov counting or when ^{90}Y is to be extracted and counted by any method. These pre-concentration and counting options are not meant to be exclusive, but are presented as illustrations of how this Sr purification scheme can be applied. Samples expected to have sufficient radioactive Sr to meet data quality objectives without pre-concentration may simply be acidified with HNO_3 , have the appropriate yield monitor added, and be loaded directly on the Sr•Spec[®] column.

8.1 Preconcentration Method 1 - Evaporation

This method is used to transpose the sample to the column feed solution where only acid soluble residues are formed by evaporation. Recovery is essentially quantitative.

- 8.1.1 An appropriately sized aliquot should be measured and transferred to a glass beaker.
- 8.1.2 A known amount of Sr carrier (e.g., 1.00 mL) and/or of ^{85}Sr is added.
- 8.1.3 The solution is evaporated to dryness on a hotplate using moderate heat.
- 8.1.4 The sides of the beaker are washed with a few mL of 8 M HNO_3 .
- 8.1.5 The solution is evaporated to incipient dryness and redissolved in a minimum volume of feed solution (5 to 10 mL); the beaker is covered with a watchglass and heated gently if necessary to dissolve the residue.

8.2 Preconcentration Method 2 - Cation Exchange

This method is used to transpose the sample to column feed solution where insoluble residues (for example, CaSO_4) are formed during evaporation. Recovery is essentially quantitative.

- 8.2.1 An appropriately sized aliquot should be measured and transferred to a bottle.
- 8.2.2 A known amount of Sr carrier (e.g., 1.00 mL) and/or of ^{85}Sr is added.
- 8.2.3 A cation exchange column containing 10 mL of AG 50W-X8 cation exchange resin (100 to 200 mesh) is prepared. This column size is adequate for 1 L of most fresh waters. Samples having high dissolved solids may need a larger column. A simple visual test of the adequacy of the column size is accomplished by adding 10 mg of copper {as $\text{Cu}(\text{NO}_3)_2$ in 0.1 M HNO_3 } to the column just before the sample is passed. Retention of the blue Cu band on the column is assurance that Sr (which is bound more strongly than is Cu) has been retained.
- 8.2.4 The column is preconditioned with 50 mL of 0.1 M HNO_3 .
- 8.2.5 The sample is passed through the column at a rate of ~1 to 2 mL/min.
- 8.2.6 The column is rinsed with 50 mL of 0.1 M HNO_3 .

- 8.2.7 The feed and rinse solutions are discarded.
- 8.2.8 The Sr and other cations are eluted with 50 mL of 8 M HNO_3 into a beaker.
- 8.2.9 The solution is evaporated to dryness on a hotplate (the sample redissolves easily if the evaporation is stopped just as the sample starts to go dry).
- 8.2.10 The salts are dissolved in a minimum volume of feed solution (5 to 10 mL), covered with a watchglass, and heated gently if necessary to dissolve the residues.

8.3 Preconcentration Method 3 - Calcium Phosphate Precipitation

This method or some variation can be used for most waters. Recovery is not quantitative, but should exceed 70%.

- 8.3.1 An appropriately sized aliquot should be measured and transferred to a beaker.
- 8.2.2 A known amount (e.g., 1.00 mL) of Sr carrier and/or of ^{85}Sr is added.
- 8.3.3 Calcium carrier is added while stirring (100 mg Ca/L of sample).
- 8.3.4 Phosphate is added while stirring (2 g phosphate/L of water, as phosphoric acid or ammonium phosphate).
- 8.3.5 The solution is neutralized with an excess of ammonium hydroxide while stirring.
- 8.3.6 The precipitate is collected by settling and/or centrifugation.
- 8.3.7 The precipitate is dissolved in a few mL of 8 M HNO_3 , transferred to a small beaker, evaporated to near dryness, and dissolved in a minimum volume of feed solution (5 to 10 mL).

8.4 Preconcentration Method 4 - Calcium Carbonate Precipitation

This method or some variation can be used for most waters. Recovery is not quantitative, but should exceed 70%.

- 8.4.1 An appropriately sized aliquot should be measured and transferred to a beaker.
- 8.4.2 A known amount (e.g., 1.00 mL) of Sr carrier and/or of ^{85}Sr is added.

- 8.4.3 Calcium carrier is added while stirring (100 mg Ca/L of sample).
- 8.4.4 The solution is neutralized to pH 10 with 6 M NaOH while stirring.
- 8.4.5 Calcium carbonate is formed by adding 200 mL of 1.5 M Na₂CO₃ per 1 L of sample while stirring.
- 8.4.6 The precipitate is collected by settling and/or centrifugation.
- 8.4.7 The precipitate is dissolved in a few mL of 8 M HNO₃, transferred to a small beaker, evaporated to near dryness, and dissolved in a minimum volume of feed solution (5 to 10 mL).

8.5 Strontium Purification Procedure

This procedure uses the solution from one of the pre-concentration options as a starting material and produces a solution from which a counting source is made.

- 8.5.1 A Sr*Spec[®] column is prepared by removing the bottom plug and the cap and pressing the top frit snugly down to the resin surface using forceps (or glass rod). The water is drained out, and the column is conditioned with 5 mL of 8 M HNO₃. The solutions are drained by gravity flow.
- 8.5.2 The sample solution is transferred to the reservoir of the column using a plastic transfer pipet. Ideally, the volume of sample feed should be less than 10 mL. Larger volumes can be used (up to about 30 mL), but at the risk of reduced chemical recoveries. The column feed solution should be allowed to drain completely before proceeding.
- 8.5.3 The sample container is rinsed with 3 mL of 8 M HNO₃, which is then added to the column.
- 8.5.4 The column is rinsed three times with 3 mL portions of 8 M HNO₃ (each solution is allowed to pass completely through before adding the next; the column reservoir is rinsed well with each addition).
- 8.5.5 The end time of the last rinse is recorded to the nearest 15 min as the start of ⁹⁰Y ingrowth.
- 8.5.6 The Sr is eluted with 10 mL of 0.05 M HNO₃ into a beaker or scintillation vial. Chemical recovery is measured on this fraction by either a) evaporating and weighing it, b) gamma counting the vial for ⁸⁵Sr, or c) removing a small aliquot,

diluting it to an appropriate volume, and measuring stable Sr by instrumental means.

The spent column can be saved and reused for the same sample if the counting option chosen involves later isolation and counting of ^{90}Y . If interferences from ^{210}Pb are possible, the Pb can be removed by passing 10 mL of 0.1 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ through the column before reuse.

8.6 Preparation of Proportional Counter Source

A source prepared by this method can be used to measure gravimetric chemical recovery and can be counted on any beta proportional counter. Reproducibility of counting geometry is $\pm 1\%$ if a dish with tapered sides is used. If instrumental analysis of stable Sr is used for monitoring chemical yield, samples do not need to be weighed.

8.6.1 A clean counting dish is weighed to the nearest tenth of a milligram, and the tare weight is recorded.

8.6.2 The counting dish is placed in the hood under a heat lamp.

8.6.3 The Sr eluate is evaporated onto the dish by adding small portions (2 to 3 mL) to the dish and allowing each portion to evaporate to near dryness between additions.

8.6.4 The dish is cooled and reweighed after all of the solution has evaporated. The $\text{Sr}(\text{NO}_3)_2$ forms an easily weighed, nonhygroscopic solid that can be weighed to 0.1 mg.

8.6.5 The net residue weight is calculated by subtracting the tare weight of the counting dish and the mass of extractant bleed (0.3 mg is the weight of crown ether in 10 mL of eluate) from the weight of the dish plus residue.

8.6.6 The chemical recovery is calculated by dividing the net residue weight by the potential $\text{Sr}(\text{NO}_3)_2$ in the sample (normally 10.0 mg from the carrier plus 2.42 times the mg of ambient Sr in the sample).

8.7 Preparation of Liquid Scintillation Counter Source

A source prepared by this method can be used to measure gravimetric chemical recovery and can be counted on any liquid scintillation counter. If instrumental analysis of stable Sr is used for monitoring chemical yield, samples do not need to be weighed.

- 8.7.1 The sample should be collected in a weighed glass liquid-scintillation vial.
- 8.7.2 The vial is evaporated to dryness on a hotplate under a heat lamp.
- 8.7.3 The vial is cooled and reweighed. The $\text{Sr}(\text{NO}_3)_2$ forms an easily weighed, nonhygroscopic solid that can be weighed to 0.1 mg.
- 8.7.4 The net residue weight is calculated by subtracting the tare weight of the vial and the mass of extractant "bleed" (0.3 mg is the weight of crown ether in 10 mL of eluate) from the weight of the vial plus residue.
- 8.7.5 The chemical recovery is calculated by dividing the net residue weight by the potential $\text{Sr}(\text{NO}_3)_2$ in the sample (normally 10.0 mg from the carrier plus 2.42 times the mg of ambient Sr in the sample).
- 8.7.6 One milliliter of water is added to the vial, the residue is dissolved, and scintillation cocktail is added.

8.8 Preparation of Cerenkov Counter Source

- 8.8.1 The vial containing the column strip solution can be used directly as the Cerenkov counting vial.

8.9 Preparation of Pure ^{90}Sr and Pure ^{90}Y for Counter Calibration Sources

- 8.9.1 An appropriate volume of calibrated ^{90}Sr standard solution should be measured into a small beaker, an appropriate amount of Sr carrier should be added {e.g., 1.00 mL, 10 mg $\text{Sr}(\text{NO}_3)_2$ }, and the solution should be evaporated to dryness. The solution should be old enough so that the ^{90}Y is in radioactive equilibrium with its ^{90}Sr parent.
- 8.9.2 The residue is dissolved in 3 mL of 2 M HNO_3 .
- 8.9.3 A Sr•Spec[®] column is prepared as above. It should be conditioned for use by passing 3 mL of 2 M HNO_3 .
- 8.9.4 The dissolved residue is transferred to the column reservoir and the solution is allowed to drain completely. The feedstock and subsequent rinses should be retained.

- 8.9.4 The original beaker is rinsed twice more with 3 mL portions of 2 M HNO_3 , adding each to the column and allowing it to drain completely before adding the next.
- 8.9.5 The combined feed and rinses contain the ^{90}Y from the original standard solution. A counting source can be made from this solution by any appropriate method, e.g., evaporation onto a planchet (with or without the addition of Sr carrier) to produce a source for a proportional counter.
- 8.9.6 The ^{90}Sr is eluted from the column with 10 mL of 0.05 M HNO_3 . A counting source can be made from this solution by any appropriate method, e.g., evaporation onto a planchet to produce a source for a proportional counter.

8.10 Suggested Counting Options

Detailed counting protocols are beyond the scope of this method. The type of counting source made, the type of counter used, and the counting times and frequencies will be dictated by the data quality objectives. Only general outlines will be discussed. Of course, appropriate corrections must be made for radioactive ingrowth and decay. Options involving more than one count will generate two or more simultaneous equations that must be solved algebraically or by the method of least squares.

- 8.10.1 If only ^{90}Sr analysis is required, the Sr eluate can be evaporated to dryness and then saved to allow ^{90}Y ingrowth. After sufficient ingrowth time (e.g., one week) the residue is redissolved, and ^{90}Y is purified as outlined in section 8.9 and counted.

This option can give very good detection limits and is independent of the presence of ^{89}Sr . The column used for the original Sr purification can be reused for this step if it is reconditioned by passing 10 mL of 0.05 M HNO_3 and then 3 mL of 2 M HNO_3 through it just before reuse.

- 8.10.2 A scintillation counting source can be made and counted on a scintillation spectrometer. By setting energy windows judiciously, ^{89}Sr and ^{90}Sr can be determined simultaneously using a single count immediately after purification.

This option has relatively poorer detection limits because of the generally higher backgrounds associated with liquid scintillation counters, but is adequate for many needs and gives very quick results. Measuring small amounts of ^{90}Sr in the presence of large amounts of ^{89}Sr is difficult because of spectral overlap.

- 8.10.3 A proportional counter source can be made and counted on a low background beta proportional counter. If ^{89}Sr is known to be absent, a single count is adequate to measure ^{90}Sr . If the presence of ^{89}Sr cannot be excluded, the first count is the total of ^{89}Sr and ^{90}Sr , and the source must be recounted after a few days (and preferably several times over the course of a few weeks) and the ingrowth of ^{90}Y and decay of ^{89}Sr fitted mathematically.

This option can give very good detection limits. As in 8.10.2, measuring small amounts of ^{90}Sr in the presence of large amounts of ^{89}Sr is difficult, this time because of the large counting interference from ^{89}Sr . If a more precise measure of ^{90}Sr is needed, the residue on the plate can be redissolved and the ^{90}Y isolated and counted as in 8.10.1.

- 8.10.4 The eluate can be counted in a Cerenkov counter shortly after purification (to measure ^{89}Sr with little interference from ^{90}Sr). The eluate can then be evaporated and saved to allow ingrowth of ^{90}Y . The ^{90}Y is isolated as in 8.10.1 and counted in the Cerenkov counter with no interference from ^{89}Sr . Alternately, after the initial count, the column effluent can be recounted one or more times during the ingrowth of ^{90}Y to allow calculation of the ^{90}Sr .

This option gives somewhat poorer detection limits because of the relatively higher backgrounds associated with Cerenkov counting. It has the advantages of being fast and has virtually no counting interference between ^{89}Sr and ^{90}Sr , even at extreme ratios.

9.0 Calculations

Calculations are beyond the scope of this purification procedure and will be dictated by the counting protocol used.

10.0 Quality Control

- 10.1 A method blank should be run with each sample set.
- 10.2 Precision and bias are determined using duplicate samples and matrix spikes.

11.0 Method Performance

- 11.1 Chemical yields are typically greater than 95% without preconcentration, greater than 90% with preconcentration by evaporation or cation exchange, and greater than 70% with preconcentration by coprecipitation (limited by precipitation efficiency).

- 11.2 Separation from all expected interferences is greater than 99%, much greater for most elements. If greater separation is needed, the column rinse volume can be increased (at the risk of lowered Sr recovery) or the column eluate can be evaporated, redissolved, and reprocessed through a second column (or a second time through the same reconditioned column).
- 11.3 Figure 1 summarizes the acid dependency of k' for alkalis, alkaline earths, actinides, and other selected ions on Sr•Spec[®] resin.
- 11.4 Table 1 indicates the separation efficiencies obtainable with the Sr•Spec[®] resin.

12.0 Reference

Horowitz, E. P., R. Chiarizia, and M. L. Dietz. 1992. "A Novel Strontium-Selective Extraction Chromatographic Resin." *Solvent Extr. and Ion Exch.*, 10(2), pp. 313-336, 1992.

13.0 For More Information

Dietz, M. L., E. P. Horwitz, D. M. Nelson, and M. A. Wahlgren. 1991. "An Improved Method for the Determination of ⁸⁹Sr and ⁹⁰Sr in Urine." *Health Phys.*, Vol. 61, No. 6, pp. 871-877.

Nelson, D. M., M. A. Wahlgren, E. P. Horwitz, M. K. Dietz, and D. E. Fisher. 1990. "Introduction of a Novel Method for Measuring ⁹⁰Sr and ⁸⁹Sr in Urine," in Proceedings of the 36th Annual Conference on Bioassay, Analytical, and Environmental Radiochemistry. Oak Ridge, Tennessee.

Figure 1. Acid Dependency of k' for Various Ions at 23-25°C Sr•Spec® (Horwitz et al. 1992).

Table 1. Sr-Spec® Elemental Selectivity

Element	Percent of Elements Eluting ^(a) by No. of Free Column Volumes							0.5 M HNO ₃	0.1 M H ₂ SO ₄
	3 M HNO ₃							30-40	40-50
	1-5	5-10	10-15	15-20	20-25	25-30			
Li	100	—	—	—	—	—	—	—	—
Na	100	—	—	—	—	—	—	—	—
Mg	100	—	—	—	—	—	—	—	—
K	65.8	35.9	—	—	—	—	—	—	—
Ca	98.7	—	1.0	—	—	—	—	—	—
Mn	100	<0.1	—	—	—	—	—	—	—
Fe	100	0.6	0.2	0.4	—	—	—	—	—
Co	99.9	—	—	—	—	—	—	—	—
Ni	100	—	—	—	—	—	—	—	—
Cu	100	0.2	—	—	—	—	—	—	—
Zn	100	0.2	—	—	—	—	—	—	—
Y	98.5	0.1	—	—	—	—	—	—	—
Zr	91.2	0.4	—	—	—	—	—	—	—
Ag	15	87.6	2.2	—	—	—	—	—	—
Cd	100	0.1	—	—	—	—	—	—	—
Ba	<0.4	<0.4	52.9	41.6	5.9	0.7	—	—	—
Hg	(6.0) ^(b)	(5.6)	18.8	45.3	19.6	14.1	(6.9)	—	—
Pb	0.8	—	—	—	—	—	—	—	32.8

Feed: 3 M HNO₃ - 0.1 M oxalic acid containing indicated elements (oxalic acid added to improve Zr solubility).

Notes:

- (a) Because of uncertainties inherent in the ICP-AES technique used for quantitation, percentages for a given element may not total 100%.
- (b) Parentheses indicate results having an uncertainty of greater than $\pm 5\%$.

RP501^(a), Rev. 1**Determination of Total Radioactive Strontium in High-Level Samples using Extraction Chromatography****1.0 Scope and Application**

This procedure is used to determine the total radioactive strontium (^{89}Sr and ^{90}Sr in combination or individually) in aqueous samples of both process and nuclear waste. It is intended for low-volume (<20 mL), high-level samples {typically >3.7 Bq/L (100 pCi/L)}. To perform this measurement, a separation and a purification of the Sr are necessary to remove radionuclides (specifically ^{90}Y) that interfere with the subsequent beta counting. Typically, large amounts of inactive substances are also present and must be removed. This method applies extraction chromatography using an Eichrom Sr-specific column (Sr•Spec[®]) that absorbs Sr at high-acid concentrations, but elutes it under low-acid conditions. The Sr•Spec[®] can be obtained as a pre-packed column consisting of an extractant, bis-t-butyl-cis-dicyclohexano-18-crown-6, dissolved in 1-octanol and supported on an inert substrate (Amberlite). The column's high selectivity for Sr is not affected by the large concentrations of other metal ions, such as Ca, Al, and Fe, which may be present in samples. Samples prepared by this method may be analyzed by either gas-flow proportional counting or liquid-scintillation counting for radioactive Sr.

2.0 Summary of Method

Two methods of analyses may be followed depending on whether ^{89}Sr and ^{90}Sr are to be determined together (total radioactive strontium) or separately. The sample preparation (Sr purification) is identical for both methods; however, the counting requirements and calculations differ.

2.1 Total Radioactive Strontium

- 2.1.1 The pre-packed column is pre-conditioned by passing a high-acid solution through it.
- 2.1.2 The sample is "spiked" with a known amount of ^{85}Sr {electron capture (EC) gamma emitter} for determining percent recovery.
- 2.1.3 A sample aliquot, the Sr content of which will not exceed the working capacity of the column, is loaded on the column in a small amount of high-acid solution

(a) This method was supplied by April Swafford Meeks and John Keller (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

followed by a larger volume “wash” of high-acid solution. The eluent is discarded.

- 2.1.4 The Sr is stripped from the column with dilute acid. The eluent can then be prepared for beta counting to determine total radioactive Sr activity and for gamma spectroscopy to measure ^{85}Sr activity.
- 2.1.5 Strontium recovery is based upon the measurement of ^{85}Sr by an independent method of detection, gamma spectrometry. The ^{85}Sr activity is subtracted from the total beta activity to determine the radioactive Sr in the sample.

2.2 Strontium-89 and Strontium-90 Determined Individually

- 2.2.1 A pre-packed column is pre-conditioned by passing a high-acid solution through it.
- 2.2.2 A sample aliquot that will not exceed the working capacity of the column is loaded on the column in a small amount of high-acid solution followed by a larger volume “wash” of high-acid solution. The eluent is discarded.
- 2.2.3 A second aliquot is spiked with a known amount of ^{85}Sr (EC, gamma emitter) and loaded on a separate prepared column using the same method as discussed in 2.2.2. This is used to determine recovery of Sr while accounting for matrix effects from the sample. {Note: ^{85}Sr or ^{90}Sr (beta emitter) may be used to determine Sr recovery; however, ^{85}Sr allows for this determination to be made using gamma spectrometry, an independent method of detection.}
- 2.2.4 The Sr is stripped from the columns with dilute acid. The unspiked sample eluent can then be prepared for beta counting by liquid scintillation or gas-flow proportional counting to determine ^{90}Sr activity and ^{89}Sr activity (if present). The spiked sample eluent is counted by gamma spectrometry for ^{85}Sr recovery determination.
- 2.2.5 Total radioactive Sr may be determined after one beta count and after applying the recovery factor. However, if ^{89}Sr is to be determined individually, a second count will need to be obtained after a 2- to 4-week waiting period to determine ^{90}Y ingrowth.

3.0 Interferences

- 3.1 To achieve efficient separation, the sample aliquot should not exceed the working capacity (20% loading capacity) of the column. A useful range for Sr loading is 2 to 4 mg, based on literature data (Horwitz et al. 1990).

- 3.2 According to literature (Horwitz et al. 1990), breakthrough of Sr can occur after 45 free-column volumes (FCVs) (1 FCV = 1.3 mL/column) pass through the column. To prevent breakthrough, the total volume (sum of sample loading plus wash) passed through the column should be maintained below 80% of the breakthrough volume.
- 3.3 The use of HCl is avoided here due to extensive use of stainless steel in radiochemical laboratories and glovebox fabrication. Only HNO₃ is used throughout this procedure.
- 3.4 Yttrium quickly grows into the separated ⁹⁰Sr. Therefore, the sample should be counted within 2 to 3 h after the separation to ensure accurate activity results of ⁸⁹Sr and ⁹⁰Sr.
- 3.5 The presence of small amounts of the crown-ether extractant due to column bleed in the Sr eluent has been observed and could cause luminescence interferences in liquid scintillation counting. To prevent this, it is recommended that the Sr eluent be passed through an Eichrom pre-filter column to remove the extractant. Pre-filters can be obtained from Eichrom Industries Inc., Darien, Illinois, cat. No. PF-C50 or PF-C200.
- 3.6 Cesium is retained up to 1% on the Sr•Spec[®] column and can cause interferences in beta counting when radioisotopes of this element are present in large excess as compared to radioactive Sr. A method for removing this interference is the precipitation of Cs by adding ammonium phosphomolybdate, which is described in *Standard Methods for the Examination of Water and Wastewater*, Edition 17, procedure 7500-Cs Radioactive Cesium (Clesceri et al. 1989). A quick alternative for Cs removal would be the use of a second Sr•Spec[®] column. The Sr eluent obtained from the first Sr•Spec[®] application could be acidified and loaded onto a second Sr•Spec[®] column.
- 3.7 Plutonium has been observed to retain up to 85% on the Sr•Spec[®] column under high-acid conditions, which causes interferences in subsequent beta counting. One method to remove this interference is by passing the sample solution through an Eichrom TRU•Spec[®] (transuranic specific) column at 2 to 6 M HNO₃ placed in series above the Sr•Spec[®] column. Plutonium is absorbed onto the TRU•Spec[®] column; the Sr fraction elutes through TRU•Spec[®] and loads onto the Sr•Spec[®]. The TRU•Spec[®] column is removed before Sr elution. (A description of Tru•Spec[®] is presented in Method MP110R.) Other methods, such as Fe(OH)₃ precipitation, may be useful as well.
- 3.8 Strontium-85 is an electron-capture gamma emitter that can also be detected by beta counting. In this method, a ⁸⁵Sr spike may be added to a sample aliquot and processed in parallel to an unspiked sample aliquot. This would allow for measurement of the unspiked sample, free of beta interference from ⁸⁵Sr, and yet permit the determination of Sr recovery by gamma spectrometry of ⁸⁵Sr from the spiked sample matrix. If ⁸⁵Sr is not available for use, a ⁹⁰Sr standard may be used as the spike. This would limit analysis to beta detection only; therefore, the counting results of the unspiked sample would need to

be subtracted from results of the spiked sample to allow for the determination of the spike recovery and ^{90}Sr in the sample.

- 3.9 An excess of radioactive K may also cause interference in subsequent beta counting due to K retention on the Sr•Spec[®] column. This interference may be removed by use of a second Sr•Spec[®] column as described in 3.6.

4.0 Safety

This method requires the use of acid solutions and radioactive materials. All necessary safety precautions, such as appropriate clothing, ventilation and containment requirements, and local applicable standards for handling radioactive materials should be followed.

5.0 Apparatus and Materials

- Eichrom Sr•Spec[®] pre-packed column, Eichrom Industries Inc., Darien, Illinois, cat. No. TR-C50 or TR-C200, or equivalent
- Column rack
- Stainless steel planchets
- Scintillation vials
- Liquid scintillation counter or gas-flow proportional beta counters
- Gamma detector, such as high-purity (HP) Ge, Ge(Li), or Na(I)

6.0 Reagents

- National Institute for Standards and Technology (NIST) traceable ^{85}Sr standardized solution, ^{90}Sr standardized solution, and ^{89}Sr standardized solution
- American Society for Testing and Materials (ASTM) type II water (ASTM D1193): Water should be monitored for impurities. Water that exceeds the purity of ASTM Type II can be substituted.
- Nitric acid, 4 M and 0.05 M
- Scintillation cocktail, such as Ultima-Gold[™] or equivalent

7.0 Sample Collection, Preservation, and Handling

It is recommended that samples be preserved with acid below pH 2 at the time of collection.

8.0 Procedure

8.1 Strontium Purification Procedure. The volumes used in this procedure are for the Eichrom pre-packed columns that have a bed volume of approximately 2 mL.

8.1.1 Total Radioactive Strontium

8.1.1.1 The tip and the cap of the Sr•Spec® column are removed. The frit is lowered to just above the top of the resin. The column is conditioned by passing 15 to 20 mL of 4 M HNO₃ through the column.

8.1.1.2 A loading solution is prepared by pipetting an aliquot of sample and an aliquot of ⁸⁵Sr standard (with an activity of the same order of magnitude as the sample) to a small beaker, being sure to maintain a total Sr concentration within the working capacity of the column (see 3.1). This solution should be adjusted to approximately 4 M HNO₃.

8.1.1.3 The loading solution is added to the pre-conditioned column. The column is washed with at least 20 mL of 4 M HNO₃, being sure to maintain a total volume through the column of less than 50 mL. The eluent is discarded.

8.1.1.4 The Sr is stripped from the column with at least 20 mL 0.05 M HNO₃. All of the eluent is collected and adjusted to a known volume.

8.1.1.5 The sample may now be analyzed by beta counting for total beta activity and by gamma spectrometry for ⁸⁵Sr determination.

8.1.2 Strontium-89 and Strontium-90 Determined Individually

8.1.2.1 The tip and cap of the Sr•Spec® column are removed. The frit is lowered to just above the top of the resin. The column is conditioned by passing 15 to 20 mL of 4 M HNO₃ through the column.

- 8.1.2.2 Two loading solutions are prepared in separate beakers. An appropriate aliquot^(a) of the sample is added to each beaker. Also, an appropriate^(a) known amount (spike) of ^{85}Sr standard with comparable activity to the sample is added to one of the beakers. Each solution is adjusted to 4 M HNO_3 .
- 8.1.2.3 Each solution is loaded onto separate pre-conditioned columns. A wash of at least 20 mL of 4 M HNO_3 on each column should then follow, being sure to maintain a total volume of less than 50 mL. The eluents are discarded.
- 8.1.2.4 The Sr is then stripped from the columns with at least 20 mL 0.05 M HNO_3 . The eluent is collected from each column and adjusted to a known volume.
- 8.1.2.5 The unspiked sample eluent is analyzed by beta counting for total beta activity according to 8.2.1 or 8.2.2. The spiked solution is analyzed by gamma spectrometry according to 8.2.3.

8.2 Counting Procedure. To determine total radioactive Sr or ^{89}Sr and ^{90}Sr individually, gas-flow proportional or beta liquid scintillation counting may be used. Both types of determinations require a beta count immediately following the Sr purification, along with ^{90}Sr detector calibrations. The determination of ^{89}Sr and ^{90}Sr individually also requires a second count after ^{90}Y ingrowth and detector calibrations for ^{89}Sr and ^{90}Y .

8.2.1 Gas Proportional Counting

- 8.2.1.1 An appropriate aliquot (enough to produce appropriate counting statistics in a reasonable amount of time, <1 h) of the eluent is pipetted evenly onto a stainless-steel planchet.
- 8.2.1.2 The sample should be counted within 3 h after completing step 8.1.1.4 or 8.1.2.4 to obtain a total beta count rate and a background count rate. If the 3-h limit is exceeded, more error will be introduced in the final determination due to ^{90}Y ingrowth.
- 8.2.1.3 For determination of ^{89}Sr and ^{90}Sr individually, the sample planchet should be saved and recounted after waiting 2 to 4 weeks. This will allow ingrowth of ^{90}Y .

(a) An appropriate aliquot would meet the restrictions discussed in 3.1.

8.2.2 Beta Liquid Scintillation Counting

An appropriate aliquot (enough to produce appropriate counting statistics in a reasonable amount of time, <1 h) of the eluent is pipetted into a scintillation vial containing a typical volume (e.g., 10 mL) of scintillation cocktail. This volume should be consistent with the standard volumes used for efficiency determination (sections 8.3 and 8.4). A total beta count rate and a background count rate are obtained. For individual determination of ^{89}Sr and ^{90}Sr , the vial is saved and recounted after waiting 2 to 4 weeks to allow for ^{90}Y ingrowth.

8.2.3 Gamma Spectrometry Counting

An appropriate aliquot (enough to produce appropriate counting statistics in a reasonable count time) of the eluent is pipetted into a container that is calibrated for ^{85}Sr efficiency for the particular detector to be used (see 8.3). The ^{85}Sr is counted and a net gamma count rate is obtained.

8.3 Detector Calibration for Strontium-85

8.3.1 A counter efficiency for ^{85}Sr should be determined for beta counting and/or for gamma spectrometry (depending on the application) by counting a known amount of NIST traceable ^{85}Sr standard on each detector for a time period to obtain reasonable counting statistics. The geometry used for determining efficiency should be consistent with the sample geometry.

8.3.2 The background count rate is subtracted from the total count rate to obtain a net count rate for ^{85}Sr .

8.3.3 The net ^{85}Sr count rate is divided by the disintegration rate of the standard to obtain a counter efficiency for this nuclide.

8.4 Detector Calibration for Strontium-89

8.4.1 A known amount of an NIST traceable ^{89}Sr standard is counted on the beta detector in a geometry consistent with the sample geometry for a time period to allow at least 10,000 counts.

8.4.2 The background count rate is subtracted from the total count rate to obtain a net count rate of ^{89}Sr .

8.4.3 The net count rate is divided by the known disintegration rate of the standard to obtain a counter efficiency for ^{89}Sr .

8.5 Detector Calibration for Yttrium-90

- 8.5.1 A known amount of ^{90}Sr standard (in equilibrium with ^{90}Y) is processed according to steps 8.1.1.1 to 8.1.1.2. If only a ^{90}Y detector calibration is desired, the ^{85}Sr spike for recovery is not necessary. If a ^{90}Sr detector calibration is desired, the ^{85}Sr spike will need to be applied as described in 8.1.1.2.
- 8.5.2 The instructions for washing the column should be followed as stated in 8.1.1.3. However, the eluent should not be discarded. This ^{90}Y eluent should be adjusted to a known volume. If also performing a ^{90}Sr detector calibration, step 8.1.1.4 should be completed to obtain the Sr eluents.
- 8.5.3 The ^{90}Y eluent is counted on a beta detector, and a net count rate is obtained by subtracting the background count rate from the total count rate.
- 8.5.4 The net ^{90}Y count rate is divided by the known disintegration rate of the ^{90}Sr standard to obtain a counter efficiency for ^{90}Y .
- 8.5.5 For a ^{90}Sr detector calibration, step 8.6.2 should be followed using the ^{90}Sr eluents obtained from 8.5.2.

8.6 Detector Calibration for Strontium-90. Due to short half-life of ^{89}Sr (50.52 d), significant levels of this nuclide are rarely detected in process and nuclear waste samples. The radioactive Sr in the sample is primarily ^{90}Sr . Therefore, for a total radioactive Sr determination, the detector calibration for ^{90}Sr is used.

- 8.6.1 A known amount of ^{90}Sr is processed according to steps 8.1.1.1 through 8.1.1.4.
- 8.6.2 The Sr eluent is counted on the beta counter by gamma spectrometry. The background count rate is subtracted from the total beta count rate to obtain a net count rate.
- 8.6.3 The Sr eluent is also counted to determine ^{85}Sr recovery. The counts due to ^{85}Sr must also be subtracted using the beta efficiency for ^{85}Sr as discussed in 8.3 and the percent recovery.
- 8.6.4 The net ^{90}Sr count rate is divided by the ^{85}Sr recovery and by the known disintegration rate of the ^{90}Sr standard to obtain a counter efficiency for this nuclide.

9.0 Calculations

9.1 Calculation Terms

- R = measured activity of ^{85}Sr divided by the theoretical 100% recovery activity of the spike
 A₁ = activity of ^{90}Sr with a decay constant of λ_1
 A₂ = activity of ^{89}Sr with a decay constant of λ_2
 A₃ = activity of ^{90}Y with a decay constant of λ_3
 C₁ = initial net count rate measured after separation of ^{90}Y (^{90}Sr count rate)
 C₂ = final net count rate measured after ingrowth of ^{90}Y
 C₃ = ^{85}Sr gamma net count rate
 C₄ = ^{85}Sr beta net count rate
 C₅ = ^{90}Sr plus ^{85}Sr net beta count rate
 E₁ = beta counting efficiency for ^{90}Sr
 E₂ = beta counting efficiency for ^{89}Sr
 E₃ = beta counting efficiency for ^{90}Y
 E₄ = gamma counter efficiency for ^{85}Sr
 E₅ = beta counting efficiency for ^{85}Sr
 t = time (h) between the measurement C₁ and C₂
 K = constant to convert from disintegration rate to reported activity units

9.2 Recovery Calculation, R

Calculation of ^{85}Sr activity measured:

$$A_4 = \frac{C_3 \cdot K}{E_4}$$

Calculation of ^{85}Sr recovery:

$$R = \frac{A_4}{\text{theoretical activity}} \times 100\%$$

9.3 Total Radioactive Sr Activity in Sample

Calculation of ^{85}Sr beta count rate, C_4

$$C_4 = \frac{C_3 \cdot E_5}{E_4} \cdot \frac{(\text{aliquot size of Sr eluent counted by beta})}{(\text{aliquot size of Sr eluent counted by gamma})} \quad (1)$$

Calculation of radioactive Sr, A_1 in sample

$$C_1 = C_5 - C_4 \quad (2)$$

$$A_1 = \frac{C_1 \cdot K}{E_1 \cdot R} \quad (3)$$

9.4 Strontium-89 and Strontium-90 Determined Individually. Calculations of the activity for both ^{89}Sr and ^{90}Sr requires measuring the sample count rate two times, separated sufficiently for ingrowth of ^{90}Y . The first count rate (C_1) should be determined as soon as possible after the ^{90}Y is separated (ideally less than 2 h), to minimize error due to ingrowth of the ^{90}Y . For the first few hours after separation, the ingrowth rate is about 1% per hour.

$$C_1 = A_1 E_1 + A_2 E_2 \quad (4)$$

$$C_2 = A_1 E_1 e^{-\lambda_1 t} + A_2 E_2 e^{-\lambda_2 t} + A_3 E_3 \quad (5)$$

$$A_3 = \frac{\lambda_3}{\lambda_3 - \lambda_1} A_1 (e^{-\lambda_1 t} - e^{-\lambda_3 t}) \quad (6)$$

since A_3 is a function of A_1 , then

$$C_2 = A_1 \left[E_1 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + \left(\frac{\lambda_3}{\lambda_3 - \lambda_1} \right) E_3 (e^{-\lambda_1 t} - e^{-\lambda_3 t}) \right] + C_1 e^{-\lambda_2 t} \quad (7)$$

With equation 4 and equation 7, we have two equations and two unknowns; then we solve for A_1 and A_2 as follows:

$$A_1 = \frac{C_2 - C_1 e^{-\lambda_2 t}}{E_1 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + \left(\frac{\lambda_3}{\lambda_3 - \lambda_1} \right) E_3 (e^{-\lambda_1 t} - e^{-\lambda_3 t})} \quad (8)$$

$$A_2 = \frac{C_1 - A_1 E_1}{E_2} \quad (9)$$

Frequently, equation 7 will be simplified by making the assumptions that

$$e^{-\lambda_1 t} \approx 1, \text{ and } \frac{\lambda_3}{\lambda_3 - \lambda_1} \approx 1 \quad (10)$$

However, these assumptions introduce a small negative bias to the ^{90}Sr activity and a small positive bias to the ^{89}Sr activity. The bias has a magnitude of several percent and increases with the ^{90}Y ingrowth time (t). With the use of personal computers and programmable calculators, no good reason exists to use the assumptions and introduce unnecessary error.

To account for recovery losses, each activity result, (A_x), should be divided by R, the recovery value of the ^{85}Sr standard.

10.0 Quality Control

- 10.1 A quality control (QC) protocol sufficient for the needs of a particular sample request should be implemented to include duplicate samples for determining precision and QC standards for measuring bias.
- 10.2 Reagent blank samples consisting of HNO_3 media alone should be applied to the Sr•Spec[®] procedure and used in the instrument calibration for background subtraction. This will account for effects of the Sr•Spec[®] matrix.

11.0 Method Performance

- 11.1 This method was tested in a single laboratory evaluation using ^{85}Sr and ^{90}Sr standards to determine total radioactive Sr. A 0.5-mL aliquot of $^{90}\text{Sr}/^{90}\text{Y}$ with a total beta activity of 4.40×10^4 Bq/mL spiked with 3.88×10^3 Bq ^{85}Sr were applied to the Sr•Spec[®] column following the procedure outlined in this method. This was performed ten times using a high-purity germanium gamma detector and a beta liquid scintillation detector for measurement. Each result is listed in Table 1 along with the average results and relative standard deviations.

11.2 The Cs precipitation method mentioned in section 3.6 was applied to a transuranic process solution containing ¹³⁷Cs and ⁹⁰Sr. The supernate from the precipitation step was then subjected to the procedure for the SrSpec[®] column. Recoveries of the two elements in the SrSpec[®] effluents are listed in Table 2.

Table 1. Recovery Performance				
Sample	⁸⁵ Sr % recovery	⁹⁰ Sr Bq/mL	⁹⁰ Sr Relative % recovery	
1	102	2.04E4	93	
2	100	2.12E4	96	
3	98	2.17E4	99	
4	96	2.13E4	97	
5	92	2.28E4	104	
6	96	2.13E4	97	
7	103	2.05E4	93	
8	102	2.07E4	94	
9	101	2.08E4	95	
10	100	2.04E4	93	
Average mean				99.0
Relative standard deviation				3.50%
				3.51%
				2.11E4
				3.45%

Table 2. SrSpec [®] Effluent Recoveries			
Nuclide	4 M HNO ₃ Effluent % Recovery	0.05 M HNO ₃ Effluent % Recovery	
⁹⁰ Sr	0.0	97.0	
¹³⁷ Cs	1.0	0.1	

11.3

The data presented Table 3 show results obtained from the application of an actual waste sample to the Sr⁹⁰Spec[®] column. The waste-sample matrix consists of a high-pH (12 to 13), high-nitrate concentration, and caustic soluble fission products. This sample had been analyzed by the U.S. Environmental Protection Agency (EPA) Method 905.0 (Radioactive Strontium in Drinking Water) applying appropriate standards to obtain a ⁹⁰Sr reference value. This reference value was 1.75 x 10⁵ Bq/mL ⁹⁰Sr in the waste sample. Table 3 shows the ⁹⁰Sr results obtained from the analysis of this sample four times using the Sr⁹⁰Spec[®] column and the percent recovery based upon the reference value obtained from the EPA Method.

Table 3. Recovery Performance of Actual Waste Sample		
Run	(x 10 ⁵ Bq/mL)	% Recovery
1	1.77	101
2	1.74	99
3	1.75	100
4	1.82	104
Average	1.77	101
Rel. Std. Dev.	2.01%	

11.4

This method was tested in a single laboratory evaluation using ⁸⁵Sr, ⁸⁹Sr, and ⁹⁰Sr standards to determine the accuracy and precision of measuring ⁸⁹Sr and ⁹⁰Sr individually. A solution containing 5.72 x 10³ Bq/mL of ⁸⁹Sr and 5.20 x 10⁴ Bq/mL of ⁹⁰Sr/⁹⁰Y was processed five times according to section 8.1.2 of this procedure with the exception of ⁸⁵Sr internal spike. A ⁸⁵Sr standard was processed twice in parallel to the unspliked sample to determine a Sr recovery factor. Liquid scintillation counting was used to determine beta activity and a high-purity germanium detector was used to measure ⁸⁵Sr. A 14-day waiting period was applied to allow for ⁹⁰Y ingrowth and consequent determination of ⁸⁹Sr and ⁹⁰Sr individually. Table 4 shows the results and relative recoveries of the Sr standards. Part of the inaccuracy and imprecision involved in the ⁸⁹Sr determination may be attributed to the difference in activity magnitude between ⁸⁹Sr and ⁹⁰Sr. However, this magnitude difference is typical in waste samples.

Table 4. Results and Relative Recoveries of the Sr Standards					
Run No.	(Bq/mL)	(Bq/mL)	⁸⁹ Sr	⁹⁰ Sr	% Recovery
1	6.48E+03	2.49E+04	113	96	
2	5.65E+03	2.56E+04	99	98	
3	5.09E+03	2.58E+04	89	99	
4	6.16E+03	2.57E+04	108	99	
5	6.20E+03	2.54E+04	108	98	
Average	5.92E+03	2.55E+04	103	98	
Rel. Std. Dev.	9.3%	1.4%			

12.0 References

Clesceri, L. S., A. E. Greenberg, and R. R. Trussell. 1989. *Standard Methods for the Examination of Water and Wastewater*, 17th Edition. American Public Health Association, Washington, DC.

Horwitz, E. P., M. L. Dietz, and D. E. Fisher. 1990. "Extraction of Strontium from Nitric Acid Solutions Using Dicyclohexano-18-Crown-6 and its Derivatives." *Solvent Extr. Ion Exch.*, Volume 8, Issues 4 and 5.

13.0 Reviewer's Comments and Suggestions

Stable Sr may be used as a tracer with yield determined subsequently by inductively coupled plasma (ICP) optical emission spectroscopy (OES) or atomic absorption spectrometer (AAS) analysis of Sr. The added Sr will need to be appropriate relative to the working capacity of the SrSpec® column. The stable Sr present in the sample matrix may need to be determined to accurately quantify Sr recovery.

RP510^(a)**Determination of Strontium-90 in Dissolved Environmental Samples Using a Chelating Resin****1.0 Scope and Application**

This procedure is for the determination of ^{90}Sr , via its daughter ^{90}Y , in environmental (aqueous, soil, vegetation, and filter) samples. Aqueous samples should be preserved in an acidic media (HCl or HNO_3) before using this method. Soil, vegetation, and filter samples need to be dissolved and/or leached before using this method. The minimal detectable activity (MDA) for ^{90}Sr in water, given a 1-L sample, 97% yield, and a 50-min count time, is 0.03 Bq/L (0.7 pCi/L). The MDA for vegetation and soil samples, given a 10-g sample, 97% yield, and a 50 min count time is 2.7 Bq/kg (73 pCi/kg). The MDA for filters is 0.03 Bq/sample (0.7 pCi/sample).

2.0 Summary

Strontium-85 tracer is added to the sample before dissolving the sample and is used to monitor the Sr yield. The Sr fraction is then gathered via a carbonate precipitate. Yttrium and rare earth hydroxides are removed with an iron hydroxide scavenge. Stable Y carrier is added to monitor the Y yield. After a suitable ingrowth period (5 to 21 days), the solution pH is adjusted for optimum Y retention on a Chelex[®] 100 column. After retention of the Y on Chelex[®] 100, interferences are washed through with 1 M ammonium acetate. Yttrium is selectively removed in 1 M HNO_3 . Yttrium oxalate is precipitated, mounted, and counted using a low-background alpha-beta gas proportional counter. The Y activity is an indirect measure of the ^{90}Sr activity originally present.

3.0 Interferences

The principle interferences for this method are the rare earths. If it is expected that a significant rare-earth contamination exists, two iron-hydroxide scavenges should be performed as well as a wash of the precipitate.

4.0 Safety

The following precautions should be considered before working with this procedure.

Acetic Acid. Solutions more concentrated than 8 M acetic acid (HOAc) should be handled in an exhaust hood or in a manner to avoid inhaling the vapors. The odor of vinegar provides adequate warning for a prompt voluntary withdrawal from excessive exposure. Contact with skin results in a burning sensation.

(a) This method was supplied by Mark W. Huntley (Westinghouse Idaho Nuclear Co., Idaho Falls, Idaho).

Ammonium Hydroxide. Solutions more concentrated than 4 M NH_4OH should be handled in an exhaust hood or in a manner to avoid inhaling ammonia. The odor of ammonia provides adequate warning for a prompt voluntary withdrawal from excessive exposure. Contact with skin results in a burning sensation.

Nitric Acid. Solutions more concentrated than 6 M HNO_3 should be handled in an exhaust hood or in a manner to avoid inhaling NO_x . Nitric acid spontaneously evolves vapors of various NO_x compounds that can be toxic. Contact with the skin results in a burning sensation and a brown discoloration of the skin.

Oxalic Acid. This chemical should be handled in a manner to avoid inhaling or ingesting the dried material or ingesting the solution. Oxalic acid is very toxic and requires wearing latex or plastic gloves to avoid skin contact.

Sodium Hydroxide. Solutions more concentrated than 4 M NaOH should be handled in an exhaust hood with rubber or plastic gloves. Solutions are slippery to the touch and result in a burning sensation.

5.0 Apparatus

- Centrifuge
- Centrifuge tubes, 50 mL
- Column: 7.5 mm (ID) x 65 mm, fritted one end, Pierce Chemical Co. or equivalent
- Counter, low background alpha-beta gas proportional
- Filter, membrane, 25 mm, Gelman 1.2 micron, Versapor 1200, or equivalent
- Filter, paper, Whatman 42, 25 mm, or equivalent
- Filtering apparatus
- Forceps
- Gamma detector (e.g., NaI 3 in. x 3 in. well detector)
- Parafilm
- pH meter, calibrated with pH 7 buffer or equivalent, or equivalent pH paper
- Pipet, disposable Eppendorf or equivalent

6.0 Reagents

All solutions should be prepared with analytical grade reagents and deionized (DI) or distilled water.

- Acetic acid, 4 M (HOAc)
- Ammonium acetate, 1 M: pH should be adjusted to 6.6 to 6.8 with dilute HOAc or dilute NH_4OH as necessary.
- Ammonium hydroxide, concentrated (conc)
- Chelex[®] 100 resin, 100 to 200 mesh, Na^+ form.
- Iron carrier, 10 mg Fe^{+3} /mL
- Methyl red indicator, 0.02%
- Nitric acid, conc, and 4 M
- Oxalic acid, 5% and 2%
- Sodium carbonate, saturated
- Sodium hydroxide, 50% (12.5 M), and 0.25 M
- Thymol blue, 0.04%
- Strontium carrier, 50 mg Sr/mL as $\text{Sr}(\text{NO}_3)_2$
- ^{85}Sr Comparator: Activity level should be such that 1% counting statistics can be achieved in 5 to 15 min.
- Yttrium carrier, 104.0 mg/mL as $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$

7.0 Sample Collection, Preservation, and Handling

Not applicable

8.0 Procedure

8.1 Concentration of Strontium-90

Before beginning, all samples should already have 50 to 100 mg of Sr carrier and an appropriate amount (to provide adequate counting statistics in a reasonable count time) of ^{85}Sr tracer. Blank samples are prepared identically with real samples; the ^{85}Sr comparitor is prepared with the same activity spike as the samples. Water samples should have been evaporated to approximately 50 mL. Soils, vegetation, and filter samples should be in solution, and made up to approximately 50 mL with 1 M HNO_3 or 1 M HCl .

8.1.1 Approximately 5 mL of saturated Na_2CO_3 are added to the sample to precipitate SrCO_3 .

8.1.2 A sufficient amount of conc NH_4OH is then added to ensure that the sample is basic.

Adding 0.5 mL is usually sufficient. If time permits, the sample is allowed to settle 1 h.

8.1.3 The sample is transferred to a 50-mL centrifuge tube and centrifuged for about 10 min.

Several transfers are made if necessary to concentrate the samples to one test tube each. The supernate solution may be saved for possible further recovery of ^{85}Sr .

8.1.4 If the precipitate is more than 1 in. deep, the precipitate should be dissolved in 3 M HNO_3 , and steps 8.1.1 through 8.1.3 should be repeated.

Caution: The acid should be slowly added to the carbonate precipitate to minimize frothing as CO_2 is given off.

8.1.5 Two to three drops of conc HNO_3 are added to the precipitate.

8.1.6 Sufficient H_2O is added to dissolve the carbonate precipitate (normally 3 to 5 mL).

If all the precipitate will not dissolve, the solution pH should be checked and adjusted with HNO_3 if necessary to below pH 3. If some precipitate still will not dissolve, the sample is centrifuged, the supernate is decanted and saved, and the precipitate is checked for ^{85}Sr activity. If there is <10% of the added ^{85}Sr

activity in the precipitate, it may be discarded. Further action may be necessary to remove ^{85}Sr entrained on an insoluble precipitate.

- 8.1.7 The sample solution should be diluted to make a working volume of approximately 10 mL.
- 8.1.8 Approximately 1 mL of Fe carrier is added to the sample.
- 8.1.9 Sufficient conc NH_4OH is added to precipitate $\text{Fe}(\text{OH})_3$, $\text{Y}(\text{OH})_3$, and rare earth hydroxides.

This step removes most rare-earth hydroxide interferences. If it is expected that significant rare earth contamination exists, as in soils, steps 8.1.8 through 8.1.16 are performed twice.

- 8.1.10 The sample is heated in a hot water bath for approximately 5 min.
- 8.1.11 The sample is centrifuged, while still hot, for approximately 10 min.
- 8.1.12 The supernate is decanted and saved in a clean 50-mL centrifuge tube. The time and date of this separation must be recorded.

This is the start of the ^{90}Y ingrowth.

- 8.1.13 The precipitate is washed with 1 to 2 mL of 3 M NH_4OH .
- 8.1.14 The sample is heated in a hot water bath for approximately 5 min.
- 8.1.15 The sample is centrifuged for approximately 10 min.
- 8.1.16 The wash solution is decanted into the test tube from step 8.1.12.
- 8.1.17 A precisely known amount (approximately 1 mL) of Y carrier is added to the sample.
- 8.1.18 The solution volume is adjusted, either by dilution (with 1 M NH_4OAc , pH=7) or concentration (by evaporation), to that of the ^{85}Sr comparator and gamma counted for ^{85}Sr yield.

A NaI(Tl) detector works well to measure the ^{85}Sr . The count rate of the ^{85}Sr 514 keV gamma rays of the sample is divided by the count rate of the comparator.

- 8.1.19 Approximately 2 to 3 drops of methyl red indicator are added to each tube.

8.1.20 To the blank sample, 3 M NH_4OH is added dropwise to the yellow endpoint of the indicator.

8.1.21 A 4 M HOAc solution is added dropwise to the first red tint.

It is critical that the pH be checked to ensure that the sample is between 6.8 and 7.0; either pH paper (graduated in 0.2 pH increments) or a pH meter may be used. Yttrium will be lost if the sample is more acidic or basic.

8.1.22 The remaining samples are adjusted to the same color as that of the blank.

8.1.23 The sample is set aside for ^{90}Y ingrowth.

Typically, the ^{90}Y ingrowth time is 5 to 21 days.

8.1.24 Once the ^{85}Sr yield is determined, all other decanted supernates may be discarded.

8.2 Resin Preparation

8.2.1 About 100 g of Chelex[®] 100 are added to a 250-mL poly bottle.

8.2.2 The resin is washed with 100 to 200 mL of 3 M NH_4OH .

This replaces the Na^+ sites with NH_4^+ sites via mass effect.

8.2.3 The NH_4OH is collected and passed through the resin at least two more times.

8.2.4 The resin is washed with 100 mL of water. The pH of the final water rinse should be between pH 7 and 8.

8.2.5 The resin is slurried with water into a suitable container for dispensing into columns.

8.3 Column Preparation

8.3.1 A sufficient amount of Chelex[®] 100 resin is slurried into a column to make a resin bed that is 65 mm in height. An additional funnel is attached to the column.

8.3.2 The column is preconditioned by washing with 10 to 25 mL of 1 M NH_4OAc , pH=7.

- 8.3.3 The pH is checked to ensure that the effluent is between pH 6.8 and 7.2.

If the effluent is not pH 6.8 to 7.2, step 8.3.2 should be repeated.

8.4 Separation of Contaminants from Yttrium-90

- 8.4.1 After a suitable ^{90}Y ingrowth period has elapsed, each sample is loaded onto a Chelex[®] 100 column. The time and date of this separation must be recorded.

This is the end of the ^{90}Y ingrowth.

- 8.4.2 After the solution has completely passed through, the column is washed with 45 to 55 mL of 1 M NH_4OAc , pH=7. The wash is discarded.

This removes all Sr, Ca, and other contaminants from the Y fraction.

- 8.4.3 After the wash has completely passed through the column, approximately 5 mL of water are loaded on the column. The wash is discarded.

This step is necessary to remove excess acetate salts.

- 8.4.4 The ^{90}Y from each column should be eluted into a clean 50-mL centrifuge tube with 6 to 10 mL of 1 M HNO_3 . The eluted solution should be checked to ensure that it is acidic.

If the pH >2, washing should be continued until the pH $\leq$ 2, to ensure that all Y is eluted.

- 8.4.5 Approximately two to three drops of thymol blue are added to the sample. The solution should be red.

- 8.4.6 Approximately 5 mL of 5% oxalic acid is added to the sample.

Some precipitate might form at this step due to the formation of $\text{Y}(\text{C}_2\text{O}_4)_3$.

- 8.4.7 To the blank, 3 M NH_4OH is added dropwise until the solution is faint pink to yellow, indicating a solution pH of 2.7.

- 8.4.8 After testing the blank sample for proper pH (with pH paper or pH meter), the other samples in the set are adjusted to the same color.

- 8.4.9 The sample is heated in a water bath for approximately 5 min.

- 8.4.10 The tare weight is determined on a Whatman 25-mm filter to ± 0.1 mg, one filter per sample.
- 8.4.11 Each sample is filtered through a tared filter.
- 8.4.12 The centrifuge tube is washed with 2% oxalic acid, and the wash solution is passed through the corresponding filter.
- 8.4.13 After the wash solution has passed completely through, the sides of the filter apparatus are rinsed with 1 to 2 mL of ethanol.

This speeds up the drying process and removes excess water. Care should be taken to not draw too much air through the filter paper, thus minimizing the collection of radon daughters on the filter paper.

- 8.4.14 The filter paper is removed and dried at 40°C for approximately 5.0 min under a heat lamp. Any higher temperature will change the waters of hydration in the weighing form.

An IR lamp positioned approximately 6 1/2 in. above the filter paper has been shown to provide a temperature of ~40°C at the filter-paper surface.

- 8.4.15 After cooling to room temperature, the filter/sample is weighed, and the gravimetric yield is determined.
- 8.4.16 The sample is then counted for a time sufficient to achieve the statistical accuracy desired. The time of sample count is recorded to correct for ^{90}Y decay.

Samples should be counted as soon as possible to minimize the decay correction factor.

9.0 Calculations

9.1 Sample Results

The Sr results are calculated using the following equations:

$$^{90}\text{Sr} = \frac{(C_Y - B_Y) \cdot k \cdot \text{DF}}{R_Y \cdot R_{\text{Sr}} \cdot E_Y \cdot V \cdot Q_2 \cdot (Q_1 - Q_3)}$$

where

^{90}Sr	=	Activity of ^{90}Sr in the sample in the applicable units
C_Y	=	Counts per second for the sample for the Y oxalate
B_Y	=	Counts per second for the blank for the Y oxalate
k	=	Factor to convert the counting results to units required in the reported results
DF	=	Dilution factor corresponding to the relationship between the original sample and the amount of sample counted
R_Y	=	Recovery of the Y oxalate (ratio of the mass of Y oxalate collected on the filter to the expected mass of Y oxalate on the filter)
R_{Sr}	=	Recovery of the Sr based on the ratio of ^{85}Sr in the sample to that of the comparator
E_Y	=	Efficiency of counter for Y oxalate mass on planchet
V	=	Volume of sample prepared for analysis
Q_1	=	Decay correction for Sr decay between start and end of ^{90}Y ingrowth ($= e^{-\lambda_1 t_1}$)
Q_2	=	Decay correction for Y decay between start and end of ^{90}Y ingrowth and counting of ^{90}Y ($e^{-\lambda_2 t_2}$)
Q_3	=	Decay correction for Y decay between start and end of ^{90}Y ingrowth ($= e^{-\lambda_3 t_1}$).

where

λ_1	=	Strontium decay constant (days) $^{-1} = 6.547 \times 10^{-5}$
λ_2	=	Yttrium decay constant (minutes) $^{-1} = 1.805 \times 10^{-4}$
λ_3	=	Yttrium decay constant (days) $^{-1} = 2.60 \times 10^{-1}$
t_1	=	Days elapsed between start and end of ^{90}Y ingrowth
t_2	=	Minutes elapsed between end of ^{90}Y ingrowth and counting of Y oxalate.

The relative uncertainty in the activity of the sample is calculated using the following equations:

$$U_{90\text{Sr}} = \sqrt{U_y^2 + U_b^2 + U_{Ry}^2 + U_{Rs}^2 + U_d^2 + U_v^2 + U_n^2}$$

- $U_{90\text{Sr}}$ = The relative uncertainty corresponding to one standard deviation of the calculated activity for ^{90}Sr from the Y oxalate
- U_y = The relative uncertainty of the counts of the sample calculated from the square root of the gross counts divided by the gross counts of the sample
- U_b = The relative uncertainty of the counts of the background calculated from the square root of the gross counts divided by the gross counts in the integrated area of the background
- U_E = The relative uncertainty of the ^{90}Y counting efficiency, including uncertainty in the standard
- U_{Ry} = The relative uncertainty in the yield of the Y. {At Westinghouse Idaho Nuclear Company (WINCO) this value has been set at 2% due to the precision of the balance and the preparation of the carrier.}
- U_{Rs} = The relative uncertainty in the yield of the Sr. (At WINCO this value is set at 2% due to the precision of the balance, the preparation of the carrier, or the comparison between the sample and comparator.)
- U_d = The relative uncertainty in the decay factors and the ingrowth corrections. (At WINCO this value has been set at 0.3%.)
- U_v = The relative uncertainty of the initial sample-volume measurement and dilutions and transfers. (At WINCO this value has been set at 3% due to the number of sample-transfer steps.)
- U_n = The relative uncertainty in the counting statistics as referenced to the current background value. As the sample count rate approaches background, the error increases exponentially. When the sample count rate is approximately three times the 1σ value of the background, this term becomes insignificant. It is calculated using

$$U_n = \frac{\sqrt{\frac{C_y}{T} + \frac{C_b}{T}}}{C_y - C_b}$$

where

T = the time the samples are counted in min.

The absolute uncertainty is calculated by multiplying the relative uncertainty by the calculated activity.

The detection limit of the analyses is calculated using the following equation:

$$DL(^{90}\text{Sr}) = \frac{[2.71 + (4.65 \cdot \sqrt{C_b \cdot T_1})] \cdot CF \cdot DF}{T \cdot R_y \cdot R_s \cdot E_y \cdot V \cdot Q_2 \cdot (Q_1 - Q_3)}$$

where

T = total seconds the Y oxalate was counted

C_b = counts of blank

T₁ = count time for blank

9.2 Instrument Calibration Calculations

For each standard counted, the efficiency is calculated using the following equation:

$$\text{EFF.} = \frac{\text{Std. Value} \cdot e^{-\lambda t}}{\left[\left(\frac{C}{S} \right)_{\text{Sple}} - \left(\frac{C}{S} \right)_{\text{Blk}} \right] \cdot R}$$

where

Std. Value	=	the disintegrations/sec (Bq) for the standard at T_0
$e^{-\lambda t}$	=	decay correction for the time elapsed between T_0 and the time of counting
$(c/s)_{\text{sple}}$	=	the counts/sec for the standard
$(c/s)_{\text{blk}}$	=	the counts/sec for the blank
R	=	the chemical recovery of the Sr or Y added

A calculator or computer linear-regression-curve fitting program should be used to determine an efficiency curve and its associated uncertainty, using the calculated efficiencies and the respective weights of the precipitate counted.

10.0 Quality Control

A laboratory control sample and a blank should be analyzed with each set of samples in the same manner that the samples are analyzed.

11.0 Method Performance

<u>STD #</u>	<u>Known d/s/g</u>	<u>Measured d/s/g</u>	<u>Recovery (%)</u>	<u>Yield (%)</u>
1	0.151 ± .004	0.17 ± .03	112	100.1
2	0.262 ± .009	0.27 ± .04	103	99.9
3	0.44 ± .013	0.25 ± .07	100	99.6
4	0.262 ± .009	0.25 ± .04	96.5	99.6
5	0.44 ± .013	0.45 ± .07	102	100.1

These five standards represent the control solutions prepared in developing this method. Since development, over 50 controls have been run. The accuracy and precision are not yet firmly established; however, the best estimate (as of March 15, 1993) is plus or minus 6% each.

Total hands-on analysis time is approximately 1.5 h before Y ingrowth, excluding the evaporation step, and 1 h after Y ingrowth, excluding the flow through the column.

RP520^(a)

Determination of Strontium-90 in Soil, Water, and Filter Samples

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method. (This method has been reviewed and comments have been resolved, but quality control data are not available.)

1.0 Scope and Application

This procedure is for the determination of ⁹⁰Sr in soil, water, air filters and a variety of other sample types. The method uses total sample dissolution and will handle samples that contain abnormally high concentrations of calcium. The detection limits for 1-g solid and 150-mL liquid samples are 1.8×10^{-2} Bq/g (0.5 pCi/g) and 1.1×10^{-1} Bq/L (3 pCi/L) respectively. The accuracy of the determination is as good as the precision of the measurement of the specific sample will allow. If greater sensitivity is required, the procedure can be scaled up to 10-g soil samples and 2-L water samples.

2.0 Summary

One gram of soil is dissolved after fusion into potassium fluoride and pyrosulfate; the fusion guarantees total sample dissolution. The pyrosulfate cake is dissolved and Sr is precipitated as the sulfate. For water samples, the Sr is separated from the bulk of the solution by direct precipitation as the sulfate. Air filter and organic samples are wet-ashed with nitric and sulfuric acids and then treated as soil samples. The strontium sulfate is dissolved in EDTA and reprecipitated to separate ⁹⁰Y, other lanthanides, and the actinides. The chemical yield of Sr is determined with ⁸⁵Sr. The strontium sulfate is redissolved in EDTA, and set aside for ⁹⁰Y ingrowth. After ingrowth, the Y is precipitated as the hydroxide, dissolved in HCl, and precipitated as the oxalate. The oxalate is filtered on a glass fiber filter paper and counted in a low-background beta counter. The chemical yield of Y is determined by gravimetric recovery of yttrium oxalate nonahydrate. Overall chemical yields are better than 96% for Y and better than 90% for Sr depending on the concentration of Ca in the sample.

This procedure is a modified version of that written by others (Martin 1979), giving higher yields and shorter analysis time.

(a) This method was supplied D. S. Sill (EG&G, Idaho Falls, Idaho).

3.0 Interference and Limitation

This method is intended for site remediation. It does not separate Ba well from the Sr fraction. If fresh fission products (e.g., ^{140}Ba) are present, an alternate analysis method should be used.

4.0 Safety

The use of a blast burner is specified for the sample fusions. This requires access to a combustible gas mixture which may entail special safety consideration. Otherwise, no significant safety problems are presented by this method other than the normal precautions for handling radioactive material, acids, and bases.

5.0 Apparatus

- Glass fiber filter, 25 mL
- Centrifuge tube, 50 mL
- Platinum dish, 60 mL
- Centrifuge tube, 100 mL
- Infrared lamp, 250 W
- Beta counter
- Centrifuge
- Filtration unit
- Blast burner, Fisher or equivalent
- Counting bottles, e.g., LSC vials
- Teflon[®] stir rods

6.0 Reagents

- Ammonium hydroxide, conc
- Anhydrous potassium fluoride
- Bromocresol green, 0.04%
- Glacial acetic acid
- Hydrochloric acid, conc
- Hydrofluoric acid, conc
- Lithium sulfate 10%. {This may be prepared by adding 50 mL of conc H_2SO_4 to a 1-L polypropylene (PP) bottle containing 200 mL of water. A 76.4-g quantity of lithium hydroxide monohydrate is dissolved in 700 mL of water in a 1-L beaker. The lithium hydroxide solution is added to the H_2SO_4 solution and the solution is swirled to mix; the final volume will be approximately 1 L.}
- Lithium sulfate, 5%. A 10% Li_2SO_4 solution is diluted 1:1 with water.
- Nitric acid, 4 M
- Oxalic acid, 2%
- Potassium hydrogen fluoride
- Sodium ethylenediaminetetraacetate (EDTA), 0.25 M. {This may be prepared by dissolving 73 g of ethylenediaminetetraacetic acid in 50 mL of 50% NaOH mixed with about 500 mL of water. The solution is diluted with 1 L of water and the pH is adjusted to 11.1 with NaOH solution. The solution is filtered through a 0.45- μm DM-450 membrane filter (Gelman Sciences, Ann Arbor, Michigan).}
- Sodium hydroxide, 0.25 M
- Sodium sulfate
- Strontium carrier, 100 mg/mL
- Strontium carrier, 5 mg/mL. A 5.0-mL volume of the 100 mg/mL Sr carrier is diluted to 100 mL with 1% HNO_3 .

- Strontium tracer. A solution of ^{85}Sr in 1% HNO_3 is prepared at an activity of about 170 cps/mL (10^4 cpm/mL).
- Sulfuric acid, conc
- Thymol blue, 0.04% (TB)
- Yttrium carrier, 10 mg/mL. (This may be prepared by dissolving 6.36 g of 99.9% Y_2O_3 in 20 mL of hot conc HNO_3 and diluting to 500 mL with water in a volumetric flask. The solution may be transferred to glass bottles with polyethylene-lined screw caps.)

7.0 Sample Collection, Preservation, and Handling

Aqueous samples should be acidified with HNO_3 to a pH of 1. Soil and filter samples need no special treatment. All samples should be protected from possibility of contamination.

8.0 Procedure

8.1 Weighing Factor for Yttrium Oxalate. Several aliquots of the Y carrier solution should be taken through the procedure to determine the average and reproducibility of the weighing form that will be used to determine the Y yield. Work with ^{88}Y has shown the yield of yttrium oxalate to be $99.93 \pm 0.02\%$. With complete recovery, the weight obtained with 10 mg of Y carrier should be very close to the theoretical value of 34 mg for yttrium oxalate nonahydrate. The weight of the experimentally determined weighing form should be used to correspond to 100% yield. This will alleviate any inaccuracies in concentration that occurred in making the carrier solution. If any question arises as to the completeness of the precipitation, ^{88}Y should be used and the minor fraction counted to determine an Y yield that will be used to calculate the weight of the oxalate precipitate that corresponds to 100% yield.

8.1.1 To a 50-mL centrifuge tube, 5 mL of 4 M HNO_3 , 1 mL of 10 mg/mL Y carrier, 5 mL of 5% oxalic acid, and 3 drops of 0.04% thymol blue are added and diluted to 20 mL with water.

8.1.2 The solution is swirled until thoroughly mixed.

8.1.3 Concentrated NH_4OH is added dropwise until the red color of the indicator just fades to pink (pH 2).

- 8.1.4 The solution is then heated in a boiling water bath for 5 min, cooled, and filtered on a well-washed, tared, 25-mm glass-fiber filter paper in an all glass filtering chimney.
- 8.1.5 The precipitate is washed with 5 mL of 2% oxalic acid at a pH of 2, then with 5 mL of acetone.
- 8.1.6 The precipitate is dried at a distance of about 4 in. from a 250-watt infrared lamp for 5 min and weighed.

8.2 Determination of Counting Efficiency for Yttrium-90 on Yttrium Oxalate. The average counting efficiency for ^{90}Y on yttrium oxalate should be determined from triplicate analyses.

- 8.2.1 To a 50-mL centrifuge tube, the following reagents are added: 5 mL of 4 M HNO_3 , 1 mL of 10 mg/mL Y carrier, 1.0 mL of 5 mg/mL Sr carrier, 1 mL of a standard solution of ^{90}Sr (in secular equilibrium with ^{90}Y) at an activity of about 5×10^2 Bq/mL (3×10^4 dpm/mL), 5 mL of 5% oxalic acid, and 3 drops of 0.04% thymol blue. The resulting solution is diluted to 20 mL.
- 8.2.2 The centrifuge tube should be swirled to mix the solution thoroughly, and NH_4OH added dropwise until the red color of the indicator just fades to pink (pH 2).
- 8.2.3 The time is recorded as the beginning of the ^{90}Y decay.

If the indicator endpoint is overshot and a yellow solution is obtained, HCl should be quickly added dropwise to the first permanent pink color. If more than 3 drops of HCl had to be added, strontium oxalate might have precipitated, contaminating the yttrium oxalate. The solution should be discarded and the procedure started over.

- 8.2.4 The solution is heated in a boiling water bath for 5 min, cooled, and centrifuged for 5 min. Then the solution should be decanted and the supernate discarded.
- 8.2.5 The precipitate is washed with about 5 mL of a 2% solution of oxalic acid. The precipitate should be centrifuged, and the supernate decanted and discarded.
- 8.2.6 The centrifuge tube may be flipped sharply to break up the packed precipitate, then 5 mL of 4 M HNO_3 are added. The solution should be heated in a boiling water bath until the precipitate has dissolved.

- 8.2.7 The solution is cooled in a cold water bath, and 5 mL of 5% oxalic acid and 3 drops of thymol blue are added. Then the solution should be diluted to 20 mL with water. Ammonium hydroxide is added to precipitate Y oxalate at a pH of 2.
- 8.2.8 The Sr-free $Y_2(C_2O_4)_3 \cdot 9 H_2O$ precipitate should be mounted on a tared 25-mm glass-fiber filter paper in an all glass filtering chimney. The precipitate should be washed with 5 mL of 2% oxalic acid and then with 5 mL of ethanol.
- 8.2.9 The precipitate is dried under an infrared lamp.
- 8.2.10 The precipitate is weighed to determine the Y yield. The mounted precipitate is counted in the low background beta counter to determine the counting efficiency of ^{90}Y . The weight determined in section 8.1 should be used as a comparator for the yield determination. However, if the weight of $Y_2(C_2O_4)_3 \cdot 9 H_2O$ is much different (>5%) than obtained in section 8.1, something is wrong and both section 8.1 and 8.2 should be repeated until constant weights are obtained.
- 8.2.11 The time at the midpoint of the count is recorded as the end of the ^{90}Y decay.
- 8.3 Soil Samples.** Indicated reagent volumes are appropriate for up to about a 1-g soil sample. To accommodate up to a 10-g soil sample, the reagent volumes need to be scaled accordingly. For a 10-g soil sample, dissolution reagents should be scaled up by a factor of ten, the Sr carrier and the EDTA by a factor of four.
- 8.3.1 To 1 g (or less) of soil in a 60-mL platinum dish, 0.5 mL conc HNO_3 and 0.5 mL conc HF should be added.
- Prewetting the soil with water may be necessary for soils high in carbonate. The resulting vigorous evolution of CO_2 may cause some loss of the sample due to spattering.*
- 8.3.2 After the evolution of CO_2 has ceased, 1 mL of 100 mg/mL Sr carrier and 1 mL of ^{85}Sr tracer are added.
- 8.3.3 An identical 1-mL aliquot of tracer is added to a counting bottle containing 20 mL of 1% HCl to serve as a standard.
- 8.3.4 The platinum dish should be heated on the hot plate until the soil is almost dry, taking care not to lose any tracer by splattering.

- 8.3.5 The solution should be cooled, and 2 g of anhydrous potassium fluoride and 1.3 g of potassium hydrogen fluoride are added.
- 8.3.6 The potassium fluorides and soil should be mixed thoroughly with a teflon stirring rod.
- 8.3.7 The dish should be placed on a ring stand, and the solution should be fused over the full heat of the blast burner until a clear melt is obtained.
- 8.3.8 The melt should be cooled to room temperature and 4 mL conc H_2SO_4 added slowly and with enough cooling to prevent the solution from frothing over the sides of the dish.

When the dissolution becomes vigorous enough for the solution to froth over the sides of the dish, the dish should be cooled in a bath of cold running water until the reaction slows, then reheated. When most of the cake has dissolved, the vigorous reactions will subside enough so that the dish can be placed on the full heat of the bare hotplate.

- 8.3.9 The dish should be heated on a hotplate until the potassium fluoride cake has dissolved and the transposition has been completed.
- 8.3.10 After all of the potassium fluoride cake has transposed, 2 g of anhydrous Na_2SO_4 should be added. The solution is mixed by swirling and heated over a small flame of the blast burner until the evolution of H_2SO_4 fumes have slowed and a clear red pyrosulfate fusion is obtained.
- 8.3.11 The dish is removed from the heat, and the melt swirled high onto the sides of the dish until the melt solidifies. The cake is allowed to cool to room temperature.

The dish should not be quenched in cold water. This practice will decrease the life of the platinum dish.

- 8.3.12 The cake is removed from the dish by gently flexing the sides of the dish; this will fracture the cake, and with minor tapping, the cake will release itself from the dish. The cake should be transferred to a beaker or Erlenmeyer flask.
- 8.3.13 A boiling mixture of 50 mL of water, 5 mL of conc HCl , and 6 g of anhydrous lithium sulfate is added to dissolve the pyrosulfate cake. Strontium and barium sulfates will precipitate at this point, but most of the Ca will remain in solution.

- 8.3.14 The solution should be boiled for 15 min to hydrolyze condensed phosphates. The Sr separation is continued under **8.7, Separation of Strontium Sulfate**.

8.4 Water Samples. Indicated reagent volumes are appropriate for up to about a 150-mL water sample. A large water sample should be evaporated to a small volume, transferred to a platinum dish, and treated as a soil sample.

- 8.4.1 Up to 150 mL of the water sample and 5 drops of 0.04% thymol blue should be added to a 250-mL Erlenmeyer flask. The pH of the solution is adjusted to the red-yellow endpoint of the indicator with either conc HCl or 50% NaOH.

If the solution is blue, HCl should be added. If the solution is red, NaOH should be added.

- 8.4.2 To the sample, 5 mL of HCl, 1 mL of the 100 mg/mL Sr carrier, and 1 mL of ^{85}Sr tracer are added.
- 8.4.3 An identical 1-mL aliquot of ^{85}Sr tracer should be added to a counting bottle containing 20 mL of 1% HCl to serve as a standard.
- 8.4.4 The volume of the water sample should be adjusted to about 50 mL by either evaporation or dilution with distilled water.
- 8.4.5 The solution should be heated to boiling on a hot plate, and 6 g of anhydrous lithium sulfate added. The solution should be boiled for approximately 10 min.
- 8.4.6 The Sr separation is continued under **8.7, Separation of Strontium Sulfate**.

8.5 Organic Air Filters

- 8.5.1 Up to one 4-in. filter paper is transferred to a 250-mL Erlenmeyer flask. One milliliter of Sr carrier, 1 mL of ^{85}Sr tracer, 10 mL of H_2SO_4 , and 10 mL of HNO_3 should be added.
- 8.5.2 An identical 1-mL aliquot of tracer is added to a counting bottle containing 20 mL of 1% HCl to serve as a standard.
- 8.5.3 The Erlenmeyer should be heated on a hotplate until the HNO_3 has oxidized the easily oxidizable organic material.

- 8.5.4 The solution is heated until the excess HNO_3 has been driven off, and the H_2SO_4 acid has charred the filter paper.
- 8.5.5 While swirling the flask, 1 mL of HNO_3 is added dropwise to oxidize the charred organic matter. After the reaction subsides, the 1 mL additions of HNO_3 should be repeated until the solution has either lightened in color or until the HNO_3 has no more effect on oxidizing the filter.
- 8.5.6 Steps 8.5.4 and 8.5.5 should be repeated until the solution no longer chars when fumed with H_2SO_4 .
- 8.5.7 The H_2SO_4 should be evaporated to about 5 mL and the solution transferred quantitatively to a 60-mL platinum dish with water.
- 8.5.8 The solution is evaporated to dryness, and the analysis proceeds with the soil preparation, Step 8.3.5.

8.6 Glass Fiber Filters. Glass fiber filters should be treated as a soil sample.

8.7 Separation of Strontium Sulfate

- 8.7.1 The precipitated solution is transferred to an appropriate centrifuge tube (e.g., 100 mL) with a 5% solution of lithium sulfate and centrifuged 5 min. The supernate is decanted and discarded.
- 8.7.2 The precipitate should be washed with 5% lithium sulfate and centrifuged for 5 min. The wash is discarded.
- 8.7.3 Ten milliliters of 0.25 M EDTA and 3 drops of thymol blue are added, and the solution is then heated in a boiling water bath until the precipitate has dissolved completely.

If the solution fades from blue during the dissolution, 50% NaOH should be added dropwise to the blue endpoint of the thymol blue.

In a sample that contains a high concentration of calcium, more EDTA will have to be used to dissolve the entire precipitate. No more EDTA should be used than is necessary to dissolve the precipitate completely, or a loss of Sr will result.

If ferric hydroxide precipitates, and after all of the sulfate precipitate has been dissolved, the solution should be centrifuged and decanted to another centrifuge

tube. The precipitate may be washed with water adjusted to pH 7 to 8 with NaOH, centrifuged, and the wash combined with the previously collected supernate. This washing step will result in a small increase in yield. The hydroxide precipitate is discarded.

- 8.7.4 The solution is mixed by swirling, and 10 mL of 10% lithium sulfate and 3 drops of bromocresol green are added.
- 8.7.5 Concentrated HCl is added dropwise until the solution turns green; then about 3 mL of glacial acetic acid are added until the yellow end point of the bromocresol green is reached to precipitate SrSO_4 (pH of 4). The time is recorded as the start of the ^{90}Y ingrowth.

If the acidity of the solution is increased much further, CaSO_4 will precipitate with the SrSO_4 and might not dissolve in the limited amount of EDTA in the subsequent dissolution. If the pH of the solution is much higher than four, the SrSO_4 will be precipitated incompletely. If there is any question as to the completeness of precipitation, the supernate may be decanted into a counting bottle and counted before discarding.

- 8.7.6 The precipitated solution should be heated in a boiling water bath for 5 min, cooled, and centrifuged. The supernate is decanted and discarded.
- 8.7.7 One milliliter of 10 mg/mL Y carrier is added to the SrSO_4 precipitate. The solution is mixed to suspend the precipitate; then 10 mL of 0.25 M EDTA and 3 drops of thymol blue are added, followed by dropwise addition of 50% NaOH to the blue endpoint of the indicator.
- 8.7.8 The centrifuge tube is heated in a bath of boiling water for 5 min to dissolve the precipitate completely.
- 8.7.9 The solution is cooled in a cold water bath and transferred quantitatively to a counting bottle (e.g., a LSC vial). The height of the sample should be adjusted with water to the same height as that of the standard.
- 8.7.10 The solution and the ^{85}Sr standard are counted by gamma spectrometry to determine the Sr yield.

Strontium-85 can be determined based on the characteristic 514 keV gamma-ray.

- 8.7.11 The solution should be set aside for at least 5 days to permit ^{90}Y to ingrow to at least 75% of equilibrium with the ^{90}Sr .

- 8.7.12 After ^{90}Y ingrowth, the solution is transferred to an appropriate centrifuge tube (e.g., 100 mL) and two 2.5 g portions of KOH added. The solution should be heated in a boiling water bath for 15 min to ensure complete precipitation of yttrium hydroxide. The time is recorded as the start of the ^{90}Y decay.
- 8.7.13 The solution should be centrifuged for 5 min while still hot. The supernate is decanted and discarded.
- 8.7.14 The precipitate should be washed with 10 mL of 0.25 M NaOH. The wash should be centrifuged, decanted, and discarded.
- 8.7.15 The hydroxide precipitate is dissolved in 5 mL of 4 M HNO_3 .
- 8.7.16 The solution should be swirled, and 3 drops of thymol blue and 5 mL of 5% oxalic acid are added, followed by 5 mL of conc NH_4OH . Ammonium hydroxide should be added dropwise with swirling to the last shade of pink, but not to the yellow endpoint of the indicator (pH 2).
- 8.7.17 The solution is heated in a boiling water bath for five min, cooled, and centrifuged for 5 min. The supernate should be decanted and discarded.
- 8.7.18 Approximately 5 mL of 4 M HNO_3 are added to the centrifuge tube to dissolve the yttrium oxalate.
- 8.7.19 The solution is transferred to an appropriate centrifuge tube (e.g., 50 mL) with 5 mL of water. Five milliliters of 5% oxalic acid and 3 drops of thymol blue are added.
- 8.7.20 The solution should be swirled and 5 mL of conc NH_4OH added. Ammonium hydroxide should be added dropwise to the pink endpoint of the indicator to reprecipitate yttrium oxalate.
- 8.7.21 The precipitated solution is heated in a boiling water bath for 5 min. The solution is cooled and the precipitate filtered on a well washed, tared, glass-fiber filter paper in an all glass filtering chimney.
- 8.7.22 The precipitate is washed with 5 mL of 2% oxalic acid at a pH of 2, followed by 5 mL of acetone.
- 8.7.23 The precipitate is dried at a distance of about 4 in. from a 250-watt infrared lamp for about 5 min.

8.7.24 The dried filter paper is weighed to determine the Y yield.

8.7.25 The filter paper is mounted in a sample holder and counted in a low background beta counter for a time long enough to obtain the statistical precision desired. The time at the mid-point of the count time should be recorded as the end of the ^{90}Y decay.

9.0 Calculations

The ^{90}Sr activity is determined as follows:

$$^{90}\text{Sr} = (Y - B_Y) / (CT_Y \cdot E_Y \cdot Q \cdot Y_{\text{Sr}} \cdot Y_Y \cdot G_Y \cdot D_Y \cdot C)$$

where

Y	=	Gross counts of ^{90}Y
B_Y	=	Background of ^{90}Y
CT_Y	=	count time of ^{90}Y
E_Y	=	counting efficiency of ^{90}Y on yttrium oxalate
Q	=	Sample quantity (e.g., g, mL, or L)
Y_{Sr}	=	Strontium Yield
Y_Y	=	Yttrium yield
G_Y	=	Yttrium growth = $1 - \exp(\ln 2 \cdot T_1 / 64)$; T_1 = Time of ^{90}Y ingrowth in hours
D_Y	=	Yttrium decay = $\exp(\ln 2 \cdot T_2 / 64)$; T_2 = Time of ^{90}Y decay in hours
C	=	factor to convert to desired reporting units.

The propagated error (S) in the ^{90}Sr activity determination is determined in the individual measurements as follows:

$$S_{^{90}\text{Sr}} = \text{SQR}(A^2 + B^2 + C^2 + D^2 + E^2 + F^2 + G^2) (^{90}\text{Sr})$$

where

A	=	$\text{SQR}(Y + B_Y) / (Y - B_Y)$	B	=	SE_Y / E_Y
C	=	SQ / Q	D	=	$SY_{\text{Sr}} / Y_{\text{Sr}}$
E	=	SY_Y / Y_Y	F	=	SQ_Y / Q_Y
G	=	SD_Y / D_Y			
SQ	=	Standard deviation of the sample quantity			
SY_{Sr}	=	St. Dev. of Y_{Sr}			
SY_Y	=	St. Dev. of Y_Y			

$$\begin{aligned} SG_Y &= \text{St. Dev. } G_Y = (\text{Ln } 2 \cdot T_1/64) \cdot \text{SQR}((ST_1/T_1)^2 + (.1/64)^2) \\ SD_Y &= \text{St. Dev. of } D_Y = (\text{Ln } 2 \cdot T_2/64) \cdot \text{SQR}((ST_2/T_2)^2 + (.1/64)^2) \\ ST_1 &= \text{St. Dev. of } T_1 \\ ST_2 &= \text{St. Dev. of } T_2 \\ SE_Y &= \text{St. Dev. of } E_Y \\ \text{SQR}() &= \text{square root of the quantity in the } () \end{aligned}$$

10.0 Quality Control

Analysis of spiked control samples and blanks should be performed with each analytical batch to help assess method performance. Other laboratory control samples, such as matrix spikes and duplicates, should be run periodically as well.

11.0 Method Performance

The accuracy of the method is as good as the precision of measurement will allow. This incorporates such items as counting errors and measurement errors made at the lab bench (e.g., error in measuring volumes). Chemical yields are typically better than 90% for Sr and better than 95% for Y. The detection limit is approximately 1.8×10^{-2} Bq/g (0.5 pCi/g) and 1.1×10^{-1} Bq/L (3 pCi/L) (based on a 1-g and 150-mL sample size, respectively) when counting for 200 min with a background count rate of 1.5 cpm.

12.0 Reference

Martin, D. B. 1979. "Determination of Strontium-89 and -90 in Soil with Total Sample Decomposition." *Anal. Chem.*, 5:1968-72.

RP530^(a)

Determination of Selenium-79 in Aqueous Samples

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method describes the isolation of Se in aqueous samples by ion exchange, distillation if necessary, and precipitation for subsequent analysis of ⁷⁹Se by liquid scintillation counting (LSC). It has been applied to high-level radioactive samples from Hanford waste tanks and on defense waste processing facility (DWPF) samples from the Savannah River Site. The separation, although difficult, provides a decontamination factor of Se from other β -emitters of about 10^6 and a chemical yield of about 50% or better.

2.0 Summary

The dissolved Se is oxidation state adjusted to an H_2SeO_3 neutral molecular form. In this form, the Se passes through a mixed bed ion exchange column onto which most other elements load. Further purification of Se is accomplished by precipitating the Se metal after reduction with hydroxylamine hydrochloride. The metal is dissolved in HNO_3 and prepared for liquid scintillation counting. A distillation process, which may be used for further purification, is also described. The chemical yield of Se can be determined gravimetrically or by elemental analysis of Se {e.g., inductively coupled plasma (ICP) optical emission spectroscopy (OES)}. Selenium-79 activity is determined from beta decay measured by LSC. A flow chart (Figure 1) indicates available paths for sample preparation.

3.0 Interferences

No interferences are known.

(a) This method was consolidated by S. K. Fadeff (Pacific Northwest Laboratory, Richland, Washington) from two analytical procedures; one from Pacific Northwest Laboratory (Maiti and Kozelisky 1990) and one from Savannah River Laboratory (1991).

Figure 1. Pathways for Sample Preparation

4.0 Safety

Selenium is considered a highly toxic material, and the carrier and sample preparative steps should be handled with appropriate safety considerations.

5.0 Apparatus and Materials

- Beaker, appropriate sizes (e.g., 400 mL)
- Vials, 7 mL and 35 mL, glass, screw-cap, or equivalent
- Liquid scintillation vials
- Heating block (100°C) or hotplate
- Ion exchange column, approximately 0.5-cm internal diameter (A 7.5-mL plastic dropper with the top cut off and plugs of glass wool on resin top and bottom works well.)
- Transfer pipettes, glass or plastic
- Filter holder
- Filters to fit filter holder, tared (e.g., Whatman 934AH glass microfiber filters)
- Vacuum flask with hole in stopper to accommodate the base of the 13-mm Swinnex filter-holder base
- Petri dishes or other suitable carriers for filters
- Centrifuge tubes
- Centrifuge

Distillation

- Selenium still (An example of a specially made still is shown in Figure 2.)
- Variac, 1.5-ampere output, 0 to 140 volts
- Heating mantle, 50 mL, round bottom
- Thermometer
- N₂ gas, 2 psi

DRAFT

Figure 2. Selenium Still

6.0 Reagents

- Selenium carrier, 10 mg/mL { This may be prepared by dissolving about 1.0 g (precisely known) of gray Se metal in a 100-mL volumetric flask using 5 to 6 mL of hot concentrated HNO_3 . When dissolution is complete, the selenium solution is diluted to slightly less than the volumetric mark with 0.5 M HNO_3 . After cooling to ambient temperature, the solution is diluted to volume with 0.5 M HNO_3 . }
- Nitric acid, fuming, 16 M, 0.5 M, and 0.1 M
- Carbon-14 Standard
- Ion exchange resin, AG 50W-X8 (Bio-Rad, Richmond, California), or equivalent, 100 to 200 mesh, H^+ form
- Ion exchange resin, AG 1-X4 (Bio-Rad, Richmond, California), or equivalent, 100 to 200 mesh, Cl^- form
- Nitric acid saturated with bromine. (This may be prepared by adding $\approx 100 \mu\text{L}$ Br_2 to 15 mL of 0.5 M HNO_3 .)
- Bromine water. (This may be prepared by adding $\approx 100 \mu\text{L}$ of Br_2 to 15 mL of deionized water.)
- Hydrobromic acid, 47% to 49%
- Liquid scintillation cocktail
- Hydroxylamine hydrochloride, 25 wt% (The shelf life is approximately two weeks.)
- Sodium hydroxide, 0.3 M
- Ethanol
- Hydrochloric acid, 9 M
- Br_2

7.0 Sample Collection, Preservation, and Handling

When handling the samples and Se carrier, appropriate precautions should be taken to handle the Se safely.

8.0 Procedure

For samples containing a high-salt matrix (e.g., fused samples), an initial sample clean-up should be performed as described in step 8.1. For low-salt samples, the initial sample clean-up can be skipped and the separation method begun at step 8.2.

8.1 Initial Cleanup of High-Salt Matrix Samples

- 8.1.1 An appropriate sample aliquot of the dissolved fused sample should be taken. The sample volume must be recorded. A precisely known quantity (e.g., 20 mg) of Se carrier and 20 μL of Br_2 are added. Using a stir bar, the sample is mixed thoroughly; then it is allowed to stand 10 min.
- 8.1.2 To the sample, 10 mL of 25% $\text{NH}_2\text{OH}\cdot\text{HCl}$ are added, and the solution is mixed.
- 8.1.3 The sample is heated until the black Se metal precipitates; this takes about 45 min. The sample is then cooled.
- 8.1.4 The solution is centrifuged for about 5 min.
- 8.1.5 The supernate is removed using a transfer pipet. The container walls and precipitate are washed with ≈ 10 mL of ethanol.
- 8.1.6 The sample is again centrifuged for about 5 min. The ethanol is removed using a transfer pipet.
- 8.1.7 The sample is slightly warmed to vaporize residual ethanol.
- 8.1.8 To the Se metal, 0.5 mL concentrated HNO_3 are added.
- 8.1.9 The sample is heated until the Se metal dissolves.
- 8.1.10 Five milliliters of water and 50 μL of Br_2 are added to the sample. The method continues with step 8.3.

- 8.2 For low salt or non-fused samples, a solution aliquot is added to a vial. A precisely known quantity (e.g., 20 mg) of Se carrier is added, along with 0.5 to 1.0 mL of 0.5 M HNO_3 , 10 to 200 μL Br_2 , and up to 0.5 mL HBr . The solution is swirled to mix thoroughly.

The excesses of Br^- and Br_2 will hold Se as H_2SeO_3 .

8.3 Ion exchange columns are prepared by placing 1 mL of the AG 1-X4 anion resin in the column and by placing 1 mL of the AG 50W-X8 cation resin on top of the anion resin. The resin column is washed with 5 mL of deionized water.

8.4 The sample solution is transferred quantitatively to the ion exchange column using 0.5 M $\text{HNO}_3 \cdot \text{HBr}$ (1 drop HBr per 1 mL 0.5 M HNO_3) to rinse the sample vial. The Se passes through the column and is collected in an appropriate vial (e.g., 35-mL screw-cap vial).

Selenium will not load onto the column, but will collect in the elution vial. Most of the other activity will load on the mixed-bed resin.

8.5 At this point, purification may continue with distillation (step 8.6) followed by precipitation (step 8.7), or purification may continue with precipitation (step 8.7).

8.6 Distillation.

8.6.1 The solution is quantitatively transferred from the vial to a Se still.

8.6.2 The vial is rinsed with two 5-mL portions of HBr, which are transferred to the still.

8.6.3 The round bottom of the still is placed in the heating mantle.

8.6.4 A vial containing 5 mL of 25% $\text{NH}_2\text{OH} \cdot \text{HCl}$ is placed in a beaker (e.g., 400 mL), which is filled with ice. The vial is positioned so that the tip of the still's exit is below the liquid level of the $\text{NH}_2\text{OH} \cdot \text{HCl}$ in the vial.

8.6.5 The still inlet is connected to N_2 , and the N_2 flow rate is adjusted to about five bubbles per sec.

8.6.6 The heating mantle variac is set to 110 V. The temperature should rise to $\approx 120^\circ\text{C}$. Distillation should be continued for about 35 min. The solution in the still should be pale yellow when distillation is complete.

8.6.7 After distillation, the variac is turned off, and the solution is allowed to cool for 2 to 3 min. Then the still is removed from the heating mantle, and the N_2 flow is shut off. The vial containing the distillate is removed. The still (shown in Figure 2) is cleaned as follows:

1. The waste in the still is discarded by vacuum suctioning through the still top into a radioactive waste jug.

2. While continuing to pull a vacuum through the top of the still, the still is flushed clean by allowing water to be pulled up the exit arm of the still. (The water in the beaker used for cooling may be used.) The still is cleaned with a series of flushes as above, with 25% $\text{NH}_2\text{OH}\cdot\text{HCl}$, deionized water, 8 M HNO_3 , and finally with deionized water.

8.6.8 The sample preparation continues with step 8.7.2.

8.7 Precipitation

- 8.7.1 If the sample was not distilled, 4 mL HBr are added to the sample solution.

Bromide provides a more reducing matrix for the subsequent reduction of Se to elemental Se.

- 8.7.2 To the sample from step 8.6.8 or 8.7.1, 5 to 10 mL 200 mg/mL $\text{NH}_2\text{OH}\cdot\text{HCl}$ are added, and the sample is heated gently for about 30 min.

The low heat will speed the reduction of Se to elemental Se. The solution will turn orange to lavender.

- 8.7.3 The solution is cooled, then centrifuged. If the Se has satisfactorily settled, the major amount of supernate may be suctioned off with a disposable pipet.

If a second precipitation is to be performed, the following steps are taken:

1. Without removing the black precipitate, the supernate is removed with a transfer pipet and discarded.
2. The precipitate is washed with ≈ 10 mL of ethanol.
3. The sample is again centrifuged for about 5 min. The ethanol wash is removed, using a transfer pipet, and the vial is warmed to vaporize the residual ethanol.
4. Slowly, 500 μL of 16 M HNO_3 are added to the vial, and then the sample is heated until the Se dissolves.
5. Ten milliliters of deionized water are added to the vial, which is swirled to mix.

6. Ten milliliters of 25% $\text{NH}_2\text{OH}\cdot\text{HCl}$ are added to the vial, which is swirled to mix.
 7. The sample is heated gently for about 30 min, cooled, then centrifuged. The major amount of supernate may be suctioned off with a disposable pipet.
- 8.7.4 Two alternatives for yield determination and LSC sample preparation are described, one in section 8.8 (gravimetric yield determination), and one in section 8.9 (spectrometric yield determination). One of these alternatives is selected for an analytical batch of samples.

8.8 Gravimetric Yield Determination and LSC Sample Preparation

- 8.8.1 A 13-mm dried, glass filter is tared, then placed on the base of a 13-mm Swinnex filter holder. While vacuum is applied, the base of the Swinnex holder, with the filter on top, is placed into the hole of the stopper in the top of the vacuum flask.
- 8.8.2 The black Se metal is mounted onto the center of the filter using a glass transfer pipet.
- 8.8.3 The vial is washed with 3 to 4 mL of ethanol, and the residual Se metal is transferred to the filter.
- 8.8.4 The filter is removed from the filter holder, and the filter plus the Se metal are placed on a petri dish, or other suitable carrier, and dried in an oven at 110°C to 120°C for about 30 min.
- 8.8.5 The filter plus Se metal are then cooled in a desiccator for at least 10 min.
- 8.8.6 The filter plus Se metal are weighed on a balance that weighs to $10\text{ }\mu\text{g}$ (0.00001 g) or better, and the mass is recorded.
- 8.8.7 The filter plus Se metal are transferred to a LSC vial.
- 8.8.8 The Se is dissolved with $150\text{ }\mu\text{L HNO}_3$.
The Se metal is allowed to dissolve completely before going to the next step.
- 8.8.9 To neutralize the acid, 1.0 mL of 0.3 M NaOH is added.
- 8.8.10 A background sample is prepared by adding a filter to an LSC vial, washing with $150\text{ }\mu\text{L HNO}_3$ and adding $1\text{ mL } 0.3\text{ M NaOH}$.

8.8.11 An appropriate liquid scintillation cocktail (e.g., Altex™, Ultima-Gold™, Opti-Flour®, etc.) is added to the Se sample solution and background sample. The vial is capped and the solution is shaken until it is clear.

8.8.12 The sample is counted by LSC to measure the ^{79}Se activity.

8.9 Yield Determination by Spectroscopy and LSC Sample Preparation

8.9.1 The sample is quantitatively transferred to a filtration unit and filtered using four 5-mL aliquots of 0.1 M HNO_3 as the vial rinse and wash solution.

8.9.2 The filter is transferred to a new vial, and the filtrate is discarded.

8.9.3 The Se precipitate is dissolved with a precisely known quantity (e.g., 2.0 mL) of fuming HNO_3 .

8.9.4 A precisely known quantity (e.g., 2.0 mL) of distilled water is added to the sample, and then the filter paper is removed and discarded.

8.9.5 A background sample is prepared by washing a blank filter paper with 2.0 mL of fuming HNO_3 , adding 2.0 mL of distilled water, and removing the filter paper.

8.9.6 A 1-mL aliquot is transferred to another vial for subsequent Se yield determination and analysis of Sr, Zr, Ni, and Na (radioisotopes that might interfere with the LSC determination) by ICP-OES (or equivalent). This step is also applied to the prepared background sample.

8.9.7 An aliquot of sample is transferred to an LSC vial and mixed with an appropriate volume of scintillation cocktail (e.g., 14 mL of Opti-Flour®). The background sample is prepared in the same way and will constitute the LSC background subtraction sample.

8.10 Standard Preparation. Since ^{79}Se standard is generally not available for calibrations, a ^{14}C standard is used. The maximum and average beta energies for ^{14}C and ^{79}Se are similar, which makes the ^{14}C standards acceptable for measuring ^{79}Se . See Radioactive Decay Data Tables (DOE/T/C-11026). Carbon-14 calibration standards are prepared in the same matrix as the samples. The ^{14}C standard activity should provide appropriate counting statistics in a reasonable count time.

8.11 Quench Factor. A series of ^{14}C standards are made up containing different amounts of Se carrier, from 0 to 20 mg, in the same matrix as the samples. These are measured by LSC to establish the quench correction.

9.0 Calculations

9.1 Gravimetric Yield Calculation

$$Y = \frac{(\text{Mass}_{\text{gross}} - \text{Mass}_{\text{filter}})}{[\text{Se}] \cdot V}$$

Y = yield as a decimal fraction

Mass_{gross} = mass of Se metal plus filter as milligrams from step 8.8.6

Mass_{filter} = mass of filter only as milligrams from step 8.8.1

[Se] = Se concentration in carrier as milligrams/milliliter

V = volume of Se carrier added in milliliters

9.2 Spectrometric Yield Calculation

$$Y = \frac{[\text{Se}]_{\text{smp}}}{[\text{Se}]_{\text{added}} \cdot \text{CF}}$$

where

[Se]_{smp} = the Se concentration found in the sample

[Se]_{added} = the Se concentration originally added to the sample

CF = correction factor for carrier dilution in preparation for the sample split
(steps 8.9.3 and 8.9.4)

For example, 2.0 mL of a 10 mg/mL Se solution are added; the sample dilution results in the 20 mg Se being diluted to 4.0 mL, resulting in a 5 mg/mL solution. The resulting correction factor is

$$\frac{2.0 \text{ mL}}{4.0 \text{ mL}} = 0.5$$

9.3 Selenium-79 Counting Efficiency

$$E = \frac{CR_{std} - CR_{bkg}}{DR_{std}}$$

E = ^{14}C and ^{79}Se counting efficiency

CR_{std} = Count rate of ^{14}C standard from liquid scintillation counting data

CR_{bkg} = Count rate of the ^{79}Se blank

DR_{std} = Disintegration rate of ^{14}C in the calibration standard

9.4 Quench Factor

$$\text{Quench factor} = \frac{CR_i}{CR_{unquenched}}$$

where

CR_i = count rate of the quenched standard

$CR_{unquenched}$ = count rate of the unquenched standard

For Altex™ scintillation cocktail, no quenching was observed from 0 to 12 mg Se; above 12 mg, a linear reduction in count rate was observed (Maiti and Kozelisky 1990). Examples of the Altex™ quench factors found are provided in Table 1.

Table 1. Quench Factors for Altex™ LSC Cocktail	
<u>mg Se recovered</u>	<u>Quench Factor</u>
12 or less	1.0
13	0.98
14	0.96
15	0.94
16	0.92
17	0.90
18	0.88
19	0.86
20	0.83

For Ultima-Gold™, no quench up to 20 mg Se was found (Maiti and Kozelisky 1990).

9.5 Sample Activity Concentration

9.5.1 If a non-fused sample is being analyzed, the activity calculation is

$$A = \frac{CR_{Se} - CR_{bkg}}{E \cdot Q \cdot Y \cdot F_q} \cdot S \cdot C$$

where

A = sample ⁷⁹Se activity concentration

CR_{Se} = sample count rate obtained from the liquid scintillation counting data

CR_{bkg} = ⁷⁹Se background sample count rate obtained from the liquid scintillation counting data

E = ¹⁴C and ⁷⁹Se counting efficiency

Q = quantity of sample (in mL)

Y = yield factor calculated for sample

F_q = quench Factor

S = sample split factor (if portion was removed for ICP yield determination)

C = conversion factor to produce the desired reporting units

9.5.2 If a fused sample is being analyzed, the calculation becomes:

$$A = \frac{CR_{Se} - CR_{bkg} \cdot V}{E \cdot Q \cdot Y \cdot F_q \cdot M} \cdot S \cdot C$$

where

V = final volume of dissolved, fused sample

M = mass of the sample that was fused, in g

10.0 Quality Control

To check for possible sample contamination, a method blank should be run with each batch of samples. A batch should not exceed 20 samples. A Se carrier is used to determine recovery for each sample. Carrier recovery should be at least 50%.

11.0 Method Performance

To be added.

12.0 References

Maiti, T. C., and A. E. Kozelisky. 1990. "Selenium-79 by Ion Exchange and Distillation Prior to Measurement by Liquid Scintillation Counting." PNL-ALO-440. *Analytical Chemistry Laboratory (ACL) Procedures Compendium*. PNL-MA-599. Pacific Northwest Laboratory, Richland, Washington.

Savannah River Laboratory. 1991. "Procedure for Separation of Selenium and Determination of Selenium-79 by Liquid Scintillation Beta Counting." WSRC-RP-91-865. Aiken, South Carolina.

13.0 Further Reading

Korkisch, J. 1989. *Handbook of Ion Exchange Resins: Their Application to Inorganic Analytical Chemistry*, Volume VI, CRC Press, Inc., Boca Raton, Florida, pages 255-273.

Marsh, K. V. 1974. *Recent Radiochemical Separation Procedures for As, At, Be, Mg, Ni, Ru, and Se*, NAS-NS-3059, National Technical Information Service, Springfield, Virginia.

RP550^(a)**Technetium-99 Analysis using Extraction Chromatography****1.0 Scope and Application**

This method is used to analyze technetium-99 (⁹⁹Tc) in up to 1-L aqueous samples under neutral or dilute (≤ 0.1 M) nitric acid conditions. Dissolved salts in the aqueous matrix are tolerated; however dissolution of particulate matter is not addressed. The method uses extraction chromatography with TEVA•Spec[®] Eichrom resin. It is fairly rapid and results in relatively little waste. Detection limits obtainable are dependent on the subsequent measuring techniques, but are on the order of 0.04 Bq/L (1 pCi/L). The total time of sample analysis is approximately 2 days for eight samples, with an estimated hands-on time of 8 h, including data reduction.

2.0 Summary of Method

The sample is heated with H₂O₂ to oxidize all technetium to pertechnetate. The aqueous sample, with acid concentration less than or equal to 0.1 M HNO₃, is then passed through TEVA•Spec[®] resin where TcO₄⁻ is strongly absorbed. The column is washed with water or up to 50 mL of 1 M HNO₃. The resin can then be transferred to a liquid scintillation counting (LSC) vial and mixed with Insta-Gel for subsequent analysis by LSC. Alternatively, the technetium can be stripped from the resin with 11 M HNO₃ for inductively coupled plasma-mass spectrometry (ICP-MS) analysis.

3.0 Interferences and Limitations

- 3.1 Organic matter that is present in the aqueous sample may be adsorbed by, and cause discoloration of, the TEVA•Spec[®] resin. This results in a potential quenching problem when counting the TEVA•Spec[®] resin by LSC. The adsorption of organics can be minimized by first passing the sample through Amberchrom[™] CG71 resin.
- 3.2 One liter of solution may be passed through a 2-mL pre-packed TEVA•Spec[®] column with no breakthrough of the ⁹⁹Tc.
- 3.3 Analysis by ICP-MS is subject to isobaric interference due to Ru. Ruthenium is not retained by TEVA•Spec[®] resin. Any Ru not washed from the resin can be corrected for if the ratio of ¹⁰¹Ru to ⁹⁹Ru is known (e.g., by process knowledge) and by assuming that

(a) This method was consolidated by S. K. Fadeff from methods supplied by D. M. Beals (Westinghouse, Savannah River Company, Aiken, South Carolina), T. (Sullivan) Davis (Argonne National Laboratory, Argonne, Illinois), and E. J. Wyse and S. K. Fadeff (Pacific Northwest Laboratory, Richland, Washington).

100% of the response at m/z 101 is due to ^{101}Ru . The corresponding response for ^{99}Ru can then be calculated and subtracted from m/z 99. The difference at m/z 99 is assumed to be due to ^{99}Tc .

- 3.4 Use of ^{97}Tc as a tracer and subsequent analysis by ICP-MS may be subject to isobaric interference due to ^{97}Mo . Most (about 99%) of the Mo should be separated out in the 1 M HNO_3 wash. Any remaining Mo can be corrected for based on the ratio of ^{97}Mo to ^{95}Mo .

4.0 Safety

No safety issues beyond traditional laboratory bench safety precautions are indicated.

5.0 Apparatus and Materials

5.1 Preparation for LSC

- TEVA•Spec[®] resin, pre-packed columns, top frit replaced with glass wool (so resin can be extruded later) or TEVA•Spec[®] resin prepared in another suitable column geometry
- Liquid scintillation counter
- LSC polyethylene vial
- Amberchrom[™] CG71 resin (TosoHaas), or Prefilter material (Eichrom)

5.2 Preparation for ICP-MS

- TEVA•Spec[®] resin, pre-packed columns or TEVA•Spec[®] resin prepared in another suitable column geometry
- Polyethylene bottle, 1 L
- Disposable column, 50 mL

6.0 Reagents

6.1 Preparation for LSC

- Nitric acid, 1 M

- Hydrogen peroxide, 30%
- Scintillation cocktail, e.g., Insta-Gel XR™, or Ultima-Gold XR™
- ^{99}Tc spike

6.2 Preparation for ICP-MS

- Nitric acid, 1 M and 11 M
- Hydrogen peroxide, 30%
- Ammonium citrate, various concentrations for neutralization
- Suitable tracer, e.g., $^{95\text{m}}\text{Tc}$, ^{97}Tc , etc.

7.0 Sample Collection and Preservation

Samples should be collected in glass or plastic bottles; acidification is not necessary; refrigeration is suggested.

8.0 Procedure

8.1 Preparation for Liquid Scintillation Counting

This method has been tested with the following yield determination process: each sample is prepared in duplicate, one of which is spiked with ^{99}Tc ; the chemical recovery is determined from the spike recovery of the duplicate.

- 8.1.1 Ten milliliters of H_2O_2 are added to each sample {up to 30 mL H_2O_2 may be added to large (e.g., 1-L samples)}; the sample is covered with a watch glass and heated to about 90°C for about 1 h, or until bubbling stops.

This step will destroy most organics, oxidize the technetium to pertechnetate, and will then destroy excess H_2O_2 . If H_2O_2 is not destroyed, bubbling in the column will occur.

- 8.1.2 To further remove organic material, the sample is passed through an Amberchrom™ CG71 resin (6 mm by 50 mm). (This can be set up in series with the TEVA•Spec® column.)

Filtering the sample before loading on the column may be required, depending on the presence of insoluble matter.

- 8.1.3 The sample is then passed through TEVA•Spec[®] resin.

Pertechnetate is strongly absorbed by the resin.

A typical gravity feed flow rate may be about 0.5 to 0.8 mL/min.

- 8.1.4 The column is washed with about 50 mL of 1 M HNO₃, which is then discarded.

- 8.1.5 The resin from the column is transferred to a polyethylene scintillation vial. This can be done as follows. The glass wool at the top of the column is removed. The column is cut open near the bottom frit with a razor blade. The entire column is rinsed into a liquid scintillation vial with four 1-mL aliquots of distilled water.

- 8.1.6 Ten milliliters of scintillation cocktail are added to the sample.

- 8.1.7 The vial is vigorously shaken for several minutes (this results in a gelatinous material in the case of Insta-Gel[™]). The vial is tapped on the bench to cause the gel sticking to the inside cap to drop down with the bulk of the material.

The resin should be evenly dispersed in the cocktail; if not, mixing should continue.

- 8.1.8 The LSC counting efficiency is determined from a known ⁹⁹Tc standard that is prepared by mixing the equivalent amount of resin, water, and scintillation cocktail used for each sample in an LSC vial. A blank is prepared the same way, but without the ⁹⁹Tc standard.

- 8.1.9 The samples and standards are then counted by LSC.

Because the standards and samples are prepared similarly, the quenching should also be similar. If the quench factor does differ significantly, a quench curve may need to be generated (refer to method RI100) to quantify the results.

8.2 Preparation for ICP-MS

- 8.2.1 The pH of a known aliquot of sample is checked and neutralized if necessary with ammonium citrate to pH 7.
- 8.2.2 The sample is spiked with an appropriate amount of ^{95m}Tc or ^{97}Tc as a recovery tracer. A 100% tracer recovery standard should be prepared at this time by pipetting an appropriate amount of tracer into an appropriate geometry.
- 8.2.3 Ten milliliters of H_2O_2 are added to each sample {up to 30 mL H_2O_2 may be added to large (e.g., 1 L) samples}; the sample is covered with a watch glass and heated to about 90°C for about 1 h or until bubbling stops.

This step will destroy most organics, oxidize the technetium to pertechnetate, and will then destroy excess H_2O_2 . If H_2O_2 is not destroyed, bubbling in the column will occur.

- 8.2.4 The sample is passed through a pre-packed TEVA•Spec[®] column.

This can be accomplished as follows. The sample is transferred to a 1-L polyethylene bottle. To the mouth of the bottle, a 50-mL disposable column is attached (this allows for the needed size reduction to the Eichrom column) followed in line by the pre-packed TEVA•Spec[®] column. The assembly is then inverted to commence sample flow. Imperfections in connections usually provide enough air exchange for satisfactory sample flow. Pinholes may be punched in the top of the polyethylene bottle to improve the flow rate.

A typical flow rate may be about 0.5 to 0.8 mL/min.

- 8.2.5 The column is washed with approximately 10 to 20 mL of water.

If using ^{97}Tc as a tracer, 50 mL 1 M HNO_3 should be used instead of water to wash the column, thus improving separation of Ru and Mo from Tc.

- 8.2.6 Technetium is eluted with 20 mL 11 M HNO_3 .

Lower HNO_3 concentrations can be used with slightly less efficiency in Tc recovery. A recovery of 91% has been found for elution with 30 mL of 4 M HNO_3 (Beals 1992). Figure 1 should be referred to for the acid dependency of k' .

- 8.2.7 The sample is brought to a known volume by sub-boiling evaporation or dilution such that the final HNO_3 concentration is low ($\leq 2 \text{ M}$).

Low HNO_3 concentrations will reduce the background for ICP-MS determination.

- 8.2.8 The chemical recovery is determined by counting the entire sample or an aliquot for $^{95\text{m}}\text{Tc}$ by gamma energy analysis, or by analysis of ^{97}Tc during the ICP-MS determination. The ^{99}Tc is then analyzed by ICP-MS.

9.0 Calculations

9.1 Technetium Activity by LSC Determination

$$\text{Yield} = \frac{(\text{spike sample CR} - \text{unspiked sample CR})}{E \cdot \text{DR}}$$

where

CR = count rate

E = counting efficiency from the standard prepared in steps 8.1.8

DR = disintegration rate of added ^{99}Tc spike

$$\text{where } ^{99}\text{Tc activity} = \frac{\text{net cpm}}{E \cdot V \cdot Y} \cdot K$$

where

net cpm = gross (unspiked) sample count rate - background count rate

V = sample volume (L)

Y = yield

K = factor to convert to the desired reporting units

9.2 Technetium Activity by ICP-MS Determination

$$\text{Yield} = \frac{\text{tracer } T_{\text{C sample}}}{\text{tracer } T_{\text{C standard}}}$$

$$^{99}\text{Tc activity (pCi/L)} = \frac{^{99}\text{Tc}_{\text{ICP-MS}}}{Y} \cdot K \cdot R$$

where

$\text{tracer } T_{\text{C sample}}$ = activity of $^{95\text{m}}\text{Tc}$ or ^{97}Tc in the sample

$\text{tracer } T_{\text{C standard}}$ = activity of $^{95\text{m}}\text{Tc}$ or ^{97}Tc in the 100% standard

$^{99}\text{Tc}_{\text{ICP-MS}}$ = ^{99}Tc concentration determined by ICP-MS in ng/mL

K = factor to convert ng $^{99}\text{Tc/mL}$ to desired reporting units

Y = yield

R = Ru correction factor:

$$\frac{\text{counts @ 99} - (\text{known } ^{99}\text{Ru}/^{101}\text{Ru ratio} \cdot \text{counts @ 101})}{\text{counts @ 99}}$$

10.0 Quality Control

A reagent blank and blank spike, as a minimum, should be run with each analytical batch.

11.0 Method Performance

Decontamination factors of selected elements are presented in Table 1 (Sullivan et al. 1991; Beals 1992). The radioisotopes were added to 1-L water samples, and processing proceeded according to the LSC sample preparation. The Mo and Ru decontamination was determined with solutions containing 10 ng/mL Mo and Ru and 1.4 pg/mL ^{99}Tc , which were processed according to the ICP-MS sample preparation.

Table 1. Decontamination Factors of Selected Elements

Isotope	Decontamination Factor
^{137}Cs	>1800
^{14}C	>9000
^{90}Sr	>1300
^{32}P	>100
^{35}S	>1100
Mo	>100
Ru	>250

Figure 1 shows the acid dependency of k' for Tc, Pu, Np, Th, U, and Am {Eichrom Industries, Inc. 1991. "Extraction Chromatographic Material for Rapid Separation of Tetravalent Actinides" (TEVA•Spec[®] product brochure), 8205 S. Cass Ave., Suite 107, Darien, Illinois 60559}. Calculation of chemical recovery by standard addition results in recoveries typically better than 80% with a range of 80% to 98% ($n = 30$). Calculation of chemical recovery by use of $^{95\text{m}}\text{Tc}$ tracer indicates recoveries of 96.4% to 101.7% (mean = 98.9%, $n = 4$) can be obtained^(a).

Precision is typically better than $\pm 10\%$. The detection limit for the LSC method is 0.04 Bq/L (1 pCi/L) for a 1- L sample, count time of 30 min, with a background count rate of 12.2 cpm. The detection limit determined by ICP-MS analysis is approximately 0.007 Bq/L (0.2 pCi/L) (1- L sample size).

(a) A draft document by E. J. Wyse and S. K. Fadeff entitled *Alternative Techniques for the Determination of Technetium-99 in Groundwaters: ICP-MS and Extraction Resin*. To be submitted for publication.

Figure 1. Acid Dependency of Various Elements on TEVA•Spec®

12.0 References

Beals, D. M. 1992. "Determination of Technetium-99 in Aqueous Samples by Isotope Dilution Inductively Coupled Plasma-Mass Spectrometry." Proceedings of the 3rd International Conference on Nuclear and Radiochemistry, Vienna, Austria.

Sullivan, T., D. Nelson, and E. Thompson. 1991. "Determination of Technetium-99 in Borehole Waters Using An Extraction Chromatographic Resin." Presented at the 37th Annual Conference on Bioassay, Analytical and Environmental Radiochemistry, Ottawa, Canada.

13.0 For Further Information

Anders, E. 1960. *The Radiochemistry of Technetium*. AEC Report, NAS-NS-3021.

14.0 Reviewer Suggestions

Technetium may be stripped from the TEVA•Spec® column and a small aliquot sampled for subsequent analysis by LSC.

A radioisotope tracer, such as ^{97}Tc or $^{99\text{m}}\text{Tc}$, may be of use when performing LSC analysis as opposed to performing a duplicate spike analysis.

RP580^(a)**Water Distillation from Soil and Aqueous Matrices Using a Micro-Distillation System for Tritium Determination**

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method describes the distillation of tritiated water from large (6 g to 50 g) and small (less than 5 g) soil samples and small volume (less than 3 mL) water samples. The weight percent moisture of soil must be known or will need to be determined to calculate the water recovery factor from soil. The method has been tested with the soil types around the Hanford site and with performance evaluation water samples from the Environmental Monitoring System Laboratory (EMSL) and the Environmental Measuring Laboratory (EML). The method is effective in separating ^3H from other radionuclides and results in a virtually unquenched sample for subsequent liquid-scintillation counting.

2.0 Summary of Method

A known mass of soil is placed in a round-bottomed flask or MICRO DIST[®] tube (depending on sample size), a layer of activated charcoal is added on top, and the void space is filled with glass wool. Water is added to the sample as a carrier. The sample is heated, and the water is distilled and collected above the Gortex[®] membrane of a MICRO DIST[®] tube. The distillation efficiency is determined by the mass of water recovered. An aliquot of the distillate is analyzed by liquid scintillation for ^3H activity.

Water analysis is performed similarly to soil. About 3 mL of water are added directly to the MICRO DIST[®] tube. The solution is made basic with NaOH, and organics are adsorbed with activated charcoal or are oxidized with KMnO_4 . The assembly is heated to distill the water that collects above a Gortex[®] membrane of the MICRO DIST[®] tube. A sample of the distillate is analyzed by liquid scintillation for ^3H activity.

^(a) This method was consolidated by S. K. Fadeff from procedures supplied by S. Catlow (Westinghouse Hanford Company, Richland, Washington), S. K. Fadeff and R. S. Strebin (Pacific Northwest Laboratory, Richland, Washington), and the *DOE Procedures Database* (Los Alamos, New Mexico).

3.0 Interferences

- Other volatile radionuclides may be distilled with the water. This problem is minimized by distilling from a basic solution (in the case of waters), and by adding activated charcoal above the sample (in the case of soils).
- Originally bound ^3H in soil may not be distilled, resulting in a potentially low bias.

4.0 Safety

The MICRO DIST[®] tubes will become pressurized during the course of distillation. This does not pose a problem by itself; however, the tube should be broken along the breakage ring with the break directed into the fume hood. The pressure release will then be directed away from the analyst.

5.0 Apparatus and Materials

- Round bottom flask, e.g., 25 mL (for large soil samples)
- Variac
- Heating mantle to fit round bottom flask
- Glass adapter for round-bottom flask and MICRO DIST[®] tubes
- MICRO DIST[®] empty tubes (Lachat Instruments, Milwaukee, Wisconsin), or equivalent
- Liquid scintillation counting (LSC) vials, plastic
- Heating block, for MICRO DIST[®] tubes with temperature controller (Lachat Instruments, Milwaukee, Wisconsin), or equivalent
- Press for sealing the MICRO DIST[®] tube assembly (Lachat Instruments, Milwaukee, Wisconsin)

6.0 Reagents

All reagents are prepared from analytical reagent-grade chemicals.

- “Dead” water - low tritiated water
- LSC cocktail - Ultima-Gold[™] or equivalent

- Powdered activated charcoal
- Sodium hydroxide (NaOH), pellets
- Potassium permanganate (KMnO₄), solid

7.0 Sample Collection, Preservation, and Handling

Samples should be collected in glass to minimize evaporative loss of water. No refrigeration is required; however, the samples in storage should not be subjected to high temperatures (e.g., above 25°C), again to minimize evaporative loss of water.

8.0 Procedure

8.1 Determination of Solids Content in Soil. Soil used to determine the solids content cannot be used for subsequent ³H analysis.

- 8.1.1 The tare mass of a clean beaker (e.g., 250 mL) is determined.
- 8.1.2 Approximately 10 g of soil are transferred to the beaker, spreading evenly across the beaker surface.
- 8.1.3 The gross beaker mass is determined, and the net soil mass is calculated.
- 8.1.4 The beaker is placed into an oven at ~110°C overnight or heated on a low setting on a hotplate overnight.
- 8.1.5 The beaker is removed from the oven or hotplate, and the soil is allowed to cool.
- 8.1.6 The gross mass of the beaker plus dried soil is determined.
- 8.1.7 The beaker is returned to the hot plate or oven and heated for an additional 3 h. The sample is cooled and reweighed. If the mass is not the same as the previously recorded mass, this step should be repeated until a constant mass (within ~1%) is obtained.

8.2 Distillation of Tritium from Soil (greater than 5 g)

- 8.2.1 The tare weight of a round-bottom flask is recorded.
- 8.2.2 Soil (e.g., 50 g) is added to the flask, and the gross mass is determined.

- 8.2.3 Approximately 5 g of water (“dead” water or Milli-Q water, precisely known) are added to the sample.

To prepare the spike, a known volume of tritiated water is added to the 5 g of water before adding it to the soil.

- 8.2.4 Powdered activated charcoal is added such that it covers the surface of the soil. The remaining void space, including the adaptor, is filled with glass wool. (This will prevent the soil and/or charcoal from contacting the Gortex[®] membrane.)
- 8.2.5 The tare mass of a MICRO DIST[®] tube is determined.
- 8.2.6 The MICRO DIST[®] tube is inserted into the glass adaptor. The MICRO DIST[®] tube/adaptor assembly is inserted into the neck of the flask. Insulating material (e.g., glass wool with foil covering) is wrapped around the top of the flask, glass adaptor, and MICRO DIST[®] tube up to the Gortex[®] membrane.
- 8.2.7 The sample is heated (distilling water into the MICRO DIST[®] tube) for about 0.5 to 3 h (until bubbling stops in the MICRO DIST[®] tube or sufficient water volume is recovered) with the variac set to ~85%. This should correspond to a distillation temperature of ~130°C once the pressure inside the flask comes to equilibrium.
- Approximately 3 to 4 mL of water are generally distilled.*
- 8.2.8 After distillation, and while the vessel is hot, the flask neck is pointed into the hood, away from the analyst, and the adaptor is removed from the flask.
- This must be done while the flask is still hot so as not to reduce pressure in the flask, thus causing the distilled water to be drawn back into the flask. (If the distillate is drawn back into the flask, the distillation may be repeated.) When the units are disjoined, a positive pressure will be released. The glass-wool layer will prevent the spread of soil and charcoal into the hood when the pressure is released.*
- 8.2.9 The adaptor is removed from the MICRO DIST[®] tube, the MICRO DIST[®] tube is cooled to room temperature, and the MICRO DIST[®] tube plus water distillate mass is determined.
- 8.2.10 The upper section tube is cut or broken in half along the breakage ring; care should be taken to avoid spilling the distillate.

- 8.2.11 An appropriate aliquot (e.g., 1 mL) of the distillate is pipetted into an LSC vial. The aliquot size will depend on the concentration of ^3H expected in the sample.
- 8.2.12 More water is added, if necessary, to bring the total aqueous volume to 1 mL. An appropriate amount (e.g., 15 mL) of LSC cocktail is added, and the sample is shaken thoroughly.

The 1-mL to 15-mL water-to-cocktail volume ratio is optimum for Ultima-Gold™. The aqueous and cocktail volumes may be changed as deemed necessary; however, the aqueous-to-cocktail volume ratio must be consistent for the samples and standards.

- 8.2.13 A background sample is prepared by adding LSC cocktail to 1 mL of water. Counting efficiency standards are prepared in the same way, except that a known volume of ^3H spike is added such that the final aqueous volume is the same as that of the samples and blank.

The note in step 8.2.12 should be referred to if aqueous and cocktail volumes of samples are changed.

- 8.2.14 The sample is ready for ^3H determination by LSC.

8.3 Distillation of Tritium from Soil (less than or equal to 5 g)

- 8.3.1 The heating block is turned on, and the thermostat setting is adjusted to provide a temperature of 115°C to 135°C.
- 8.3.2 The tare weight of the lower sample vial section of the MICRO DIST® tube is determined.
- 8.3.3 Soil (e.g., 5 g) is added to the MICRO DIST® tube sample section, and the gross mass is determined.
- 8.3.4 Approximately 5 g of water ("dead" water or Milli-Q water, volume precisely known) are added to the sample.

To prepare the spike, a known volume of tritiated water is added to the 5 g of water before adding it to the soil.

- 8.3.5 Activated charcoal is added to cover the surface of the soil. The remaining void space is filled with glass wool. (This will prevent the soil and/or charcoal from contacting the Gortex® membrane on disassembly of the apparatus.)

It is important to avoid contaminating the Gortex® membrane of the MICRO DIST® tube. Contamination can be avoided by adding no more than 5 g of soil to the tube. If contamination does occur, the tube may be replaced.

- 8.3.6 The upper section of a tared distillation tube is placed on the sample vial section; these are pressed until they lock together. The assembly is transferred to the heating block.
- 8.3.7 The sample is heated until over 1 mL of water has distilled into the collection section (generally 30 to 45 min).
- 8.3.8 Using leather gloves or some other means of protecting the hands from the heat of the MICRO DIST® tube assembly (~100°C), the assembly is removed from the heating block, and the upper and lower sections are quickly separated such that the break points away from the analyst and into the fume hood.

If this separation is not performed quickly, while the system is hot, the distilled water fraction will be drawn back down into the lower section. If the distillate is drawn back into the lower section, the distillation may be repeated.

- 8.3.9 The distilled fraction is cooled, and the gross MICRO DIST® tube mass is determined.
- 8.3.10 The upper section tube is cut or broken in half along the breakage ring; care should be taken to avoid spilling the distillate.
- 8.3.11 An appropriate aliquot (e.g., 1 mL) of the distillate is pipetted into an LSC vial. The aliquot size will depend on the concentration of ³H expected in the sample.
- 8.3.12 Enough water is added, if necessary, to bring the total aqueous volume to 1 mL. An appropriate volume (e.g., 15 mL) of LSC cocktail is added, and the sample is then shaken thoroughly.

The 1-mL to 15-mL water-to-cocktail volume ratio is optimum for UltimaGold™. The aqueous and cocktail volumes may be changed as deemed necessary. The aqueous-to-cocktail volume ratio must be consistent for the samples and standards.

- 8.3.13 A background sample is prepared by adding 15 mL of LSC cocktail to 1 mL of water. Counting efficiency standards are prepared in the same way, but a known volume of ³H spike is also added such that the final aqueous volume is the same as that of the samples and blank.

The note in step 8.3.12 should be referred to if aqueous and cocktail volumes of samples are changed.

8.3.14 The sample is ready for ^3H determination by LSC.

8.4 Distillation of Tritium from Aqueous Matrices

8.4.1 The heating block is turned on, and the thermostat setting is adjusted to provide a temperature of 115°C to 135°C.

8.4.2 Approximately 4 to 5 mL of sample are added to the sample vial section; the exact quantity does not need to be known. For spiked samples, the exact sample volume *does* need to be known/recorded.

8.4.3 The pH is adjusted to basic by adding a small amount of solid NaOH. A small amount (to give a light purple color) of solid KMnO_4 is added to oxidize organics, or activated charcoal may be added to absorb organics. The actual amounts added are not critical.

It is important to avoid contaminating the Gortex[®] membrane of the MICRO DIST[®] tube. Contamination can be avoided by adding no more than 5 mL of liquid to the tube. If contamination does occur, the MICRO DIST[®] tube should be replaced.

8.4.4 Using the lower section of a clean MICRO DIST[®] tube, the Gortex[®] filter is pushed up the tube (~1 cm). This reduces the chance of filter contamination by the sample.

8.4.5 The upper section of the distillation tube is placed on the sample vial section, and the assembly is pressed until the parts lock together. The assembly is transferred to the heating block.

8.4.6 The sample is heated until 1 to 3 mL of water have distilled into the collection section.

8.4.7 Using leather gloves or some other means of protecting the hands from the heat of the MICRO DIST[®] tube assembly (~100°C), the assembly is removed from the heating block, and the upper and lower sections are quickly separated such that the break points away from the analyst and into the fume hood.

If this separation is not performed quickly, while the system is hot, the distilled water fraction will be drawn back down into the lower section.

- 8.4.8 The distilled fraction is cooled.
- 8.4.9 The upper section tube is cut or broken in half along the breakage ring; care should be taken to avoid spilling the distillate.
- 8.4.10 An aliquot of the distillate (e.g., 1 mL) is pipetted into an LSC vial. The aliquot size will depend on the concentration of ^3H expected in the sample.
- 8.4.11 Enough water is added, if necessary, to bring the total aqueous volume to 1 mL. An appropriate amount (e.g., 15 mL) of LSC cocktail is added, and the sample is shaken thoroughly.

Note: The 1-mL to 15-mL water-to-cocktail volume ratio is optimum for Ultima-Gold™. The aqueous and cocktail volumes may be changed as deemed necessary. The aqueous-to-cocktail volume ratio must be consistent for the samples and standards.

- 8.4.12 A background sample is prepared by adding 15 mL of LSC cocktail to 1 mL of water. Counting efficiency standards are prepared in the same way; however, a known volume of ^3H spike is added such that the final aqueous volume is the same as that of the samples and blank.

The note in step 8.4.11 should be referred to if aqueous and cocktail volumes of samples are changed.

- 8.4.13 The sample is ready for ^3H determination by LSC.

9.0 Calculations

9.1 Determination of Water Content of the Soil

$$\text{water}_{\text{soil}} = \text{wet}_{\text{mass}} - \text{dry}_{\text{mass}}$$

where:

$$\text{water}_{\text{soil}} = \text{mass of water in sample aliquot}$$

$$\text{dry}_{\text{mass}} = \text{mass of dry sample}$$

$$\text{wet}_{\text{mass}} = \text{mass of sample as received}$$

9.2 Determination of Soil Sample Activity

$$A_{\text{soil}} = \frac{(CR_{\text{smp1}} - CR_{\text{bkg}})}{E \cdot M} \cdot \frac{m_i}{m_s} \cdot C$$

where:

A_{soil} = sample activity

CR_{smp1} = sample count rate

CR_{bkg} = background count rate

E = detection efficiency {e.g., (standard count rate)/(standard disintegration rate)}

M = sample mass analyzed, g

m_i = mass of water in original sample ($\text{water}_{\text{soil}}$) plus water added as carrier, g

m_s = mass of water sampled for LSC, g

C = conversion factor to adjust to the desired reporting units

9.3 Determination of Water Sample Activity

$$A_{\text{soil}} = \frac{(CR_{\text{smp1}} - CR_{\text{bkg}})}{E \cdot V_s} \cdot C$$

where:

A_{water} = sample activity

V_s = sample volume prepared for LSC

10.0 Quality Control

The following criteria are generally used to determine if the data from an analytical batch are acceptable.

- The distilled water fraction should not have the purple color of KMnO_4 . If the distillate is colored purple, then the sample is assumed to have contacted the filter and contaminated the distillate.
- It is recommended that one reagent blank, one sample duplicate, and one blank spike or matrix spike be run with each analytical batch to provide an estimate of the bias and precision.
- The spectrum should show minimal interference from other beta-emitting peaks in the ^3H region. The presence of other beta emitters may be evaluated by quantifying the energy region from 20 keV to 2000 keV in addition to their tritium region.

11.0 Method Performance

Results of the water distillation method applied to two EMSL performance evaluation (PE) samples are presented in Table 1.

Known Value (Bq/L)	Analytical Result (Bq/L)	Bias	n
364.2 $\pm$ 36.4	371.3 $\pm$ 58.9	+1.9%	3
273.7 $\pm$ 27.4	272.8 $\pm$ 6.2	-0.3%	3

12.0 Source Procedures

Catlow, S. 1992. "Tritium by Lachat Micro-DistTM and Liquid Scintillation Counting," LA-218-114, Westinghouse Hanford Company, Richland, Washington.

Fadoff, S. K., and R. S. Strebin, Jr. 1993. "Tritium Determination in Soil and Water Using a Lachat Micro-DistTM System," PNL-ALO-418, PNL-MA-599, Pacific Northwest Laboratory, Richland, Washington.

Los Alamos National Laboratory (LANL). "Extraction of Tritated Water from Soil Samples for Liquid Scintillation Counting." *DOE Procedures Database*. Los Alamos, New Mexico. {Taken from: U. S. Department of Energy (DOE). 1989. *The Environmental Survey Manual*. Appendix D - Part 4 (Radiochemical Analysis Procedures), Second edition. DOE/EH-0053.}

RP710^(a)

Laboratory Method for Gross Alpha and Beta Activity Determination

1.0 Scope and Application

This method is used to rapidly screen a variety of matrices for both high and low activities of alpha and beta emitting radionuclides in waters, air filters, soils, sludges, waste waters, and solvents. The purpose of this method is three-fold: 1) to provide adequate information concerning the activity within samples, and thus determine if further, more detailed analyses are required, 2) to support accountability of radioactive material and ensure that a receiving laboratory's radioactive materials licenses or limits are not exceeded, and 3) to ensure that Department of Transportation regulations concerning the transport of radioactive materials have not been exceeded.

Gross screening analyses are not expected to be as accurate nor as precise as more detailed radiochemical separations. Rather, they are intended to provide rapid information associated with a particular action level with minimal chemical preparation. Additionally, these types of analyses are not intended to give "absolute" activity measurements, but rather "order-of-magnitude" estimates.

This method is intended to be complementary to other gross alpha/beta "rapid" screening methods, such as field methods or certain liquid scintillation methods. It is intended to provide more detailed information when samples are thought (or known) to be close to a given action level. In addition, this method does not produce any by-products (other than the sample itself), an advantage as opposed to liquid scintillation methods (i.e., scintillation cocktail).

2.0 Summary of Method

Samples are leached with acids, and organic matter is oxidized, if necessary. An aliquot of the sample or leachate is then evaporated to dryness on a stainless steel planchet and counted for alpha and/or beta radioactivity on a low-background gas-flow proportional counter. Calculated activities depend on sample mass and are based on calibration of specific isotopic standards.

(a) This method was consolidated by W. P. Brug (Los Alamos National Laboratory, Los Alamos, New Mexico). Appendixes 1 and 2 were prepared in collaboration with K. D. McCroan (National Air Radiation Environmental Laboratory, Montgomery, Alabama).

3.0 Interferences and Limitations

The problems discussed below should be recognized as inherent interferences and limitations of the method.

- High hygroscopic salt content in evaporated samples can cause the sample mass to fluctuate due to moisture absorption. To minimize this interference, the salts are converted to oxides by heating the sample intensely until it glows with a characteristic dull-red color.
- Self-absorption and scattering will occur when large mass, high density solid samples are analyzed for gross alpha activity.
- Volatile radioisotopes of C, ^3H , Tc, Po, Cs, and adsorbed Rn may be lost when samples are heated, especially to a dull-red heat.
- The crosstalk correction method for differentiating beta from alpha radiation may not adequately protect from misidentification for samples containing very low-energy alpha or high-energy beta energies.
- Moderate to high levels of gamma radiation can be misinterpreted as alpha or beta activity by gas-flow proportional counters; this interference can be minimized by using a guard detector and employing anti-coincident counting techniques.
- Proportional counters operated in the “windowed” mode are limited to detecting (beta) particles with an energy of 0.1 MeV or greater. To detect “soft” betas, the counter must be operated in the “windowless” mode.

4.0 Safety

Samples may contain a variety of hazards in addition to radioactivity and should be handled accordingly. Reagents and apparatus used in this method are standard for chemistry labs, and counting rooms and standard safety practices apply. For more information, one may refer to Chapter 4, Safety.

5.0 Apparatus and Materials

5.1 Sample Preparation

- Infrared heating lamp
- Hotplate

- Transfer pipettes
- Glass (Pyrex or equivalent) beakers
- Watch glasses to fit beakers
- Mylar film: 0.0064-mm (0.00025-in.) maximum thickness; or acrylic solution: 50-mg Lucite dissolved in 100-mL acetone, or other appropriate means to fix activity to planchet
- Stainless steel planchets
- Centrifuge and centrifuge tubes or filtering apparatus

5.2 Sample Counting

- Gas flow proportional counting system or scintillation detection system
- Guard detector operated in the anti-coincidence mode (usually a part of a typical proportional counter)
- Ionizing gas (counter specific, P-10 for example)

6.0 Reagents

- Nitric acid (conc, 70%)
- Nitric acid (12 M) • hydrochloric acid (1 M), store in a polyethylene bottle
- Nitric acid (8 M)
- Hydrochloric acid (conc)
- Hydrogen peroxide (30%)

7.0 Sample Collection, Preservation, and Storage

Aqueous samples should be acidified with HNO_3 so that the pH is less than 2. Adding the acid precludes the formation of precipitates and thus analyte loss. In addition, lowering the pH will minimize the adsorption of radionuclides on container walls by creating relatively non-polar surfaces.

No preservation is necessary for soil, sludge, air filter, or organic samples before analysis.

8.0 Procedure

Aliquot size. A general guideline for the aliquot size is that it should be chosen such that the coverage density (g/cm^2) on the planchets does not exceed $5 \text{ mg}/\text{cm}^2$ for gross alpha determinations and $10 \text{ mg}/\text{cm}^2$ for gross beta determinations.

Sample drying. The sample should be heated carefully so spattering does not occur. To avoid spattering, samples are first heated with a low temperature, and then the temperature is slowly ramped upwards. If the mass of the sample fluctuates or appreciable salt content is expected, the mass should be stabilized by heating the sample until it glows with a characteristic dull red color, which converts the hygroscopic salts into their respective oxide forms.

Fixing activity to planchet. Some sample residues contain particles that can become airborne and thus need to be fixed to the planchet to prevent sample cross-contamination and/or detector contamination (especially when counting in the “windowless” mode). Suggestions include covering the sample with a thin (0.0064-mm thickness) mylar film, or treating it with an acrylic solution (e.g., a few drops of 50-mg Lucite dissolved in 100 mL acetone). Whatever technique is employed (if any), the efficiency curves and crosstalk curves generated should be based on the sample configuration.

8.1 Waters

The waters analysis method presented here is intended to be equivalent to other standard methods {SW-846 Method 9310 (EPA 1986); EPA Method 900.0 (EPA 1980); *Standard Methods for the Examination of Waters and Wastewaters* Method 7110 (Clesceri et al. 1992)}.

8.1.1 If the sample is known or suspected to contain significant chloride (acid or salts), the chloride should be converted to nitrate before transferring to a stainless steel planchet. (*Chlorides will attack the stainless steel, depositing heavy metal ions on top of the sample, thereby increasing inelastic scattering. Subsequently, no correction can be made for this effect.*) Chloride salts can be converted to nitrates by adding 5 mL 16 M HNO_3 and evaporating to near dryness (chloride ions will be oxidized to gaseous chlorine). One repeat of this step is usually sufficient.

8.1.2 A sample should be evaporated directly on a tared counting planchet, or for larger samples, it should be evaporated in a beaker and transferred quantitatively to a counting planchet, using 8 M HNO_3 to wash down beaker walls.

- 8.1.3 The sample is dried by heating on a hot plate or under an infrared lamp. If hygroscopic salts are present, the sample should be heated until it glows with a characteristic dull red color to stabilize the mass.
- 8.1.4 The dried planchet is weighed, and the net residue mass is determined.
- 8.1.5 The sample is fixed to the planchet, if necessary, and counted for an appropriate time.

8.2 Sludge

- 8.2.1 An aliquot of sludge is placed into a tared beaker, and the wet weight is determined if required. The sample is dried (under an infrared lamp or drying oven for example) and weighed to determine the dry weight.
- 8.2.2 Approximately 40 mL of 12 M HNO_3 • 1 M HCl are added to 1 g of dried sample (i.e., 0.5 g of dried sample requires approximately 20 mL of acid solution). The sample is covered with a watchglass and digested on a hotplate for about 20 min.
- 8.2.3 The sample is removed from the hotplate, and the leachate is separated by centrifuging, filtering, or decanting.
- 8.2.4 Steps 8.2.2 and 8.2.3 are repeated. The resultant leachates are combined.
- 8.2.5 Approximately 20 mL of 8 M HNO_3 per 1 g of dried sample are added to the remaining residue in the beaker. The sample is covered with a watchglass and digested on a hotplate for an appropriate time (i.e., roughly 10 min).
- 8.2.6 After cooling, the leachate is separated by centrifuging, filtering, or decanting and is combined with the previously collected leachates and brought to a known volume with 8 M HNO_3 .
- 8.2.7 An aliquot of the leachate is dried onto a tared stainless steel planchet. The sample is heated until it glows with a characteristic dull red color to stabilize the mass, if necessary, and the sample is cooled. The residual weight is recorded.
- 8.2.8 The sample is fixed to the planchet, if necessary, and counted for an appropriate time.

8.3 Organics

This section is applicable to all organic samples that can be evaporated to dryness by simple convective heating; other samples, such as high boiling point organics and oils, should be determined by other methods.

- 8.3.1 An aliquot of the sample (e.g., 5 mL) is pipetted onto a tared stainless steel planchet.
- 8.3.2 The sample is dried by heating on a hot plate or under an infrared lamp. If hygroscopic salts are present, the sample is heated until it glows with a characteristic dull red color to stabilize the mass.
- 8.3.3 The dried planchet is weighed, and the net residue mass is determined.
- 8.3.4 The sample is fixed to the planchet, if necessary, and counted for the appropriate time.

8.4 Air Filters

- 8.4.1 The filters are mounted directly on a planchet (no chemical processing) with the loaded face of the filter exposed.
- 8.4.2 The sample is counted for an appropriate time.

8.5 Soils

- 8.5.1 An aliquot (e.g., 2 g) of homogenized soil is placed into an appropriately sized tared beaker, and the weight is determined. The soil may be dried (under a heat lamp for example) and the dry weight determined.
- 8.5.2 The sample is covered with conc HNO_3 , and 3 to 5 drops (per 1 g of dried sample) of conc HCl are added to the beaker. The sample is swirled carefully and allowed an appropriate amount of time (generally overnight) to leach at room temperature. Alternatively, the sample can be heated with stirring to reduce leaching time to about 30 min.
- 8.5.3 The sample is heated until the yellow-orange NO_2 fumes no longer appear, indicating HCl is no longer present.

- 8.5.4 The soil residue is separated from the leachate (e.g., by centrifuging, filtration, etc.). The soil residue is rinsed with (~ 5mL) 8 M HNO_3 , adding the rinse to the leachate.
- 8.5.5 The leachate is either quantitatively transferred to a tared planchet, or it is brought to a known volume, and an aliquot is transferred to a tared planchet.
- 8.5.6 The solution is evaporated on the planchet to dryness under a heat lamp. The heating rate is controlled so that the sample does not spatter.
- 8.5.7 The planchet is allowed to cool; then it is reweighed, and the weight is recorded.
- 8.5.8 The activity is fixed to the planchet, if necessary, and counted for an appropriate time.

8.6 Sewage, Waste Water, and Aqueous Slurries

- 8.6.1 An appropriate aliquot of the sample is poured into a tared beaker, reweighed, and the wet weight is determined.
- 8.6.2 The sample is evaporated to dryness and re-weighed. The dry weight is then determined.
- 8.6.3 The sample is heated on a hotplate and carefully treated with conc HNO_3 and H_2O_2 until all organic material has been oxidized.

The sample should not have a black tarry consistency (due to remaining organics), but may still have a grayish or reddish appearance. If the sample is black or tarry, the wet ashing (as described in the previous step) should continue to complete the oxidation of organics.

- 8.6.4 Approximately 20 mL of conc HNO_3 and approximately 10 mL of conc HCl are added, and it is boiled until all HCl has been driven off (the yellow-orange NO_2 fumes will no longer appear). Continued addition of conc HNO_3 and evaporation may be necessary to eliminate Cl^- from the matrix.
- 8.6.5 Evaporation is continued until approximately 3 mL of solution remain.
- 8.6.6 Approximately 10 to 15 mL of 8 M HNO_3 are added to the sample.
- 8.6.7 Any residue is separated from the leachate (e.g., by centrifuging, filtration, etc.). The residue is rinsed with 8 M HNO_3 , adding the rinse to the leachate.

- 8.6.8 The leachate is either quantitatively transferred to a tared planchet, or it is brought to a known volume, and an aliquot is transferred to a tared planchet.
- 8.6.9 The solution is evaporated on the planchet to dryness under a heat lamp. The heating rate is controlled so that the sample does not spatter.
- 8.6.10 The planchet is allowed to cool, reweighed, and the weight is recorded.
- 8.6.11 The activity is fixed to the planchet, if necessary, and counted for an appropriate time.

8.7 **Calibration and Standards** *(A more in-depth discussion of efficiency and crosstalk determination is presented in Appendix 1.)*

To ensure accurate measurements, it is necessary to determine both detector efficiency and crosstalk as a function of sample mass. (Efficiency determination as a function of sample mass is equivalent to determining a zero-mass efficiency with an associated self-absorption factor.) While most modern detector systems allow the crosstalk to be minimized via manual discriminator (or window) adjustment, it is only at the expense of reduced detection efficiency. If instrumental parameters are adjusted to minimize or eliminate crosstalk, crosstalk curves still need to be generated to ensure that crosstalk factors are negligible throughout the entire analytical sample mass range. Finally, when the sample mass exceeds coverage density guidelines, or crosstalk is deemed significant, the curves should be determined to generate the requisite correction factors. The same data used to generate the efficiency curves can also be used to generate the crosstalk curves.

- 8.7.1 Calibration standards should be prepared from matrices similar to those to be measured, and the mode of fixing the activity to the planchet should also be the same as that used for the sample. Two tracer solutions are used: one from a measured amount of any NIST traceable alpha emitting secondary standard (for example $^{238}\text{Pu}/^{239}\text{Pu}$) and the other from a measured amount of NIST traceable beta emitting standard (for example $^{90}\text{Sr}/^{90}\text{Y}$). *Some laboratories have suggested using a pure alpha emitting standard, such as ^{210}Po , to accurately determine alpha to beta crosstalk. Other alpha standards also have gamma and x-ray emissions associated with them, which will be detected as beta counts, and thus overestimate the crosstalk factor. Other laboratories argue that using standards that contain x-rays etc. more accurately represent real world samples and thus better estimate detector performance. If a measured sample contains no interferences (x-rays etc.), then the resultant activity will be underestimated. The decision of which type of standard to be used is left up to the individual laboratory, but one must be aware of the limitations associated with the choice selected.*

The resultant solutions should have sufficient activity so that acceptable counting statistics from a standard mount can be achieved with a reasonable count time. (For example 10,000 total counts have an associated 1% counting error, and 100 counts have a 10% counting error.)

8.7.2 To generate the calibration curves (alpha efficiency, beta efficiency, alpha-to-beta crosstalk, and beta-to-alpha crosstalk) as a function of sample mass, two groups of matrix (e.g., soil) standards (one for alpha and one for beta) are prepared with the same amount of radioactive tracer while the amount of residue is varied so that the masses encompass the target sample masses.

8.7.3 The individual measured alpha and beta efficiencies are calculated as follows:

$$\varepsilon_x(m) = \frac{N_x}{D_x}$$

where

$\varepsilon_x(m)$ = measured efficiency for mass, m
 x = α or β (dependent on the emission source)
 N_x = measured net count rate in channel x
 D_x = known disintegration rate for either an alpha or beta standard.

Additionally, the alpha to beta crosstalk factors are determined using the alpha standards, and the beta to alpha crosstalk factors are determined using the beta standards. These factors are calculated as follows:

$$X_{\alpha\beta}(m) = \frac{N_\beta}{N_\alpha}$$

$$X_{\beta\alpha}(m) = \frac{N_\alpha}{N_\beta}$$

where

$X_{\alpha\beta}(m)$ = alpha to beta crosstalk for mass m
 $X_{\beta\alpha}(m)$ = beta to alpha crosstalk for mass m
 N_α = measured net alpha counts
 N_β = measured net beta counts.

8.7.4 Equations or graphical plots should be derived to describe all four calibration curves (note: these curves are generally not linear). This is usually done with the help of a computer or some plotting device. Therefore, the desired data for any arbitrary sample mass can be interpolated from any one of these curves.

9.0 Calculations *(A more complete and rigorous discussion of the calculations is provided in Appendix 2.)*

If crosstalk has been determined to be negligible, then all the references to $X_{\alpha\beta}$ and $X_{\beta\alpha}$ are equal to zero and thus can be disregarded. However, the crosstalk forms of the equations are the most general.

9.1 The crosstalk corrected net count rates are calculated by the following equations:

$$N_{x\alpha} = \left(\frac{C_\alpha}{t_{C_\alpha}} - \frac{B_\alpha}{t_{B_\alpha}} \right) - X_{\beta\alpha}(m) \left(\frac{C_\beta}{t_{C_\beta}} - \frac{B_\beta}{t_{B_\beta}} \right)$$
$$N_{x\beta} = \left(\frac{C_\beta}{t_{C_\beta}} - \frac{B_\beta}{t_{B_\beta}} \right) - X_{\alpha\beta}(m) \left(\frac{C_\alpha}{t_{C_\alpha}} - \frac{B_\alpha}{t_{B_\alpha}} \right)$$

where

$N_{x\alpha}$ and $N_{x\beta}$	=	crosstalk corrected net alpha and beta count rates, respectively
C_α and C_β	=	measured alpha and beta sample counts
t_{C_α} and t_{C_β}	=	alpha and beta sample count time
B_α and B_β	=	measured alpha and beta background counts
t_{B_α} and t_{B_β}	=	alpha and beta background count time
$X_{\alpha\beta}$ and $X_{\beta\alpha}$	=	alpha to beta crosstalk and beta to alpha crosstalk for a given mass, m .

9.2 The equations for the alpha activity, A_α , and the beta activity, A_β are

$$A_\alpha = \frac{N_{x\alpha}}{\epsilon_{x\alpha}(m) \cdot Q} \cdot k$$
$$A_\beta = \frac{N_{x\beta}}{\epsilon_{x\beta}(m) \cdot Q} \cdot k$$

where

A_α	=	alpha activity
A_β	=	beta activity
$N_{x\alpha}$	=	crosstalk corrected net alpha count rate
$N_{x\beta}$	=	crosstalk corrected net beta count rate
k	=	factor to convert to the desired reporting units

Q	=	sample size (volume or mass)
$\varepsilon_{X\alpha}(m)$	=	crosstalk corrected alpha detector efficiency at mass m
$\varepsilon_{X\beta}(m)$	=	crosstalk corrected beta detector efficiency at mass m .

Note: the crosstalk corrected efficiencies are given by

$$\varepsilon_{X\alpha} = \varepsilon_{\alpha}(m) \cdot [1 - X_{\alpha\beta}(m) X_{\beta\alpha}(m)]$$

$$\varepsilon_{X\beta} = \varepsilon_{\beta}(m) \cdot [1 - X_{\alpha\beta}(m) X_{\beta\alpha}(m)]$$

9.3 The alpha and beta counting errors, $\sigma_{N_{X\alpha}}$ and $\sigma_{N_{X\beta}}$, are calculated as

$$\sigma_{N_{X\alpha}} = \sqrt{\left(\frac{C_{\alpha}}{t_{C_{\alpha}}^2} + \frac{B_{\alpha}}{t_{B_{\alpha}}^2}\right) + X_{\beta\alpha}^2(m) \left(\frac{C_{\beta}}{t_{C_{\beta}}^2} + \frac{B_{\beta}}{t_{B_{\beta}}^2}\right) + \sigma_{X_{\beta\alpha}(m)}^2 \left(\frac{B_{\beta}}{t_{B_{\beta}}} - \frac{C_{\beta}}{t_{C_{\beta}}}\right)^2}$$

$$\sigma_{N_{X\beta}} = \sqrt{\left(\frac{C_{\beta}}{t_{C_{\beta}}^2} + \frac{B_{\beta}}{t_{B_{\beta}}^2}\right) + X_{\alpha\beta}^2(m) \left(\frac{C_{\alpha}}{t_{C_{\alpha}}^2} + \frac{B_{\alpha}}{t_{B_{\alpha}}^2}\right) + \sigma_{X_{\alpha\beta}(m)}^2 \left(\frac{B_{\alpha}}{t_{B_{\alpha}}} - \frac{C_{\alpha}}{t_{C_{\alpha}}}\right)^2}$$

9.4 The total error or the uncertainty in the alpha and beta activity calculations, $\sigma_{A_{\alpha}}$ and $\sigma_{A_{\beta}}$, can be expressed by the following equations:

$$\sigma_{A_{\alpha}} = \sqrt{\left(\frac{\sigma_{N_{X\alpha}}}{k^{-1} \cdot \varepsilon_{X\alpha}(m) \cdot Q}\right)^2 + \left(\frac{A_{\alpha} \cdot \sigma_{\varepsilon_{X\alpha}(m)}}{\varepsilon_{X\alpha}(m)}\right)^2 + \left(\frac{A_{\alpha} \cdot \sigma_Q}{Q}\right)^2}$$

$$\sigma_{A_{\beta}} = \sqrt{\left(\frac{\sigma_{N_{X\beta}}}{k^{-1} \cdot \varepsilon_{X\beta}(m) \cdot Q}\right)^2 + \left(\frac{A_{\beta} \cdot \sigma_{\varepsilon_{X\beta}(m)}}{\varepsilon_{X\beta}(m)}\right)^2 + \left(\frac{A_{\beta} \cdot \sigma_Q}{Q}\right)^2}$$

where

$\sigma_{A_{\alpha}}$	=	error in the alpha activity
$\sigma_{A_{\beta}}$	=	error in the beta activity
A_{α}	=	measured alpha activity
A_{β}	=	measured beta activity

$\sigma_{EX\alpha(m)}$	=	uncertainty in the crosstalk corrected alpha detector efficiency/self-absorption factor
$\sigma_{EX\beta(m)}$	=	uncertainty in the crosstalk corrected beta detector efficiency/self-absorption factor
σ_Q	=	uncertainty in the sample quantity.

10.0 Quality Control

Quality control (QC) and instrument verification vary greatly between laboratories, and this section is only meant to provide guidance. However, minimal QC guidelines (from EPA SW-846 Method 9310) are 1) all QC data should be maintained and made available for easy reference; 2) one method blank per sample batch should be employed; and 3) one sample duplicate should be run for every 10 samples. Control samples such as matrix spikes, blank spikes and/or performance evaluation samples should also be run periodically.

11.0 Method Performance

The following single laboratory based performance data measurements were made on aqueous, soil, and filter samples. The known analyte concentration levels are listed, along with the obtained precision and bias and associated number of replicate samples. No performance data are available for organic, sewage, or sludge matrices.

Gross Alpha Single Laboratory Performance Data							
Matrix	Known Activity	Bias (%)				Precision (%)	Total Analyses
	Range	Minimum	Maximum	Average	Median	(Std Dev of Bias)	
Water	0-0.37 Bq/L	-13.04	69.81	42.01	50.95	±28.16	10
	0.37-01.1 Bq/L	-46.67	26.05	-18.20	26.67	±28.21	9
	1.9 kBq/L	-5.88	19.61	7.13	5.88	±5.91	24
Soil	0-0.19 Bq/g	-77.55	150.00	17.87	6.25	±78.82	8
	0.19-0.56 Bq/g	-34.21%	60.71	15.00	17.56	±31.93	10
Air Filter	0.78 Bq/filter	-19.05	0.00	-10.19	-9.52	±4.71%	50

Gross Beta Single Laboratory Performance Data							
Matrix	Known Activity	Bias (%)				Precision (%)	Total Analyses
	Range	Minimum	Maximum	Average	Median	(Std Dev of Bias)	
Water	0.19-1.9 Bq/L	-27.66	15.63	-6.33	-4.41	±13.68	14
	0.005-2.3 kBq/L	-10.32	8.06	1.85	1.617	±3.61	24
Soil	0-0.19 Bq/g	-17.65	93.02	29.58	18.37	±40.99	11
	0.19-0.56 Bq/g	-46.43	23.46	1.60	1.14	23.12	7
Air Filter	2.3 Bq/filter	-22.58	-16.31	-19.52	-19.35	±1.54	50

12.0 References

Clesceri, L. D., A. E. Greenberg, and R. R. Trussell, eds. 1992. "Method 7110, Gross Alpha and Gross Beta Radioactivity (Total, Suspended, and Dissolved)." *Standard Methods for the Examination of Water and Wastewaters*. American Public Health Association, 18th edition.

Krieger, H. L. and E. L. Whittaker. 1980. *Prescribed Procedures for Measurement of Radioactivity in Drinking Water*, EPA-600/4-80-032, U.S. Environmental Protection Agency.

U.S. Environmental Protection Agency (EPA). 1986. "Method 9310, Gross Alpha and Gross Beta." *Test Methods for Evaluating Solid Waste*, Third Edition. EPA/SW-846. Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

13.0 Reviewer Modifications/Suggestions

A reviewer suggested that a modification of the sludge, air filters, and soils preparation be as follows:

A single or double mixed acid digestion may be performed with 25 mL of 16 M HNO₃, 5 mL of 12 M HCl, and 2 to 3 mL of HF to moist salts. The solution is heated in 15 to 20 mL of 8 M HNO₃ to dissolve the contents, transferred to a centrifuge tube, centrifuged and decanted into a 100 mL volumetric flask, and diluted to 100 mL with deionized water. The sample is evaporated onto a tared stainless steel planchet.

Appendix 1

Self-Absorption and Crosstalk Curve Determinations

Alpha and Beta Self-Absorption/Efficiency Determinations

The presence of appreciable sample mass results in attenuation of alpha and beta particles and loss of counting efficiency. This phenomenon is more significant for alpha particles than for beta particles because of the more highly ionizing nature and consequent shorter path of alpha particles in matter. For example, a 3 MeV alpha particle only has a range of approximately 1.6 cm in air, while a 1 MeV electron will travel approximately 3 m.

The presence of additional sample mass can result in complete attenuation of the alpha particle (self-absorption with loss of counting efficiency) or alternatively, degradation of the alpha particle energy to the point that it deposits energy equivalent to a beta particle (cross-talk, again with loss of alpha particle counting efficiency). To compensate for these effects, the instrument efficiency and crosstalk for both alpha and beta particles must be determined as a function of sample mass.

Determination of alpha/beta self-absorption curves. The parameters that are required for the determination of alpha and beta activities are derived from curves that plot both the absolute detector efficiency and alpha/beta self-absorption as a function of the sample mass residue. Note: this method combines the absolute zero-mass detector efficiency, $\epsilon(0)$, with a self-absorption factor, $A(m)$, to yield the detector efficiency/self-absorption factor, $\epsilon(m)$.

$$\epsilon(m) = \epsilon(0) \cdot A(m)$$

This is equivalent to methods that determine these two factors separately since $\epsilon(0)$ is a constant. From the preceding equation, a boundary condition must exist so that $A(0) = 1$, which gives the zero-mass or absolute efficiency of the instrument.

At 2.5 mg/cm² surface coverage (50 mg for a 2 in. planchet), a distinct inflection point occurs in the self-absorption curve, which makes it more viable to model this phenomena with two curves (one for 0 to 50 mg and the other for 50 mg and higher). The theoretical origins for this inflection point can be traced to the fact the 2.5 mg/cm² is roughly the surface coverage necessary to completely attenuate an alpha particle originating from the bottom of the planchet with a trajectory normal to the planchet surface.

Fitting Functions. While many fitting functions can be used, some of the more common equations are a) linear, b) exponential, and c) 1/x.

$$\text{a) } \varepsilon(m) = a \cdot m + b$$

$$\text{b) } \varepsilon(m) = a \cdot e^{-b \cdot m}$$

$$\text{c) } \varepsilon(m) = \frac{a}{2 \cdot m}$$

where

a, b = adjustable parameters
 m = sample mass
 $\varepsilon(m)$ = detector efficiency/self-absorption factor

The parameters for the fitting function are generally found by least-squares regression. Note: each portion of the curve can be fitted with a unique function. The following example shows the low- mass portion of the curve being fitted by a linear function and the high-mass portion being fitted as $1/x$.

$$\varepsilon(m) = \left. \begin{array}{l} b - \frac{m}{2 \cdot a} \\ \frac{a}{2 \cdot m} \end{array} \right\} \begin{array}{l} m \leq 50 \text{ mg} \\ m > 50 \text{ mg} \end{array}$$

Crosstalk

In simultaneous gross alpha/beta determinations, two types of counting efficiencies can be defined mathematically. First of all, the traditional counting efficiency, $\varepsilon_x(m)$, where $x = \alpha$ or β , which is simply the ratio of the measured counts in a particular channel to the known disintegration rate, is

$$\varepsilon_x(m) = \frac{N_x}{D_x}$$

where

$\varepsilon_x(m)$ = measured "traditional" efficiency for mass, m
 x = α or β (dependent on the emission source)
 N_x = measured net count rate in channel x
 D_x = known disintegration rate for either an alpha or beta standard.

The second type of detection efficiency is the detection of an emission event of one type in the other channel (i.e., an alpha particle is mistakenly counted in the beta channel or window). This "cross-efficiency" term is unique to simultaneous gross alpha/beta measurements. The

“efficiency” of mistakenly measuring an alpha particle in the beta channel, $\varepsilon_{\alpha\beta}(m)$, is very similar to the previous equation, except it is the ratio of the measured beta count rate to the known alpha disintegration source. Likewise, the beta-alpha efficiency, $\varepsilon_{\beta\alpha}(m)$, is the ratio of the measured alpha count rate to the known beta disintegration source. Mathematically, these two “cross-efficiencies” can be summarized as

$$\varepsilon_{xy}(m) = \frac{N_y}{D_x}$$

where

$\varepsilon_{xy}(m)$	=	measured “cross” efficiency at mass, m
x, y	=	α or β ($x \neq y$)
N_y	=	measured net count rate in channel y
D_x	=	known disintegration rate for either an alpha or beta standard.

To simplify the calculation and correctly deduce the actual count rates (crosstalk corrected count rates) from the measured count rates, two crosstalk terms, $X_{\alpha\beta}(m)$ and $X_{\beta\alpha}(m)$, are defined as the ratio of the respective “cross-efficiency” to the “traditional efficiency.”

$$X_{\alpha\beta}(m) = \frac{\varepsilon_{\alpha\beta}}{\varepsilon_{\alpha}} = \frac{N_{\beta}}{N_{\alpha}}$$

$$X_{\beta\alpha}(m) = \frac{\varepsilon_{\beta\alpha}}{\varepsilon_{\beta}} = \frac{N_{\alpha}}{N_{\beta}}$$

where

$X_{\alpha\beta}(m)$	=	alpha to beta crosstalk for mass m
$X_{\beta\alpha}(m)$	=	beta to alpha crosstalk for mass m
N_{α}	=	measured net alpha counts
N_{β}	=	measured net beta counts.

As can be seen from the previous set of equations, the crosstalk terms simplify to a ratio of net counts of the alpha and beta channels for a single measurement of a given disintegration source. Therefore, to experimentally measure the alpha to beta crosstalk for a given mass, $X_{\alpha\beta}(m)$, an alpha source with a standardized disintegration rate is prepared at the desired mass and counted for an appropriate amount of time. The crosstalk term is calculated simply by dividing the net measured beta counts by the net measured alpha counts. The beta to alpha crosstalk term, $X_{\beta\alpha}(m)$, can be determined in a similar fashion by using a beta standard. Note: since particle scattering should increase in a non-linear relationship with sample mass, crosstalk curves must be derived as a function of mass in a similar fashion to the self-absorption curves.

Typically, the counting system should be set up so that less than 1% of the beta events are counted in the alpha channel. This is accomplished by varying the discriminator window values and the operating voltage values. Note: not all systems provide this type of variability in instrument setup. In such cases, the system has been optimized by the manufacturer to minimize the alpha to beta crosstalk factor or to provide a correction factor within the data reduction algorithm.

Appendix 2

Derivation of the Measured Alpha and Beta Disintegration Rate, Activity, and Error Calculations

Observed Net Count Rate

At the end of each counting cycle, the net count rate is calculated for the alpha and beta channels. The net count is the counts/min with background subtracted. In general, the count rate is calculated as

$$N_x = \frac{C_x}{t_{C_x}} - \frac{B_x}{t_{B_x}}$$

where

x	=	α or β channel
C_x	=	measured gross counts in channel x
t_{C_x}	=	sample counting time in channel x
B_x	=	measured background counts in channel x
t_{B_x}	=	background counting time in channel x
N_x	=	measured net x count rate.

Measured Alpha and Beta Disintegration Rate

Due to the crosstalk phenomena, the measured disintegration rate is represented by two linear equations.

$$\begin{aligned}N_\alpha &= \varepsilon_\alpha(m)D_\alpha + \varepsilon_{\beta\alpha}(m)D_\beta \\N_\beta &= \varepsilon_\beta(m)D_\beta + \varepsilon_{\alpha\beta}(m)D_\alpha\end{aligned}$$

where

$\varepsilon_\alpha(m)$	=	measured alpha efficiency for mass, m
$\varepsilon_\beta(m)$	=	measured beta efficiency for mass, m
$\varepsilon_{\alpha\beta}(m)$	=	alpha-beta cross-efficiency for mass, m
$\varepsilon_{\beta\alpha}(m)$	=	beta-alpha cross-efficiency for mass, m
D_α	=	actual alpha disintegration rate
D_β	=	actual beta disintegration rate
N_α	=	measured net alpha count rate
N_β	=	measured net beta count rate.

These equations have two similar terms. The first term is the “traditional” counting situation where the measured count rate is a result of the actual disintegrations multiplied by the detection efficiency. The second term incorporates the cross-efficiency term. This term gives

the measured counts from the other disintegration source that ideally should not have been measured in the given channel. The sum of these two terms is simply the observed count rate for each channel. The two quantities that need to be calculated are D_α and D_β – the actual sample alpha and beta disintegration rates, respectively. In this simple linear system, two equations and two unknowns exist. The desired quantities can be calculated by simple substitution and some algebra as

$$D_\alpha = \frac{N_\alpha - \left[\frac{\varepsilon_{\beta\alpha}(m)}{\varepsilon_\beta(m)} \right] \cdot N_\beta}{\varepsilon_\alpha(m) \cdot \left[1 - \frac{\varepsilon_{\alpha\beta}(m) \varepsilon_{\beta\alpha}(m)}{\varepsilon_\alpha(m) \varepsilon_\beta(m)} \right]}$$

$$D_\beta = \frac{N_\beta - \left[\frac{\varepsilon_{\alpha\beta}(m)}{\varepsilon_\alpha(m)} \right] \cdot N_\alpha}{\varepsilon_\beta(m) \cdot \left[1 - \frac{\varepsilon_{\alpha\beta}(m) \varepsilon_{\beta\alpha}(m)}{\varepsilon_\alpha(m) \varepsilon_\beta(m)} \right]}$$

Substituting the crosstalk terms for the efficiency ratios in the previous equations yields the desired result:

$$D_\alpha = \frac{N_\alpha - X_{\beta\alpha}(m) N_\beta}{\varepsilon_\alpha(m) \cdot [1 - X_{\alpha\beta}(m) X_{\beta\alpha}(m)]}$$

$$D_\beta = \frac{N_\beta - X_{\alpha\beta}(m) N_\alpha}{\varepsilon_\beta(m) \cdot [1 - X_{\alpha\beta}(m) X_{\beta\alpha}(m)]}$$

Note as the crosstalk values approach zero, these equations simplify into the more typical case where the measured dpm is equal to the measured net count rate divided by the detection efficiency.

Crosstalk Corrected Count Rate and Efficiency

By closely examining the preceding dpm equations, D_α and D_β , the numerators are the crosstalk corrected net count rates, $N_{x\alpha}$ and $N_{x\beta}$, and the denominator is the crosstalk corrected efficiency/self-absorption factors, $\varepsilon_{x\alpha}(m)$ and $\varepsilon_{x\beta}(m)$.

$$\varepsilon_{x\alpha} = \varepsilon_\alpha(m) \cdot [1 - X_{\alpha\beta}(m) X_{\beta\alpha}(m)]$$

$$\varepsilon_{x\beta} = \varepsilon_\beta(m) \cdot [1 - X_{\alpha\beta}(m) X_{\beta\alpha}(m)]$$

By substituting for the observed count rates into the crosstalk corrected count rates, the final desired equations are obtained:

$$N_{x\alpha} = \left(\frac{C_\alpha}{t_{C_\alpha}} - \frac{B_\alpha}{t_{B_\alpha}} \right) - X_{\beta\alpha}(m) \left(\frac{C_\beta}{t_{C_\beta}} - \frac{B_\beta}{t_{B_\beta}} \right)$$

$$N_{x\beta} = \left(\frac{C_\beta}{t_{C_\beta}} - \frac{B_\beta}{t_{B_\beta}} \right) - X_{\alpha\beta}(m) \left(\frac{C_\alpha}{t_{C_\alpha}} - \frac{B_\alpha}{t_{B_\alpha}} \right)$$

Uncertainty in the Crosstalk Corrected Counting Rates

Using the fact that the counting error is simply the square root of the number of counts, the uncertainties for the crosstalk corrected counting rates, $\sigma_{N_{x\alpha}}$ and $\sigma_{N_{x\beta}}$, are calculated as

$$\sigma_{N_{x\alpha}} = \sqrt{\left(\frac{C_\alpha}{t_{C_\alpha}^2} + \frac{B_\alpha}{t_{B_\alpha}^2} \right) + X_{\beta\alpha}^2(m) \left(\frac{C_\beta}{t_{C_\beta}^2} + \frac{B_\beta}{t_{B_\beta}^2} \right) + \sigma_{X_{\beta\alpha}(m)}^2 \left(\frac{B_\beta}{t_{B_\beta}} - \frac{C_\beta}{t_{C_\beta}} \right)^2}$$

$$\sigma_{N_{x\beta}} = \sqrt{\left(\frac{C_\beta}{t_{C_\beta}^2} + \frac{B_\beta}{t_{B_\beta}^2} \right) + X_{\alpha\beta}^2(m) \left(\frac{C_\alpha}{t_{C_\alpha}^2} + \frac{B_\alpha}{t_{B_\alpha}^2} \right) + \sigma_{X_{\alpha\beta}(m)}^2 \left(\frac{B_\alpha}{t_{B_\alpha}} - \frac{C_\alpha}{t_{C_\alpha}} \right)^2}$$

Activity Calculations

The activity and error calculations are performed at the end of each counting cycle. The activity of the sample is in pCi per unit volume (mass). The equations for the alpha activity, A_α , and the beta activity, A_β , are

$$A_\alpha = \frac{N_{x\alpha}}{\varepsilon_{x\alpha}(m) \cdot Q} \cdot k$$

$$A_\beta = \frac{N_{x\beta}}{\varepsilon_{x\beta}(m) \cdot Q} \cdot k$$

where

$$\begin{array}{ll} A_\alpha & = \text{alpha activity} \\ A_\beta & = \text{beta activity} \end{array}$$

$N_{X\alpha}$	=	crosstalk corrected net alpha count rate
$N_{X\beta}$	=	crosstalk corrected net beta count rate
k	=	factor to convert to the desired reporting units
Q	=	sample size (volume or mass)
$\varepsilon_{X\alpha}(m)$	=	crosstalk corrected alpha detector efficiency/self-absorption factor at mass, m
$\varepsilon_{X\beta}(m)$	=	crosstalk corrected beta detector efficiency/self-absorption factor at mass, m

Activity Error Calculations

The uncertainty in the alpha and beta activity calculations, σ_{A_α} and σ_{A_β} , can be expressed by the following equations:

$$\sigma_{A_\alpha} = \sqrt{\left(\frac{\sigma_{N_{X\alpha}}}{k^{-1} \cdot \varepsilon_{X\alpha}(m) \cdot Q}\right)^2 + \left(\frac{A_\alpha \cdot \sigma_{\varepsilon_{X\alpha}(m)}}{\varepsilon_{X\alpha}(m)}\right)^2 + \left(\frac{A_\alpha \cdot \sigma_Q}{Q}\right)^2}$$

$$\sigma_{A_\beta} = \sqrt{\left(\frac{\sigma_{N_{X\beta}}}{k^{-1} \cdot \varepsilon_{X\beta}(m) \cdot Q}\right)^2 + \left(\frac{A_\beta \cdot \sigma_{\varepsilon_{X\beta}(m)}}{\varepsilon_{X\beta}(m)}\right)^2 + \left(\frac{A_\beta \cdot \sigma_Q}{Q}\right)^2}$$

where

σ_{A_α}	=	error in the alpha activity
σ_{A_β}	=	error in the beta activity
A_α	=	measured alpha activity
A_β	=	measured beta activity
$\sigma_{\varepsilon_{X\alpha}(m)}$	=	uncertainty in the crosstalk corrected alpha detector efficiency/self-absorption factor
$\sigma_{\varepsilon_{X\beta}(m)}$	=	uncertainty in the crosstalk corrected beta detector efficiency/self-absorption factor
σ_Q	=	uncertainty in the sample quantity.

RP720^(a)**Rapid Determination of Gross Alpha, Gross Beta, and Gross Tritium in Water Samples Using a Liquid Scintillation Counter**

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method describes the simultaneous determination of gross alpha, gross beta, and gross tritium (i.e., tritium and other low-energy beta emitters) activities by liquid scintillation spectrometry. It applies to all clear liquid samples, and the method can be completed in a short period of time (1 to 2 h) once efficiency curves have been established. Liquid scintillation counting systems are designed to detect and measure low-energy beta particles (e.g., ^3H), medium to high energy beta particles (e.g., $^{90}\text{Sr}/^{90}\text{Y}$), and alpha particles (e.g., ^{239}Pu). This method is designed for liquid scintillation counters (LSC) that are not equipped to perform time-resolved analysis to discriminate between alpha and beta particles.

Since LSC systems are now available (e.g., Packard Tri-Carb 2550TR/AB) that are equipped with pulse-decay discrimination electronics to perform time-resolved liquid scintillation analysis, distinction between alpha and beta particles is possible, and alpha and beta counts can be recorded in different counting windows. The methods described herein for window calibration and alpha correction will not apply. Users of these systems should refer to the operating manual to select the windows and adjust the optimum pulse decay discriminator settings.

2.0 Summary of Method

The ^3H , alpha, and beta spectral ranges or window settings are first defined. The total alpha activity is obtained by subtracting the beta contribution to the alpha spectrum. This correction is possible because the contribution by beta emitters to the alpha channel is independent of the beta energy within the range of 0.25 to 1.2 MeV.

The counting efficiencies are then determined by using efficiency curves (quench curves). The efficiency curve is a plot of the counting efficiency as a function of the external ratio (ER). The external ratio is also known as the automatic external standardization (AES) number or the transformed spectral index of the external standard (TSIE).

(a) This method was supplied by Kelvin L. Wright (Waste Policy Institute, Germantown, Maryland).

A sample aliquot is prepared with a measured volume of scintillation cocktail that is then placed in a programmed liquid scintillation counter for spectrum analysis.

3.0 Interferences

- 3.1 Medium- and high-energy beta emitters interfere with the alpha count. A correction for this interference is performed.
- 3.2 Interference in the beta count by alpha activity is minimal provided the alpha window is properly adjusted.
- 3.3 Using this procedure, the calculated ^3H concentration may be higher than the actual concentration because of possible interferences from other low-energy beta emitters and the beta continuum of high-energy beta particles. A ^3H distillation should be performed if information more accurate than gross tritium is needed.
- 3.4 Samples with excessively high count rates (e.g., greater than 1,000,000 cpm) should be reanalyzed using less sample material.
- 3.5 Deep color in samples may cause severe quenching that will lower the counting efficiency. If quenching causes the efficiency to drop to one fourth of the highest efficiency, an alternate method should be used for that particular sample.

4.0 Safety

- 4.1 Many of the solvents and scintillators used in liquid scintillation cocktails are highly flammable and toxic. They should only be used with all of the necessary precautions. For example, the scintillation cocktail should be handled in a well ventilated area.
- 4.2 Some of the quenching agents listed are highly toxic and/or carcinogens (e.g., carbon tetrachloride), and the safety of handling and disposal is the responsibility of the user.
- 4.3 After the samples have been counted, they should be stored in a well-ventilated area until they are ready for disposal.

5.0 Apparatus and Materials

- Liquid scintillation counter
- Scintillation vials
- Refrigerator

- Tritium source (sealed 20-mL scintillation vial with cocktail)
- Carbon-14 source (sealed 20-mL scintillation vial with cocktail)
- Background source (sealed 20-mL scintillation vial with cocktail)

6.0 Reagents

- Low ^3H water or “dead” water
- Scintillation cocktail
- Ethanol (95%)
- Quenching agent (e.g., chloroform, nitromethane, carbon tetrachloride, nitric acid, etc.)

7.0 Sample Collection, Preservation, and Handling

Samples should be preserved as specified in the sample collection program. Samples should be in glass containers where ^3H is of concern to minimize evaporative loss of water.

8.0 Procedure

8.1 Determination of Window Settings

Before counting samples and backgrounds, the window settings are determined for the three regions of interest (i.e., ^3H , beta, and alpha).

- 8.1.1 Unquenched ^{239}Pu , ^{90}Sr , and ^3H standards are prepared in the same geometry as the analytical samples. Using guidance found in the applicable Liquid Scintillation Counter Manual, the energy regions are set for ^3H (Region A), alpha emitters (Region B), and high energy beta emitters (Region C) (usually 0 to 19 keV, 200 to 400 keV, and 450 to 2000 keV respectively).
- 8.1.2 Using again guidance found in the operating manual, the three energy regions are optimized (the figure of merit is a common way to optimize the regions of interest). Alternatively, the following procedure may be followed (steps 8.1.3 to 8.1.5).
- 8.1.3 Using the ^3H standard, a spectrum analysis is performed, and the energy range of Region A (0 to 19 keV, ^3H) is visually adjusted to maximize count rate and

minimize energy range. A balance between count rate and energy range should be obtained.

A properly adjusted ^3H range should not contain any interference from alpha particles. However, there will be interference from low energy beta particles with the same energy as ^3H as well as the beta continuum from high energy beta particles.

- 8.1.4 A spectrum analysis is performed using the ^{239}Pu standard, and Region B (200 to 400 keV, ^{239}Pu) energy range is visually adjusted to maximize the count rate and minimize energy range. A balance between count rate and energy range should be obtained.

A properly adjusted alpha range should not interfere with ^3H or gross beta analysis. However, gross beta (middle-to-high range) will interfere with the gross alpha.

- 8.1.5 A spectrum is recorded using the $^{90}\text{Sr}/^{90}\text{Y}$ standard; and Region C (450 to 2000 keV) energy range is adjusted such that the beginning of the range is about 25 to 50 keV above the end of the alpha energy range. The end value should be the highest energy of the spectrum (2000 keV).

8.2 Determination of Efficiency as a Function of Quenching

Efficiency curves (efficiency vs external ratio) are established for alpha, beta, and ^3H respectively. The efficiency curve should be checked annually and regenerated if any major component of the instrumentation is replaced.

Calibration for Gross Alpha

- 8.2.1 A volume of ^{239}Pu tracer solution that has sufficient activity to give a counting error of less than one percent (1%) in 50 min, but also less than 100,000 counts per minute (cpm) is pipetted into several (e.g., 11) scintillation vials. Deionized water is used to dilute the aqueous standard to a volume consistent with the sample set preparation (e.g., 2 mL).

Tracer information (including volume, activity concentration, reference date, etc.) needs to be recorded. An example of a form (Liquid Scintillation Gross Alpha Efficiency Calibration Form) to use for this activity is given in Appendix 1.

- 8.2.2 To obtain a range of quenching from high to low efficiency, various volumes of a quenching agent are pipetted into the vials, separately labeled. The following

quenching agent volumes are presented as an example: 0.01, 0.03, 0.05, 0.07, 0.09, 0.11, 0.13, 0.15, 0.17 and 0.19 mL. The 11th vial serves as an unquenched standard.

- 8.2.3 Enough scintillation cocktail is dispensed into each plastic vial to make up the final volumes consistent with the sample set to be analyzed (e.g., 20 mL).
- 8.2.4 The scintillation vials are capped and shaken vigorously for 10 to 20 sec. The vials are wiped clean with ethanol and a paper towel. The samples should then be refrigerated for at least 10 min.
- 8.2.5 The LSC stability and operational order are checked before running the standards and samples. This can be done by counting background, a ^3H standard, and a ^{14}C standard by an appropriate program, and then comparing the count rate of these standards with previously determined standard data according to criteria currently in use at the laboratory.
- 8.2.6 A background sample (prepared similarly to the standards) and the ^{239}Pu standards are counted for 50 min (or until 1% counting statistics are obtained) in the three regions selected on the LSC. The corresponding ERs given by the instrument should be recorded.
- 8.2.7 The net count rate for each vial is calculated by subtracting the prepared background count rate in Region B from the measured gross count rates in Region B.
- 8.2.8 The gross alpha efficiency (Eff_α) is determined for each vial in units of counts per min/disintegration per min by dividing the net activity measured in cpm by the calculated activity added in dpm. Also, the uncertainty in the gross alpha efficiency, $\sigma_{\text{Eff}_\alpha}$, should be estimated for each vial.
- 8.2.9 The gross alpha efficiency curve is generated by plotting $\ln(\text{Eff}_\alpha)$ versus the ER. Many LSC systems are equipped with programs to generate efficiency curves; to use these applications, the operating manual should be referenced.
- 8.2.10 A least squares fit on the plot may be performed. The coefficients a_α and b_α for the equation $\text{Eff}_\alpha = a_\alpha \cdot \exp(b_\alpha \cdot \text{ER})$ (obtained from the intercept $[\ln a]_\alpha$ and the slope $[b_\alpha]$), and the fitting coefficient, R^2 , should be recorded.

Calibration for gross beta is performed in an identical fashion to the calibration procedure for gross alpha (section 8.2), except a tracer solution of $^{90}\text{Sr}/^{90}\text{Y}$ is used instead of ^{239}Pu , and count rates are measured in Region C rather than Region B. An example of a calibration form (Liquid Scintillation Gross Beta Efficiency Calibration Form) is given in Appendix 1.

Calibration for gross tritium is performed in an identical fashion to the calibration procedure for gross alpha (section 8.2), except a tracer solution of ^3H is used instead of ^{239}Pu , and count rates are measured in Region A rather than Region B. An example of a calibration form (Liquid Scintillation Tritium Efficiency Calibration Form) is given in Appendix 1.

8.3 Sample Analysis

8.5.1 Appropriate scintillation vials are marked with the sample ID.

If marking the side of the vial, a marker with ink that is removable using ethanol should be used.

8.5.2 A known amount (e.g., 2.0 mL) of each sample is pipetted individually into the appropriate scintillation vials.

8.5.3 An appropriate amount (e.g., 18 mL) of scintillation cocktail is dispensed into each scintillation vial.

8.5.4 The cap is secured onto each of the scintillation vials, the vials are then shaken vigorously for 10 to 20 s, and the outside of each vial should then be wiped with a paper towel wet with ethanol to remove any sample identification and fingerprints.

8.5.5 Samples should be checked for phase separation. If phase separation is evident, solubilizing or complexing agents will be required to produce a stable solution (Parmentier and Ten Haaf 1969; Fox 1976).

8.5.6 Samples should be refrigerated for at least 10 min before counting. Samples may also need to be "dark adapted" to minimize the potential for delayed scintillations. These are usually performed as a function of the LSC system.

8.5.7 A background sample is prepared in the same manner as the samples.

A prepared background sample is one that has been developed using stable compounds (e.g., dead water) and has a matrix as similar as possible to that of the samples being analyzed.

8.5.8 The samples are counted for an appropriate time (e.g., 100 min) in the three regions specified in section 8.1. The ERs given by the instrument are recorded.

8.5.9 When sample counts are completed, the samples should be returned to a well-ventilated area and stored until disposal.

9.0 Calculations

The following notation is used in the calculations:

The terms BACK, BETA, and SAMP represent the count rates (in cpm, counts per minute) obtained when the background, the beta standard, and the samples are counted, respectively.

The subscripts α , β , and trit are the count rates in the alpha (region B), beta (C), and ^3H (A) regions respectively.

9.1 The net count rates for the beta standard in the alpha and beta regions are

$$\text{BETA}_{\alpha}^{\text{NET}} = \text{BETA}_{\alpha} - \text{BACK}_{\alpha}$$

$$\text{BETA}_{\beta}^{\text{NET}} = \text{BETA}_{\beta} - \text{BACK}_{\beta}$$

The net count rates for the sample in the alpha and beta regions are

$$\text{SAMP}_{\alpha}^{\text{NET}} = \text{SAMP}_{\alpha} - \text{BACK}_{\alpha}$$

$$\text{SAMP}_{\beta}^{\text{NET}} = \text{SAMP}_{\beta} - \text{BACK}_{\beta}$$

9.2 The adjusted alpha count rate, in unit of cpm, for the sample is

$$\text{Adjusted } \alpha \text{ cpm} = \text{SAMP}_{\alpha}^{\text{NET}} - \left[\frac{\text{BETA}_{\alpha}^{\text{NET}}}{\text{BETA}_{\beta}^{\text{NET}}} \cdot \text{SAMP}_{\beta}^{\text{NET}} \right]$$

9.3 The gross alpha, gross beta, and tritium activities of the sample are calculated according to the following expressions:

$$\alpha_{\text{GROSS}} = \frac{\text{Adjusted } \alpha \text{ cpm}}{K \cdot \text{Eff}_{\alpha} \cdot V}$$

$$\beta_{\text{GROSS}} = \frac{\text{SAMP}_{\beta}^{\text{NET}}}{K \cdot \text{Eff}_{\beta} \cdot V}$$

$$\text{TRIT}_{\text{GROSS}} = \frac{\text{SAMP}_{\text{TRIT}} - \text{BACK}_{\text{TRIT}}}{K \cdot \text{Eff}_{\text{TRIT}} \cdot V}$$

where

α_{GROSS} , β_{GROSS} and $\text{TRIT}_{\text{GROSS}}$ are the gross alpha, gross beta, and gross ^3H activities respectively in units of pCi per mL

V is the volume of sample in mL

Eff_{α} , Eff_{β} and Eff_{TRIT} (alpha, beta, and tritium counting efficiencies) are determined from the efficiency curves together with the corresponding ERs recorded when the samples were counted

K is a factor to convert to desired reporting units.

- 9.4 The uncertainties in the gross alpha, gross beta, and ^3H activities of the sample are calculated according to the following expressions:

$$\sigma_{\alpha_{\text{GROSS}}} = \alpha_{\text{GROSS}} \cdot \sqrt{\left(\frac{\sqrt{\text{SAMP}_{\alpha} t_{\alpha}^{\text{SAMP}} + \text{BACK}_{\alpha} t_{\alpha}^{\text{BACK}}}}{\text{SAMP}_{\alpha} t_{\alpha}^{\text{SAMP}} - \text{BACK}_{\alpha} t_{\alpha}^{\text{BACK}}} \right)^2 + \left(\frac{\sigma_{\text{Eff}_{\alpha}}}{\text{Eff}_{\alpha}} \right)^2}$$

$$\sigma_{\beta_{\text{GROSS}}} = \beta_{\text{GROSS}} \cdot \sqrt{\left(\frac{\sqrt{\text{SAMP}_{\beta} t_{\beta}^{\text{SAMP}} + \text{BACK}_{\beta} t_{\beta}^{\text{BACK}}}}{\text{SAMP}_{\beta} t_{\beta}^{\text{SAMP}} - \text{BACK}_{\beta} t_{\beta}^{\text{BACK}}} \right)^2 + \left(\frac{\sigma_{\text{Eff}_{\beta}}}{\text{Eff}_{\beta}} \right)^2}$$

$$\sigma_{\text{TRIT}_{\text{GROSS}}} = \text{TRIT}_{\text{GROSS}} \cdot \sqrt{\left(\frac{\sqrt{\text{SAMP}_{\text{TRIT}} t_{\text{TRIT}}^{\text{SAMP}} + \text{BACK}_{\text{TRIT}} t_{\text{TRIT}}^{\text{BACK}}}}{\text{SAMP}_{\text{TRIT}} t_{\text{TRIT}}^{\text{SAMP}} - \text{BACK}_{\text{TRIT}} t_{\text{TRIT}}^{\text{BACK}}} \right)^2 + \left(\frac{\sigma_{\text{Eff}_{\text{TRIT}}}}{\text{Eff}_{\text{TRIT}}} \right)^2}$$

where

t_{α}^{SAMP} , t_{β}^{SAMP} , and $t_{\text{TRIT}}^{\text{SAMP}}$ are the times of measurement of the sample activity in minutes in the alpha region, beta region and ^3H region respectively

t_{α}^{BACK} , t_{β}^{BACK} and $t_{\text{TRIT}}^{\text{BACK}}$ are the times of measurement of the background activity in minutes in the alpha region, beta region and ^3H region respectively, and

$\sigma_{\text{Eff}_{\alpha}}$, $\sigma_{\text{Eff}_{\beta}}$ and $\sigma_{\text{Eff}_{\text{TRIT}}}$ are the estimated uncertainties in the alpha, beta and ^3H efficiencies respectively.

When uncertainties arising from sources other than counting statistics and efficiencies are known or can be estimated, they should be included in the calculation.

10.0 Quality Control

Quality control criteria to be developed and included.

11.0 Method Performance

11.1 Liquid scintillation counting is normally used to quantify a radionuclide that has been separated from all other radionuclides. The bias and precision of this method are affected by the number and type of interfering radionuclides.

11.2 The gross alpha, gross beta, and ^3H method detection limits (MDLs), as defined by NUREG 0472, are ~0.01 Bq/mL (0.3 pCi/mL), ~0.02 Bq/mL (0.5 pCi/mL) and ~0.04 Bq/mL (1.0 pCi/mL), respectively using the liquid scintillation counter. Detection limits are based on little or no quenching. Detection limits will vary proportionally to the amount of quencher in the samples.

12.0 References

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13.0 For Further Information

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Laboratory/Radiochemistry

Appendix 1

Liquid Scintillation Tritium Efficiency Calibration Form (LSTECF)

Nuclide _____

Detector _____

Date _____

Analyst _____

Tracer Information

Stock # _____ Dilution # _____

Activity _____ Bq/mL Ci/mL dpm/mL (Circle one)

Reference Date _____ Count Date _____

Decay Correction Factor _____

Decay Corrected Activity _____ dpm/mL

Volume Added to Each Vial _____ mL

Activity Added to Each Vial _____ dpm

Measurement Data

Background Activity _____ cpm

Activity of Empty Vial _____ cpm

Activity of Standard _____ cpm

Sample No.	Gross ^3H Activity cpm	Net ^3H Activity cpm	Eff_{Trit} cpm/dpm	σ_{EffTrit} cpm/dpm	ER
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

Efficiency Curve Coefficients ($\text{Eff}_{\text{Trit}} = a_{\text{Trit}} \cdot \exp(b_{\text{Trit}} \cdot \text{ER})$):

$a_{\text{Trit}} =$ _____

$b_{\text{Trit}} =$ _____

$R^2 =$ _____

DRAFT

Liquid Scintillation Gross Alpha Efficiency Calibration Form (LSGAECF)

Nuclide _____

Detector _____

Date _____

Analyst _____

Tracer Information

Stock # _____

Dilution # _____

Activity _____ Bq/mL Ci/mL dpm/mL (Circle one)

Reference Date _____ Count Date _____

Decay Correction Factor _____

Decay Corrected Activity _____ dpm/mL

Volume Added to Each Vial _____ mL

Activity Added to Each Vial _____ dpm

Measurement Data

Background Activity _____ cpm

Activity of Empty Vial _____ cpm

Activity of Standard _____ cpm

Sample No.	Gross α Activity cpm	Net α Activity cpm	Eff $_{\alpha}$ cpm/dpm	$\sigma_{\text{Eff}\alpha}$ cpm/dpm	ER
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

Efficiency Curve Coefficients ($\text{Eff}_{\alpha} = a_{\alpha} \cdot \exp(b_{\alpha} \cdot \text{ER})$): $a_{\alpha} =$ _____ $b_{\alpha} =$ _____ $R^2 =$ _____

DRAFT

Laboratory/Radiochemistry

Liquid Scintillation Gross Beta Efficiency Calibration Form (LSGAECF)

Nuclide _____
Date _____

Detector _____
Analyst _____

Tracer Information

Stock # _____ Dilution # _____
Activity _____ Bq/mL Ci/mL dpm/mL (Circle one)
Reference Date _____ Count Date _____
Decay Correction Factor _____
Decay Corrected Activity _____ dpm/mL
Volume Added to Each Vial _____ mL
Activity Added to Each Vial _____ dpm

Measurement Data

Background Activity _____ cpm
Activity of Empty Vial _____ cpm
Activity of Standard _____ cpm

Sample No.	Gross β Activity cpm	Net β Activity cpm	Eff $_{\beta}$ cpm/dpm	$\sigma_{\text{Eff}\beta}$ cpm/dpm	ER
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

Efficiency Curve Coefficients ($\text{Eff}_{\beta} = a_{\beta} \cdot \exp(b_{\beta} \cdot \text{ER})$):

$a_{\beta} =$ _____
 $b_{\beta} =$ _____
 $R^2 =$ _____

RP725^(a)

Group Actinide Screening Using Extraction Chromatography

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method provides a fast group separation of Am, Cm, Pu, U, and Np in aqueous samples. It is intended to screen samples for actinide identification and concentration. The method applies to simple and complex aqueous matrices. It has been used on soil leachates of up to 1 g equivalent soil and urine samples prepared by calcium phosphate precipitation. Applicability should also extend to other prepared materials, such as wipe and air-filter samples.

2.0 Summary of Method

The sample matrix is converted to 2 M HNO₃. The oxidation states of the actinides and Fe are reduced because the pentavalent actinides do not extract onto the column. The sample is loaded on a prepared TRU•Spec[®] column. Most lanthanides, U, Th, Am, Cm, Pu, and Np, are retained on the column, and impurities are washed through the column. The actinides and lanthanides are eluted with 0.1 M ammonium biocalate. The sample is then prepared for alpha spectrometry by electrodeposition or precipitation plating.

3.0 Interferences

- 3.1 Polonium may not be well separated and could cause a positive interference on the ²⁴³Am and ²³²U spectral peaks.
- 3.2 Bismuth follows the actinides, and large masses of Bi in the sample will interfere with electrodeposition mounting techniques.
- 3.3 Interferences may result in the alpha energy analysis (AEA) spectrum due to isotopes with unresolved peak energies (e.g., ²⁴¹Am and ²³⁸Pu).
- 3.4 High phosphate or fluoride concentrations and chelators present in the sample solution {such as ethylenediaminetetraacetic acid (EDTA), diethylhexylphosphoric acid

(a) This method was consolidated by S. K. Fadeff (Pacific Northwest Laboratory, Richland, Washington).

(HDEHP), etc.) may complex the actinides such that they will not extract into the substrate. In such cases, the organics may need to be destroyed by wet ashing or oxidation in a muffle furnace before the separations chemistry. The phosphate and fluoride can be bound with Al if $\text{Al}(\text{NO}_3)_3$ is present in the feed solution.

- 3.5** The column capacity is limited to approximately 2 to 4 mg of actinides and lanthanides on a 2-mL prepacked TRU•Spec® column (product literature, Eichrom Industries, Inc., Darien, Illinois). Samples with excessive amounts of lanthanides or actinides will need to be diluted and small aliquots taken before analysis.

4.0 Safety

No special safety precautions are indicated for this method.

5.0 Apparatus and Materials

- TRU•Spec® pre-packed column (Eichrom Industries, Inc., 8205 S. Cass Ave., Suite 107, Darien, Illinois, 60559), or equivalent
- Column support rack

6.0 Tracers and Reagents

- 6.1 Tracers.** Yields may be traced with ^{242}Pu (4.90 MeV), ^{236}Pu (5.76 MeV), ^{236}U (4.49 MeV), ^{243}Am (5.28 MeV), or ^{244}Cm (5.81 MeV), as appropriate for the matrix.

- 6.2 Reagents.** All reagents are prepared from analytical reagent-grade chemicals. Concentrations are not critical and need only be within $\pm 10\%$ of stated values.

- Nitric acid, 8 M, 2 M HNO_3 , 1 M HNO_3 , and 0.025 M HNO_3
- Column feed solution (one of two options in step 8.2 may be used)
 - 2 M HNO_3 (If phosphate or fluoride are present, this feed solution may result in reduced tetravalent isotope yields, especially for Np.)
 - 2 M $\text{HNO}_3 \cdot 0.5 \text{ M Al}(\text{NO}_3)_3$
- Ammonium hydroxide, (NH_4OH) (option for step 8.2)
- Fe^{+3} carrier, 10 mg/mL (as an option in steps 8.2 and 8.3) {For example, 18.08 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is diluted in 250 mL H_2O ; another ferric salt or another

concentration may be used as long as the indicated mass of Fe^{+3} is added to the sample.}

- Phosphate solution, 300 mg PO_4^{-3} /mL (as an option in step 8.2) {This may be prepared by dissolving 41.6 g $(\text{NH}_4)_2 \text{HPO}_4$ in 100 mL water.}
- Reducing solution (One of two options in step 8.3 may be used.)
 - 1 to 2 M HNO_3 saturated with ascorbic acid (This solution is made just before use. Solid ascorbic acid is added to approximately 5 mL 1 to 2 M HNO_3 until no more will dissolve and some solid ascorbic acid remains. Greater than 2 M HNO_3 will begin to destroy the ascorbic acid.)
 - 0.1 M $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ -0.2 M $\text{NaHSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$ {ferrous ammonium sulfate and sodium formaldehyde-sulfoxylate (rongalite)} in 2 M HNO_3 .
- Ammonium bioxalate, 0.1 M $\text{NH}_4\text{HC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ {This may be prepared by dissolving 1.26 g $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and 1.42 g $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ into 200 mL H_2O .}
- Hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$

7.0 Sample Collection, Preservation, and Handling

Water samples collected for actinide determination should be preserved with HNO_3 . No refrigeration is required.

8.0 Procedure

- 8.1 An appropriate radionuclide tracer may be added (if not previously added), as required by the analysis, to an appropriately sized aliquot of prepared sample (e.g., soil leachate, aqueous sample, prepared urine). If used, the exact amount of tracer added needs to be recorded.
- 8.2 The sample matrix is converted to the column feed solution {2 M HNO_3 or 2 M $\text{HNO}_3 \cdot 0.5 \text{ M Al}(\text{NO}_3)_3$ }. Examples of the conversion process are described below. The first option may be most appropriate for small-volume, high-radioactive samples. The second option is best applied to large-volume samples. The third option is applicable to most sample types, including soil leachates. However, because $\text{Fe}(\text{OH})_3$ precipitation is not quantitative for pentavalent isotopes, an initial oxidation-state reduction is used. The fourth option is applicable to most matrices, including urine.

- A small aliquot (e.g., <0.5 mL) is added to a beaker containing 5 mL of column feed solution.
- The sample is evaporated to a low volume and brought up to a 5-mL volume with column feed solution.
- A small mass (e.g., 2 mg) $\text{NH}_2\text{OH}\cdot\text{HCl}$ is added to the sample to reduce the actinide oxidation states. Ten milligrams of Fe^{+3} carrier are (if Fe is not already present), and the Fe and actinides are precipitated as the hydroxides with the addition of NH_4OH . The precipitate is centrifuged, and the supernate is decanted and discarded. The $\text{Fe}(\text{OH})_3$ precipitate is dissolved with an excess of column feed solution such that the NO_3^- concentration is essentially equivalent to that of the column feed solution.
- Fifty milligrams of Ca^{+2} carrier are added to each sample. After mixing, 1500 mg of phosphate are added. The basic calcium phosphate precipitate is formed by adding NH_4OH until the solution is basic. The precipitate is centrifuged, and the supernate is decanted and discarded. The basic calcium phosphate precipitate is dissolved in the column feed solution (containing Al).

8.3 One of two options may be employed to reduce the valence state of the actinides and any Fe present. If Fe is already present in the sample (e.g., in the case of soil leachates), the ascorbic acid option will be preferred. If Fe is an insignificant fraction of the sample, then the rongalite/ferrous ammonium sulfate may be preferred.

8.3.1 Ascorbic Acid Reduction

- To the solution, an equivalent of 10 mg Fe are added (if not already present), and the solution is gently mixed.

At this point, the sample should have a yellow color typical of iron complexed with nitrate.

- Saturated ascorbic acid•2 M HNO_3 is added to the solution 1 to 3 mL at a time. The ascorbic acid will make the solution turn blue momentarily. The ascorbic acid•2 M HNO_3 addition is continued until further addition ceases to cause the blue-color production.

This step reduces Fe^{+3} to Fe^{+2} . The Pu is stabilized to the +3 oxidation state, and Np^{+6} is reduced to Np^{+4} by the Fe^{+2} , ensuring their retention on the TRU•Spec[®] column. The Fe^{+2} is eluted without interfering with the retention of other actinides.

8.3.2 **Rongalite/Ferrous Ammonium Sulfate Reduction.** The rongalite/ferrous ammonium sulfate is prepared fresh, and 0.5 mL is added to the sample. The sample is allowed to sit for about 15 min.

8.4 An Eichrom TRU•Spec[®] column is prepared for each sample as follows:

8.4.1 The tip is broken off an Eichrom TRU•Spec[®] disposable column, and the water is allowed to drain.

8.4.2 The column is washed with 5 to 10 mL 2 M HNO₃. The column is now ready to use for sample separation.

8.5 The sample (from step 8.3) is added to the column using 2 M HNO₃ to quantitatively transfer the sample.

The column may change color; this is a matrix effect and should not affect the performance of the column.

8.6 If the Po interference needs to be eliminated, the column may be washed with 10 mL 8 M HNO₃. The column is then washed with 15 to 20 mL of 1 M to 2 M HNO₃; the wash is discarded.

8.7 The actinides are eluted with either of the following:

- Fifteen milliliters of 0.025 M HNO₃ followed by 10 to 15 mL of 0.1 M NH₄HC₂O₄, combining eluents.

The initial elution with HNO₃ will elute the rare earths and Am; otherwise, the oxalate may precipitate the rare earths on the column.

- 10 mL of 0.1 M NH₄HC₂O₄.

This is used if the rare earth concentration is known to be very small.

8.8 The sample is ready for precipitation plating or electrodeposition and analysis by AEA.

9.0 Calculations

Using a tracer and AEA, the isotope activity can be calculated as follows:

$$\text{Activity} = \frac{C_{\text{analyte}} \cdot \text{TR}}{C_{\text{TR}} \cdot F} \cdot \frac{C}{Q}$$

where

C_{analyte}	=	net analyte counts
TR	=	added tracer activity
C_{TR}	=	net tracer counts
Q	=	sample quantity analyzed
C	=	factor to convert to desired reporting units
F	=	fraction of decay events in the region.

Where chemical yields are well characterized, activity concentration in the sample may be determined without the use of a tracer.

$$\text{Activity} = \frac{CR_s}{E \cdot Y \cdot F \cdot Q} \cdot C$$

where

CR_s	=	net count rate of the analyte in the sample
E	=	counter efficiency
F	=	fraction of decay events in the region
Q	=	sample quantity
C	=	factor to convert to desired reporting units
Y	=	chemical yield.

10.0 Quality Control

10.1 It is recommended that, at a minimum, one reagent blank and one blank spike be run with each analytical batch to evaluate the effectiveness of the full analytical process, including data reduction.

10.2 The blank should indicate no (or insignificant) contamination of the analytes of interest.

10.3 The blank spike (yield corrected) should indicate low (<10%) method bias.

11.0 Method Performance

Matrix blank urine samples were spiked with ^{244}Cm , ^{239}Pu , ^{237}Np , and ^{236}U ; then they were prepared by calcium phosphate precipitation and wet ashing. The samples were dissolved in 2 M

HNO_3 -0.5 M $\text{Al}(\text{NO}_3)_3$ and loaded on the prepared TRU-Spec[®] column. The Po was eluted off the column with 8 M HNO_3 , and other impurities were washed off with 1 M HNO_3 . The actinides were eluted with 10 mL of 0.1 M $\text{NH}_4\text{HC}_2\text{O}_4$, then electroplated and counted by AEA. Table 1 summarizes the bias and precision of the method.

Table 1. Bias and Precision of Group Actinide Screening Using Extraction Chromatography			
Analyte	Recovery (%)	Precision (%)	Number of Determinations
²³⁶ U	89	4	48
²³⁷ Np	94	3	48
²³⁹ Pu	94	2	48
²⁴⁴ Cm	96	2	48

12.0 Further Reading

Horwitz, E. P., M. L. Dietz, D. M. Nelson, J. J. LaRosa, and W. D. Fairman. 1990. "Concentration and Separation of Actinides from Urine Using a Supported Bifunctional Organophosphorus Extractant." *Anal. Chim. Acta*, 238:263-271

Horwitz, E. P., R. Chiarizia, M. L. Dietz, and H. Diamond. 1993. "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography." *Anal. Chim. Acta*, 281:361-372.

13.0 Source Procedures for the Consolidation

Strebin, R. S. 1993. "Separation of Am and Pu and Actinide Screen by Extraction Chromatography," PNL-AL0-417, *Analytical Chemistry Laboratory Procedures Manual* MA-599, Pacific Northwest Laboratory, Richland, Washington.

Nelson, D. M. 1993. "Measurement of Actinides in Urine," Rev. 0, DARC-0013, Radiochemistry Laboratory, Environment, Safety and Health Division, Argonne National Laboratory, Argonne, Illinois.

RP730(a)

Gross Gamma Screening for Environmental Matrices

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method is for rapidly screening a variety of matrices for both high and low activities of gamma emitting radionuclides. The purpose of this method is to provide a quick, inexpensive, "order-of-magnitude" estimate concerning the activity within the samples to subsequently determine 1) sample handling for both laboratory safety and counting configurations and 2) if further, more in-depth isotopic analysis is required.

Disclaimer: Gross screening analyses are not expected to be as accurate nor as precise as their isotopic counterparts. Rather, they are intended to provide rapid information associated with a particular action level with minimal chemical preparation. Also, no isotopic information is given as a result of this method—only a measure of the total gamma activity in the sample. Only in cases where the sample and calibration standards are identical in composition and configuration and the isotopes are known can the results be accurately converted to absolute disintegration rate.

2.0 Summary of Method

Samples are packaged in appropriate counting geometries (usually laboratory and detector specific—LANL uses 500-mL plastic bottles) and are counted in an appropriate gamma detector (for example, intrinsic Ge, Ge(Li), NaI(Tl) well-type or planar detectors). Currently, for gross gamma analyses, the well-type NaI(Tl) have proven to be the most cost effective. Samples are then placed directly into the detector (without chemical processing) and counted for a suitable amount of time.

Note: Sample size is usually determined by the specific container that is used (i.e., LANL liquid sample sizes are typically 500 mL).

(a) This method was consolidated by W. Patrick Brug (Los Alamos National Laboratory, Los Alamos, New Mexico).

3.0 Interferences

Although the method is intended to measure gamma-emitting isotopes, the wall thickness of the detector is such that high-energy beta particles from the sample will also be counted.

4.0 Apparatus and Materials

- An appropriate gamma counter of any type: i.e., Model No. 550 EG&G Ortec, equipped with a 10.16-cm-dia x 15.24-cm (4 in. dia x 6in.) NaI[Tl] well-type scintillation detector, with a 7.62-cm-dia x 13.97-cm-dia (3 in. dia x 5.5 in.) well and a single-channel analyzer. The system window is adjusted to observe 0- to 2-MeV gamma rays.
- Amplifier (if not part of detector): i.e., Model No. 572, EG&G Ortec
- Timer/counter (if not part of detector): i.e., Model No. 871, EG&G Ortec
- Bias supply (if not part of detector): i.e., Model No. 459 EG&G Ortec
- Sample containers—specific to detector and laboratory requirements: i.e., 500-mL polyethylene bottles
- Analytical balance of the appropriate minimum capacity (i.e., 300 g) to accurately weigh solid samples
- Bags: Low-density polyethylene (LDPE) clear bags, sized to fit sample containers. The bags protect the detector from surface contamination on the bottles.
- Funnel

5.0 Reagents

No reagents are required.

6.0 Sample Collection, Preservation, and Handling

No special collection and storage requirements are necessary.

7.0 Calibration and Standards

- 7.1 Preparation.** All standards should be prepared from National Institute for Standards and Technology (NIST) Standard Reference Material (SRM) 4233-B, ¹³⁷Cs Burn-up standard. When doing isotopic gamma analysis, it is found that the efficiency of

detecting a gamma ray is energy dependent. To correctly calibrate the detection efficiency, a mixed-energy gamma source that completely encompasses the target analyte's energy is used. For gross-gamma analysis, a ^{137}Cs standard is chosen since its detection efficiency relationship closely represents the average detection efficiency for all the gamma-emitting isotopes of interest.

7.1.1 The liquid standard should be prepared by diluting an aliquot of the stock solution to the desired volume (i.e., 500 mL) with distilled water. The standard is poured into the sample container (i.e., polyethylene bottle).

7.1.2 The soil standard should be prepared by evaporating an aliquot of the stock solution on an appropriate aliquot (i.e., 100 g) of blank soil under an infrared lamp. The solution must not contact the walls or bottom of the container. The dry standard should be thoroughly blended with a stainless steel spatula and transferred to the target sample container (i.e., a polyethylene bottle) with the aid of a polyethylene powder funnel and a small brush.

7.2 **Blanks.** The liquid blank is an appropriate volume (i.e., 500 mL) of distilled water, and the soil blank is an appropriate quantity (i.e., 100 g) of washed deep-well sand.

7.3 Usage

7.3.1 An appropriate quality control (QC) material should be counted with each sample set to record detector system performance.

7.3.2 The appropriate blank should be counted with each sample set. The data should be used to calculate the background count of the counter.

7.4 **Efficiency Determinations.** When making efficiency calibration standards, the activity loading of the resultant standard should be such that the number of total counts in the desired count time is sufficiently high enough to minimize the statistical counting error (i.e., a general criterion is a total of 10,000 counts, which yields a 1% counting error).

8.0 Procedure

8.1 Backgrounds

8.1.1 The appropriate matrix blank should be placed in the gamma detector and the background count rate recorded.

8.1.2 Ideally, background counting times are usually performed overnight to improve the counting statistics. For field analyses where long background counts are not feasible, backgrounds should be counted for at least as long as a sample.

8.1.3 Background counts are generally performed daily. For field analyses, backgrounds are generally performed before and after each sample batch. The average background count rate is used to determine the net analyte counts.

8.2 Soils, Waters, etc.

8.2.1 An appropriate quantity (i.e., 100 g for soils, 500 mL for waters) of a sample should be weighed into the sample container (i.e., the polyethylene bottle). Soil samples should be dried if possible.

8.2.2 The bottle is tightly capped, and any exterior contamination is cleaned off.

8.2.3 The sample is placed into a plastic bag to prevent any accidental cross-contamination, and the container is inserted into the gamma detector.

8.2.4 The sample should be counted for an appropriate length of time.

8.3 Quality Control Samples

8.3.1 Quality control samples should be handled in exactly the same fashion as a typical sample.

8.3.2 A general guideline is to count a QC sample with each daily sample batch.

9.0 Calculations

Calculations of radiometric counting data for determinations are made without a radiotracer. Most data values are assumed to have Poisson distributions, and all time-measurement errors are assumed to be insignificant.

9.1 **Counting Efficiency.** The counting efficiency of the counter for a single standard run is calculated using the following equation:

$$E = \frac{\left(\frac{C_s}{t_s} \right) - \bar{B}}{A_s}$$

where

E	=	efficiency (counts per disintegration)
C_s	=	gross counts for the standards
t_s	=	counting time for standard
$\bar{B}$	=	average background count rate
A_s	=	activity of the standard.

The average counter efficiency is calculated from a running average of the last n values of individual E determinations using the following equation:

$$\bar{E} = \frac{\sum_{i=1}^n E_i}{n}$$

where

$\bar{E}$	=	the running average of the counting efficiency
E_i	=	the individual counting efficiencies
n	=	the number of measurements used for calculation.

The standard deviation of $\bar{E}$ is calculated as follows:

$$\sigma_{\bar{E}} = \bar{E} \cdot \sqrt{\frac{\sum_{i=1}^n (E_i - \bar{E})^2}{n(n-1)\bar{E}^2} + \frac{\sigma_{A_s}^2}{A_s^2}}$$

where

$\sigma_{\bar{E}}$	=	standard deviation of the average efficiency
A_s	=	activity of the standard
σ_{A_s}	=	stated standard deviation associated with the known value of A_s .

The standard deviation of an individual efficiency, E , is calculated as follows:

$$\sigma_E = \frac{1}{A_s} \cdot \sqrt{\frac{C_s}{t_s^2} + \sigma_{\bar{B}}^2 + E^2 \sigma_{A_s}^2}$$

where

σ_E	=	standard deviation of E (counts per disintegration)
$\sigma_{\bar{B}}$	=	standard deviation of the average background count rate.

9.2 Background. The background count rate is calculated as follows:

$$B = \frac{C_b}{t_b}$$

where

B	=	background count rate
C _b	=	gross counts of background
t _b	=	counting time of the background.

A running average of the background count rate is calculated using the following equation:

$$\bar{B} = \frac{\sum_{i=1}^n B_i}{n}$$

where

$\bar{B}$	=	average background count rate
B _i	=	background count rate
n	=	number of values used.

The standard deviation of the average background count rate is calculated using the following equation:

$$\sigma_{\bar{B}} = \bar{B} \cdot \sqrt{\frac{\sum_{i=1}^n (B_i - \bar{B})^2}{n(n-1) \cdot \bar{B}^2}}$$

where

$\sigma_{\bar{B}}$	=	standard deviation of the running average of the background
$\bar{B}$	=	average background
B _i	=	ith background count rate.

9.3 Sample Activity. The activity in the samples is calculated as follows:

$$A_x = \frac{\left(\frac{C_x}{t_x} \right) - \bar{B}}{E}$$

where

A_x	=	sample activity
C_x	=	gross counts for the sample
t_x	=	counting time for the sample.

The standard deviation of the activity in the sample is calculated as follows:

$$\sigma_{A_x} = \bar{E}^{-1} \cdot \sqrt{\frac{C_x}{t_x^2} + \sigma_{\bar{E}}^2 + A_x^2 \sigma_{\bar{E}}^2}$$

where

σ_{A_x}	=	standard deviation of sample activity
$\sigma_{\bar{E}}$	=	standard deviation of the average efficiency
$\sigma_{\bar{B}}$	=	standard deviation of the average background count rate.

The reported activity calculation to put the radiometric measurement into the required form for final reporting is as follows:

$$R_x = \frac{A_x}{K \cdot Q}$$

where

R_x	=	sample activity in correct units for reporting
K	=	factor to convert to desired reporting units
Q	=	sample quantity analyzed (i.e., 0.5 L or 100 g).

The propagated uncertainty of the reported activity is calculated using the following equation:

$$\sigma_{R_x} = \sqrt{\frac{\sigma_{A_x}^2}{K^2 Q^2} + R_x^2 \left(\frac{\sigma_Q^2}{Q^2} \right)}$$

where

σ_{R_x}	=	propagated uncertainty of the reported activity
σ_{A_x}	=	standard deviation of sample activity
σ_Q	=	standard deviation of the sample quantity aliquoted.

10.0 Method Performance

- 10.1** The limits of detection are 22.2 Bq/L (600 pCi/L) for aqueous solutions and 0.11 Bq/g (3 pCi/g) for solids at the 661 keV ^{137}Cs line.

- 10.2 This method is intended as a qualitative assessment of gross-gamma activity, but the accuracy and precision have been assessed using ^{137}Cs standards. For 0.5-L water samples, the accuracy at 51.3 Bq/L (1400 pCi/L) is $108\% \pm 53\%$. For 100-g soil samples at 8.14 Bq/g (220 pCi/g), the accuracy is $104\% \pm 3\%$.

11.0 Further Reading

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Los Alamos National Laboratory (LANL). "Gross Gamma in Environmental Matrices," ER-150. *DOE Procedures Database*. Los Alamos, New Mexico {for access contact W. Patrick Brug (505-665-7409; e:Mail - brug@lanl.gov)}.

RP735^(a)

Determination of Total Fissile Content by Neutron Activation Followed by Delayed Neutron Counting

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method is useful for determining the concentration of any fissile element or the total fissile concentration in a mixture of fissile elements. It can be used in a variety of matrices. However, the method cannot be used to quantify individual radionuclides in a mixture of radionuclides. This method is also useful as a screening technique for large numbers of samples.

The determination of gross fissile content in samples such as contaminated soil, waste, or biological materials has become an important part of current environmental-restoration efforts. This method considers the fissions induced in materials by neutron bombardment followed by counting the delayed neutrons, emitted during fission, with boron trifluoride tubes. The method is especially applicable to those materials that do not activate to form high levels of long-lived radionuclides. These materials include soil, rocks, certain ores, and many biological materials, such as leaves.

2.0 Summary of Method

- 2.1 A homogenized sample is weighed and placed into a clean irradiation capsule.
- 2.2 The sample is bombarded with neutrons, allowed to decay for a short time, and transferred to a counting station for analysis.
- 2.3 Comparative standards, containing a known amount of the fissile material of interest, and laboratory control standards are also irradiated and counted.
- 2.4 The neutron bombardment flux, irradiation time, and counting geometry must remain constant throughout analysis of samples and comparative standards.

(a) This method was submitted by D. C. Glasgow (Oak Ridge National Laboratory, Oak Ridge, Tennessee).

- 2.5 The fissile material in a sample is quantified as equivalents of fissile material based on the delayed neutron counts accumulated for the comparative standard. Therefore, as an example, if the comparative standard is composed of 50 μg of ^{235}U , the total fissile content in the sample would be expressed as μg of ^{235}U .

3.0 Interferences

- 3.1 If the irradiation capsule is contaminated with fissile elements, error will be introduced into the measurement. Chemical contamination by substances other than those that are fissile has no effect on the determination.
- 3.2 The time between the end of irradiation and the beginning of the count, or decay time, must be kept constant for all samples and standards.
- 3.3 Assumptions about the level of enrichment and identity of fissile material (e.g., Pu, U, Np, etc.) of the samples may have to be made as part of the comparative analysis technique. If necessary, the isotopic ratio for two isotopes can be verified by an alternate technique. Uranium-235 is generally assumed to exhibit its natural abundance of 0.72% of ^{238}U .
- 3.4 The counting geometry must be reproducible and constant throughout a batch of samples so that counting errors are minimized. A short delay (10 to 20 sec) may be necessary if high levels of fissile elements or if high gamma activity creates a dose problem.

4.0 Safety

This method is intended for use with samples that do not contain macro amounts of fissile elements. The irradiation of U ore, enriched U, and large samples having percent amounts of fissile material is discouraged under this method. Such irradiations may promote unsafe conditions and should be strictly avoided. Careful adherence to the nominal material safety limits for the neutron source will help decrease the likelihood of criticality problems.

5.0 Apparatus and Materials

- Neutron source - ^{252}Cf , reactor, etc.
- High purity irradiation capsules, such as polyethylene or graphite
- BF_3 , neutron detectors with associated amplifiers, power supplies, and analog-to-digital converters
- Fissile material standards and flux monitors if desired

6.0 Reagents

None

7.0 Sample Collection, Preservation, and Handling

- 7.1 Care should be taken to avoid cross contamination of the samples as well as contamination by other fissile elements.
- 7.2 Samples that have been sealed in irradiation capsules can be stored for extended periods as no losses can occur.

8.0 Procedure

- 8.1 Before irradiating samples, three comparative neutron-activation standards should be irradiated. The relative agreement of the counts between these standards should be within 2%. The amount of fissile material should be chosen such that the neutron count is precisely and accurately measured, thus minimizing analytical bias after comparison with these standards. These standards should be representative of the element(s) to be measured.
- 8.2 About 0.5 g of sample (depending on neutron flux, irradiation time, and expected concentration) are placed in an irradiation capsule. No sample dissolution is necessary. The capsule is sealed by melting the lid to the body, forming an air-tight enclosure.
- 8.3 The samples are irradiated long enough to yield the desired fluence, but irradiation times longer than about 120 sec are not helpful since the lifetime of the delayed neutrons emitted is approached during the irradiation.
- 8.4 The delayed neutrons are counted after some reproducible decay time (e.g., 15 sec). Decay time can be chosen such that sample travel time to the neutron counter is taken into account. The decay time must be kept constant between samples and standards as delayed neutron emission is both time and element dependent.

The count time should be delayed such that prompt neutrons are not counted. Only delayed neutrons should be counted.

If necessary, the samples should be shielded after irradiation and during counting as they will be emitting radiation. Any applicable procedures for the handling and disposal of radioactive solids should be observed.

9.0 Calculations

- 9.1 The neutron counts for the comparative standards are averaged, and a calibration factor is determined in the following way:

$$F = \frac{(\mu\text{g of Standard})}{(\text{Avg. Neutron Count})} \quad \text{Eq. 1}$$

- 9.2 The average background value is then subtracted from the neutron count for the sample and multiplied by the factor generated by Eq. (1). The sample concentration is calculated as follows:

$$[\text{Sample}] = \frac{(\text{Counts} - \text{Bkgd.}) \cdot F}{M} \quad \text{Eq. 2}$$

In this case, "F" is the calibration factor and "M" is the sample mass in grams. Since the units on "F" are $\mu\text{g}/\text{count}$, this equation yields concentrations in units of $\mu\text{g}/\text{g}$.

10.0 Quality Control

- 10.1 A quality control (QC) protocol sufficient for the needs of a particular sample request should be implemented to include the desired level of quality assurance.
- 10.1.1 Empty irradiation containers (e.g., three) should be irradiated and counted for delayed neutrons such that a blank value can be established.
 - 10.1.2 Because samples need to be counted quickly after irradiation, the neutron detectors and associated electronics should be evaluated by counting a standard source of neutrons.
 - 10.1.3 Standard reference materials should be periodically irradiated and counted during a batch of samples. The isotopic concentration of fissile elements in the standards should be comparable to those in the samples to be analyzed.
 - 10.1.4 Spiked and duplicate samples are recommended as needed.

11.0 Method Performance

- 11.1 In a single laboratory evaluation, several standard reference materials were analyzed; the results are summarized in Table 1. A depleted U Standard (Spex U) was used for calibration. Except for the Spex U material, the test material contained natural isotopic

U. The measured values are corrected for the difference in U enrichment. The accuracy and precision of the method makes it an excellent technique for determining fissile content.

Table 1. Delayed Neutron Analysis of U in National Institute for Standards and Technology Standard Reference Materials

Material Identification	True U ($\mu\text{g/g}$)	Measured U ^(a) ($\mu\text{g/g}$)	Standard Deviation ($\mu\text{g/g}$)	Number of Observations	Percent Difference
2709 Soil	(3)	3.15	.08	7	5
1633a Fly ash	10.2	10.31	.12	7	1.1
Spec U ^(b)	20	20.08	.15	14	0.4
1575 Pine needles	0.02	0.021	0.002	14	6.5
4353 Soil	3.1	2.91	.20	3	6.1
3164 Soil	50	48.6	.02	316	2.8
(a) Mean values					
(b) Uranium inductively coupled plasma standard from Specpure (depleted U)					

11.2 Seven samples were prepared from high-purity silica gel (a standard support material free of fissile material) spiked with $0.0677 \mu\text{g } ^{235}\text{U}$. In the same manner, various amounts of ^{235}U were spiked in duplicate onto silica gel. The spike recovery and duplicate performance data are displayed in Tables 2 and 3, respectively. The recoveries are typically better than 95% for the spikes, and the relative percent differences are typically less than 5% for the duplicates.

11.3 The detection limit of the delayed-neutron-analysis method is on the order of a few hundred nanograms, depending on the bombardment flux, the neutron cross section, and the absence of a significant neutron background.

11.4 Though much of the work described here involved the determination of U, virtually any fissile nuclide can be determined. Table 4 is a partial list of fissile nuclides that can be determined by the delayed neutron method. Note: Values in parentheses are calculated or theoretical values. Notice that each nuclide has a characteristic delayed-neutron yield for both thermal-fission and fast-fission processes. The ratios of these yields to those of ^{235}U can be used to calculate the concentrations of the element of interest when ^{235}U is used as the comparative standard. Correction of spontaneous fission (SF) must also be performed.

Table 3. Duplicate Analyses by Delayed Neutron Counting

Sample Number	Duplicate $\mu\text{g } ^{235}\text{U}$	Sample $\mu\text{g } ^{235}\text{U}$	Relative % Difference
1	0.0210	0.0204	3.18
2	0.0257	0.0253	1.71
3	0.0233	0.0243	4.14
4	0.0447	0.0433	3.33
5	0.0346	0.0338	2.34
6	0.0343	0.0345	1.00
7	0.0315	0.0320	1.60
Standard Deviation			1.21

Table 2. Spike Recovery Data for Delayed Neutron Counting

(a) Based on a spike value of 0.0677 $\mu\text{g } ^{235}\text{U}$

Sample Number	^{235}U Spike (μg)	% Recovery of Spike (a)
1	0.0679	100.3
2	0.0682	96.8
3	0.0604	85.5
4	0.0683	100.1
5	0.0673	99.5
6	0.0674	99.5
7	0.0669	98.9
Standard Deviation		5.30
Based on a spike value of 0.0677 $\mu\text{g } ^{235}\text{U}$		

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Table 4. Compilation of Fissile Nuclide Data

Nuclide	SF(%)	Neutron Yield per fission by fast n	Ratio to ²³⁵ U fission by fast n	Neutron Yield per fission by thermal n	Ratio to ²³⁵ U fission by thermal n
²³² Th	2.37	.06 ^(a) , .0496 ^(b)	3.3	.0527 ^(c)	3.2
²³³ U	1.3E-10	.0077 ^(b) , .00779 ^(d) , .007 ^(b)	.47	.0074 ^(c) , .0066 ^(a,b)	.43
²³⁵ U	WEAK	.0165 ^(b) , .0164 ^(e)	1.0	.0158 ^(b) , .0167 ^(e)	1.0
²³⁸ U	WEAK	.049 ^(a) , .0412 ^(b) , .0439 ^(e)	2.7	.046 ^(c)	2.8
²³⁶ Np	N	(.0077) ^(b)	(.47)	(.00648) ^(f)	(.40)
²³⁷ Np	N	.0122 ^(d) , (.011) ^(f)	.74	.0107 ^(e)	.66
²³⁸ Pu	1.84E-7	.00406 ^(d) , (.0053) ^(f)	2.5	.0046 ^(c)	.28
²³⁹ Pu	4.4E-10	.0069 ^(a) , .0063 ^(b) , .00598 ^(e)	.40	.0061 ^(a,b) , .0065 ^(c)	.39
²⁴⁰ Pu	N	.00911 ^(d) , .0088 ^(b)	5.4	.0090 ^(c)	.55
²⁴¹ Pu	N	.0160 ^(d)	.97	.0157 ^(c)	.96
²⁴¹ Am	4.1E-10	.00394 ^(d) , (.0053) ^(f)	.24	.0044 ^(c)	.27
^{242m} Am	WEAK	(.0077) ^(f)	(.47)	(.00648) ^(f) , .0069 ^(e)	.42
²⁴³ Cm	N			(.00267) ^(f)	(.16)
²⁴⁴ Cm	1.347E-4	(.0053) ^(f)	(.32)		
²⁴⁵ Cm	WEAK	(.0077) ^(f)	(.47)	(.00648) ^(f) , .0059 ^(e)	.36
²⁴⁷ Cm	N	(.0158) ^(f)	(.96)	(.0157) ^(f)	(.96)
²⁴⁹ Cf	2.5E-7	(.0037) ^(f)	(.22)	(.00267) ^(f) , .0027 ^(e)	.16
²⁵¹ Cf	N	(.0077) ^(f)	(.47)	(.00648) ^(f)	(.40)
²⁵² Cf	3.092	.86 by SF ^(b)	52	.86 by SF ^(b)	53

Note: Values in () are calculated values.

(a) Keepin, 1972.
 (b) ANL-5800, 1963
 (c) Waldo, 1981.
 (d) Benedetti, 1982.
 (e) Bersant, 1977.
 (f) Ronen, 1989.

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13.0 Further Reading

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U.S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste: Volume 1B, Laboratory Manual Physical/Chemical Method*. 3rd Edition, EPA/SW-846, Office of Solid Waste and Emergency Response, Washington, DC. Available from the National Technical Information Service, Springfield, Virginia.

RP800^(a)

Sequential Separation of Americium and Plutonium by Extraction Chromatography

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method is a fast sequential separation for Am/Cm and Pu in aqueous samples. Additionally, provision has been made for eluting Np off the extraction column following the Pu and Am elution. The method applies to simple and complex aqueous matrices. It has been used on Hanford tank-waste samples and soil leachates of up to 1 g equivalent soil.

2.0 Summary of Method

The sample matrix is converted to 2 M HNO₃. An Fe⁺³ carrier is added, and the oxidation state of the actinides and Fe are adjusted with ascorbic acid. The sample is loaded on a prepared TRU•Spec[®] column. Most lanthanides, Am, Cm, Pu, and Np, are retained on the column and impurities are washed through the column. The Am and Cm are selectively eluted with 9 M HCl and 4 M HCl. The Pu is eluted with 4 M HCl•0.1 M hydroquinone. Neptunium may be eluted next from the TRU•Spec[®] column with 0.1 M ammonium bioxalate. The Pu and Am fractions can be prepared for alpha spectrometry electrodeposition or precipitation plating.

3.0 Interferences

3.1 Chelators present in the sample solution {such as ethylenediaminetetraacetic (EDTA), diethylhexyl-phosphoric acid (HDEHP), etc.} may complex the actinides such that they will not extract into the substrate. In such cases, the chelators may need to be destroyed by wet ashing or oxidation in a muffle furnace.

(a) This method was consolidated by R. S. Strebin and S. K. Fadeff (Pacific Northwest Laboratory, Richland, Washington).

- 3.2 High phosphate or fluoride concentrations may complex the actinides such that they will not extract into the substrate. The phosphate and fluoride can be bound with Al if $\text{Al}(\text{NO}_3)_3$ is present in the feed solution, thus minimizing interference with tetravalent isotope extraction.
- 3.3 The column capacity is limited to approximately 2 to 4 mg of actinides and lanthanides on a 2-mL prepacked TRU•Spec[®] column (product literature, Eichrom Industries, Inc., Darien, Illinois). Samples with excessive amounts of lanthanides or actinides will need to be diluted, and a small aliquot will need to be taken before analysis.

4.0 Safety

No special safety precautions are indicated for this method.

5.0 Apparatus and Materials

- Eichrom TRU•Spec[®] pre-packed column
- Column support rack

6.0 Tracers and Reagents

6.1 Tracers

- Plutonium yields may be traced with ^{242}Pu (4.90 MeV) or ^{236}Pu (5.76 MeV).
- Americium yields may be traced with ^{243}Am (5.28 MeV) or ^{244}Cm (5.81 MeV).

6.2 Reagents

- All reagents are prepared from analytical reagent-grade chemicals. Concentrations are not critical and need only be within $\pm 10\%$ of stated values.
- Nitric acid, concentrated (16 M), 2 M HNO_3 , and 0.025M HNO_3
- Column feed solution (one of two options in step 8.2 may be used)
 - 2 M HNO_3 (If phosphate or fluoride are present, this feed solution may result in reduced tetravalent isotope yields, especially for Np.)
 - 2 M $\text{HNO}_3 \cdot 0.5 \text{ M Al}(\text{NO}_3)_3$

- Hydrochloric acid, concentrated (12 M), 9 M HCl, and 4 M HCl
- Sulfuric acid, concentrated (18 M) H_2SO_4
- Fe^{+3} carrier, 10 mg/mL (For example, 18.08 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is diluted in 250 mL H_2O ; another ferric salt may be used or another concentration as long as the required milligrams of Fe^{+3} are added to the sample as indicated.)
- 2 M HNO_3 saturated with ascorbic acid (This solution is made just before use. Solid ascorbic acid is added to approximately 5 mL 2 M HNO_3 until no more will dissolve and some solid ascorbic acid remains.)
- 0.1 M hydroquinone•4 M HCl (This solution may be prepared by dissolving 1.1 g hydroquinone $\{\text{C}_6\text{H}_4(\text{OH})_2\}$ in 100 mL 4 M HCl.)
- Sodium nitrite (NaNO_2)
- Ammonium bioxalate, 0.1 M $\text{NH}_4\text{HC}_2\text{O}_4$ (This may be prepared by dissolving 1.2 g ammonium oxalate and 0.9 g oxalic acid in 200 mL water.)

7.0 Sample Collection, Preservation, and Handling

Water samples collected for Pu and Am determination should be preserved with HNO_3 . No refrigeration is required.

8.0 Procedure

- 8.1 Radionuclide tracers are added as required by the analysis to an appropriate size aliquot or aqueous sample. The tracer activity should be appropriate for the sample activity (e.g., a 1:1 ratio of tracer to analyte works well). The exact amount of tracer added needs to be recorded.
- 8.2 The sample matrix is converted to the column feed solution {2 M HNO_3 or 2 M HNO_3 •0.5 M $\text{Al}(\text{NO}_3)_3$ }. Examples of the conversion process are described below. The first option may be most appropriate for small-volume, highly-radioactive samples. The second option is best applied to large-volume aqueous samples. The third option is applicable to most sample types, including soil leachates. However, because $\text{Fe}(\text{OH})_3$ precipitation is not quantitative for pentavalent isotopes, an initial oxidation state reduction is used. The fourth option is applicable to urine and water matrices.
 - A small aliquot (e.g., <0.5 mL) is added to a beaker containing 5-mL column feed solution.

- The sample is evaporated to a low volume and brought up to a 5-mL volume with column feed solution.
- A small volume of dissolved $\text{NH}_2\text{OH}\cdot\text{HCl}$ is added to the sample to reduce the actinide oxidation states. Ten milligrams of Fe^{+3} carrier may be added (if Fe is not already present), and the Fe and actinides are precipitated as the hydroxides with the addition of NH_4OH . The precipitate is centrifuged, and the supernate is decanted and discarded. The $\text{Fe}(\text{OH})_3$ precipitate is dissolved with an excess of column feed solution such that the NO_3^- concentration is essentially equivalent to that of the column feed solution.
- Fifty milligrams of Ca^{+2} carrier are added to each sample. After mixing, 1500 mg of PO_4^{-3} are added. The $\text{Ca}_3(\text{PO}_4)_2$ precipitate is formed by adding NH_4OH until the solution is basic. The precipitate is centrifuged and the supernate is decanted and discarded. The $\text{Ca}_2(\text{PO}_4)_3$ precipitate is dissolved in the column feed solution (containing Al).

- 8.3 To the solution, 10 mg Fe carrier are added (if not already present), and the solution is gently mixed.

At this point, the sample should have a yellow color typical of Fe-nitrates.

- 8.4 Then 2 M HNO_3 , saturated with ascorbic acid, is added to the solution 1 to 3 mL at a time. The ascorbic acid will make the solution turn blue momentarily. The ascorbic acid solution addition is continued until further addition ceases to cause the blue color.

This step reduces $\text{Fe}^{(+3)}$ to $\text{Fe}^{(+2)}$ and complexes $\text{Fe}^{(+2)}$ with ascorbic acid. The Pu is stabilized to the +3 oxidation state, and $\text{Np}^{(+6)}$ is reduced to $\text{Np}^{(+4)}$, ensuring their retention on the TRU•Spec[®] column. The $\text{Fe}^{(+2)}$ is eluted without interfering with the retention of other actinides.

- 8.5 An Eichrom TRU•Spec[®] column is prepared for each sample as follows:

8.5.1 The tip is broken off an Eichrom TRU•Spec[®] disposable column and the water is allowed to drain.

8.5.2 The column is washed with 5 to 10 mL 2 M HNO_3 . The column is now ready to use for sample separation.

- 8.6 The sample (from step 8.4) is added to the column.

The column may change color; this is a matrix effect and should not affect the performance of the column.

- 8.7 The column is washed with 2 to 5 mL 2 M HNO₃. The wash is discarded.
- 8.8 Approximately 500 mg NaNO₂ are mixed into 5 mL H₂O. Then 100 µL of this solution are added to 5 mL 2 M HNO₃. This latter solution is mixed and added to the column.
- The column may turn blue as this is added. The Pu is oxidized to the +4 oxidation state.*
- The wash is discarded.
- 8.9 The column is washed with 20 mL of 2 M HNO₃; the wash is discarded.
- 8.10 Americium is eluted with 2 mL 9 M HCl followed by 13 mL 4 M HCl.
- 8.11 Plutonium is eluted with 15 mL 4 M HCl•0.1 M hydroquinone.
- Np may be eluted next from the TRU•Spec[®] column with 15 mL 0.1 M acid ammonium oxalate. Further cleanup of the Np eluent will need to be performed before analysis. This may include wet-ashing and an anion-exchange separation. Thorium and uranium will also elute with this Np fraction.*
- 8.12 The Am and Pu fractions are ready for precipitation plating or electrodeposition and analysis by alpha spectrometry.

9.0 Calculations

Using a tracer and alpha spectrometry, the isotope activity can be calculated as follows

$$\text{Activity} = \frac{C_{\text{analyte}} \cdot \text{TR}}{C_{\text{TR}}} \cdot \frac{K}{Q}$$

where

C_{analyte}	=	net analyte counts
TR	=	added tracer activity
C_{TR}	=	net tracer counts
Q	=	sample quantity analyzed
K	=	factor to convert to desired reporting units.

10.0 Quality Control

10.1 It is recommended that, at a minimum, one reagent blank and one blank spike be run with each analytical batch to evaluate the effectiveness of the full analytical process, including data reduction.

10.2 The blank should indicate no contamination if the analytes of interest are present.

10.3 The blank spike (yield corrected) should indicate low (<10%) method bias.

11.0 Method Performance

The method performance for two different matrices, organic phase from a Hanford waste tank and soil leachate solutions, is presented.

Tank Waste

Four samples of a Hanford organic waste tank were analyzed according to this method. To each 50 μL sub-sample, ^{242}Pu and ^{243}Am tracers and Ca carrier were added. A blank spike sample was prepared with an organic simulant and was spiked with 11.97 pCi/g ^{239}Pu and 9.55 pCi/g ^{241}Am . The samples were heated to evaporate volatile organics, then muffled overnight at 500°C to oxidize remaining organics. The method as described was followed, and the analyte fractions were precipitation plated and counted by alpha spectrometry. The method performance is summarized in Table 1.

Identification	pCi/g ^{238}Pu	RSD*	pCi/g $^{239+240}\text{Pu}$	RSD*	Bias	pCi/g ^{241}Am	RSD*	Bias
X11	83.6 $\pm$ 3.4		191 $\pm$ 5.8			182 $\pm$ 3.8		
X11 dup	93.7 $\pm$ 3.8		196 $\pm$ 6.2			177 $\pm$ 4.0		
X12	96.4 $\pm$ 3.3	6%	199 $\pm$ 5.5	3%		183 $\pm$ 4.2	2%	
X14	84.9 $\pm$ 3.6		186 $\pm$ 6.0			175 $\pm$ 4.0		
X15	92.2 $\pm$ 6.0		199 $\pm$ 6.0			179 $\pm$ 4.0		
Blank	<0.7		0.73 $\pm$ 0.28			0.92 $\pm$ 0.29		
Blank Spike	na		12.6 $\pm$ 0.34		+5%	9.41 $\pm$ 0.23		-1.5%

*relative standard deviation

Soil

Two 10-g aliquots of soil samples were acid leached. The equivalent soil mass analyzed was approximately 1 g. The blank spike sample was spiked with 23 pCi ^{239}Pu and 9.4 pCi ^{241}Am . The matrix spike sample was spiked with 17.8 pCi/g ^{239}Pu and 7.06 pCi/g ^{241}Am . Because the

samples contained a large U concentration, an initial U separation was performed. This was done by passing the sample through a prepared U/TEVA-Spec[®] column. The duplicate sample results and the matrix and blank-spike recoveries are provided in Table 2.

Table 2. Method Performance on Soil Leachate Samples

Identification	PC/fg ^a 239+240Pu	RPD ^(a)	Bias	pg/fg ^a 241Am	RPD ^(a)	Bias
1156	4.40 ± 0.20			0.098 ± 0.0073		
1156 duplicate	4.16 ± 0.15	5.6		0.132 ± 0.0085	30	
Blank	<0.5			<0.05		
Matrix spike	20.4 ± 0.49		-10%	6.85 ± 0.16		-4%
Blank spike (pCi)	24.2 ± 0.57		+2%	9.14 ± 0.20		-3%
(a) Relative percent difference						

Horowitz, et al. (1993) published the elution behavior of various elements on a TRU-Spec[®] column. This table is reproduced on the following page.

12.0 Reference

Horwitz, E. P., R. Chiarizia, M. L. Dietz, and H. Diamond. 1993. "Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," *Anal. Chim. Acta*, 281, 361-372.

13.0 Further Reading

Eichrom Industries, Inc., 8205 S. Cass Ave Suite 107, Darien IL, 60559; Product literature

Horwitz, E. P., M. L. Dietz, D. M. Nelson, J. J. LaRosa, and W. D. Fairman. 1990. "Concentration and Separation of Actinides from Urine Using a Supported Bifunctional Organophosphorus Extractant," *Anal. Chim. Acta*, 238, pp. 263-271.

Kaye, J. H., R. S. Streb, and R. D. Orr. "Rapid, Quantitative Analysis of Americium, Curium, and Plutonium Isotopes in Hanford Samples Using Extraction Chromatography and Precipitation Plating," *J. Radioanal. Nucl. Chem.* In press.

14.0 Source Procedures

"Analysis of Americium in Soil and Bottom Sediment, DAR-C-0007," Radiochemistry Laboratory, Dosimetry and Analytical Services Section, Argonne National Laboratory, Argonne, Illinois.

"Analysis of Plutonium in Soil, Bottom Sediment, and Plants," Procedure DARC-0008, Radiochemistry Laboratory, Dosimetry and Analytical Services Section, Argonne National Laboratory, Argonne, Illinois.

Strebin, R. S. August 1993. "Separation of Am and Pu and Actinide Screen by Extraction Chromatography," PNL-AL0-417, Analytical Chemistry Laboratory Procedures Manual PNL-MA-599, Pacific Northwest Laboratory, Richland, Washington.

Table 3 Elution Behavior of Selected elements on a TRU-Spec[®] Column^(a) (Conditions: T = 23°C, particle size = 50 to 100 µm diameter, 1 FCV = 0.60 mL/Number of Free Column Volumes)

Element	1 to 5 ^b	6 to 10 ^b	11 to 15 ^b	16 to 20 ^b	21 to 25 ^b	26 to 30 ^b	31 to 40 ^c
Li	98.4 ^e	<19	-	-	-	-	-
Na	92.8	<1.2	-	-	-	-	-
Mg	100	-	-	-	-	-	-
Al	99.8	<2.9	-	-	-	-	-
K	81.8	40.9	-	-	-	-	-
Ca	100	-	-	-	-	-	-
Cr	100	-	-	-	-	-	-
Mn	100	-	-	-	-	-	-
Fe	102	<12.3	-	-	-	-	-
Co	100	-	-	-	-	-	-
Ni	100	-	-	-	-	-	-
Cu	100	-	-	-	-	-	-
Zn	100	-	-	-	-	-	-
Sr	100	-	-	-	-	-	-
Y	23.4	76.8	3.5	-	-	-	-
Zr	-	-	-	-	-	-	75.0
Ru	82.6	<19.2	-	-	-	-	-
Rh	100	-	-	-	-	-	-
Ag	100	-	-	-	-	-	-
Cd	100	-	-	-	-	-	-
Ba	100	-	-	-	-	-	-
La	-	-	-	-	-	30.0	72.0
Ce	-	-	-	-	-	<25.0	75.0
Pr	-	-	-	-	-	-	100
Nd	-	-	-	-	-	-	96.0
Sm	-	-	-	-	-	-	100
Eu	-	-	-	-	-	-	>99
Hg	(100)	(60)	(19)	-	-	-	-
Pb	100	-	-	-	-	-	-
Am ^d	-	-	-	-	-	-	>99

a Because of uncertainties inherent in the ICP-AES method, the fractions shown for each element may not total 100%. Values in parentheses are subject to considerable uncertainty and are intended only as a rough guide.

b 2 M HNO₃

c 0.05 M HNO₃

d radiometric determination

e percent eluted

RI010(a)

Gamma-Ray Spectrometry

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This method is intended to provide analytical support for the qualitative/quantitative determination of gamma-ray emitting nuclides in a variety of matrices. This is accomplished with laboratory based instrumental gamma-ray spectrometry systems using either Lithium Drifted Germanium {Ge(Li)}, or High-Purity Intrinsic Germanium type (HPGe) detectors. While a wide variety of radioisotopes can be determined via gamma spectroscopy, the gamma emitting radionuclides of particular interest to DOE are listed in Table 1.

Qualitative identification of radionuclides is derived by examining the samples' specific "fingerprint" of decay schemes and comparing this to known libraries of defined decays and branching ratios. Quantitative data are obtained by determining the net gamma-ray peak areas of the cleanest gamma-ray transitions and correcting for an appropriate matrix blank, peak-specific branching ratios, and decay of the sample from time of collection. They are also obtained by using matrix-based efficiency curves for the sample activity determination.

The accuracy for environmental matrices depends on sample density, geometry, self-absorption characteristics, the isotope of interest, and the specific detector used. Precision can be a function of the variation associated with the peak/background (Peak/Compton) ratios. By examining these factors, along with data generated from secondary standards, characteristic uncertainties can be determined for routine analyses of these specific matrices. For other samples where a more elaborate sample preparation occurred (i.e., concentration and evaporation, elution, or co-precipitation onto a standard media), the accuracy and precision may be more limited by the statistical uncertainty of the counting process than that of background count rates or the sample preparation process.

(a) This method was supplied W. P. Brug and G. Brooks (Los Alamos National Laboratory, Los Alamos, New Mexico).

Table 1. Gamma Emitting Isotopes of Particular Interest to DOE

Nuclide	Half-Life
²⁴¹ Am	432.02 years
⁷ Be	53.29 days
¹⁴⁴ Ce	284.5 days
⁵⁷ Co	271.65 days
⁶⁰ Co	5.2719 years
¹³⁴ Cs	2.062 years
¹³⁷ Cs	30.174 years
¹⁵² Eu	13.2 years
¹³¹ I	8.040 days
⁵⁴ Mn	312.20 days
²² Na	2.062 years
²³³ Pa	26.95 days
²²⁶ Ra	1599 years
¹⁰³ Ru	39.35 days
⁷⁵ Se	118.45 days
⁶⁵ Zn	244.0 days

The sensitivity is limited by such factors as the specific counter background, sample self-absorption, half-lives, and occasionally by direct gamma-ray interferences. In that it is rare that any two Ge crystals have exactly the same gamma-ray sensitivity characteristics, the sensitivity must be determined individually for each crystal.

2.0 Interferences

2.1 Potential gamma-ray spectral interferences are found when the gamma energies are so close that more than one photon is included in the energy window. For example, ¹⁵⁴Eu interferes with the ⁵⁷Co photoppeak at 122 keV and the ²²Na photoppeak at the 1.275 MeV area. These interferences can sometimes be corrected by using non-interfering lower-yield photoppeaks.

2.2 Alternate methods for correcting background interferences can be obtained by using an anti-coincidence type counting system. This system, which can be an array of scintillation detectors around an HPGe type detector, can discriminate and exclude from the counting process any high-energy cosmic-ray charged particles that interact with the counting system during the counting process.

- 2.3 Other forms of signal interference can arise from such sources as direct detector contamination from improperly prepared samples, poorly shielded high-level sources in or near the counting facility, or in the event of ^{241}Am analysis, the interference of the 59 keV line from the lead shielding itself. This latter problem can be adjusted by lining the inside dimensions of the shield with lower Z materials (graded shielding) that will absorb the characteristic X-rays emitted by the bulk of the shield. These potential problem areas can be monitored by systematically counting detector backgrounds each week.

3.0 Sample Collection and Storage

- 3.1 For water or other aqueous samples, the samples should be filtered and acidified soon after collection to minimize the formation of precipitates and optimize sample homogeneity.
- 3.2 No special collection or storage requirements exist for other matrices (silicates, biologicals, filters, etc.).

4.0 Apparatus

- Filter apparatus for filters
- Pipettes with disposable tips
- Polyethylene bottles
- Analytical grade balance
- Graduated cylinders
- Filter media
- Grinding mill
- Gamma-ray spectrometer counting system. This includes the following:

A Ge(Li) or HPGe type detector with a moderate efficiency rating ($>20\%$), peak resolution (<2.0 keV), and signal to noise ratios (>60). These detectors can be cooled by either a conventional type dewar that is maintained on a routine basis with liquid nitrogen, or configured with an automated cryogenic type cooling system.

- Appropriate counting electronics:
 - Nuclear instrumentation module bin and power supply ($\pm 6, 12, 24$ V)
 - Bias supply (0 to 5 keV)
 - High resolution spectroscopy amplifier
 - Ge resolution enhancer for increased signal response
 - Precision pulse generator
 - Coaxial BNC and SHV type cables to carry the signal between the system components
 - Signal processing system
 - Hardware-type multichannel analyzer (MCA). This type of system, characteristic of the early developmental stages associated with gamma spectroscopy, will require that the user provide some means of data storage off-line (either dumped to an alternate computing system, tape, or disk) after the data collection process is completed. Users will have to possess the necessary programs to provide for the data interpretation, reduction, and reporting processes.
 - Software-type multichannel analyzer. This system requires a high performance (386 or faster) personal computing system with a high resolution color monitor for spectrum interpretation, including the specific manufacturers' electronic interface (cards) to massage the signal for the software. This configuration will also require ancillary programs that interpret the signal, such as an MCA emulator, and the necessary software to provide data reduction and reporting capabilities.

5.0. Reagents

- Nitric acid (conc, reagent-grade)
- Hydrochloric acid (conc, reagent-grade)
- Dilute hydrochloric acid (0.1 M)

6.0 System Calibration

- 6.1** To provide adequate accountability within the counting systems, maintaining some form of traceability {primarily from the National Institute of Standards and Technology (NIST)} throughout the calibration procedures is required. Radioactive standard solutions can be acquired directly from NIST, the U.S. Environmental Protection Agency (EPA)-Las Vegas, Amersham Inc., Isotope Products Laboratory (IPL), or a variety of other commercial vendors of radioactive standards. In most cases, the vendors can provide some form of formal traceability to NIST for a minimal cost.
- 6.2** Counter efficiencies should be generated for each environmental matrix encountered. This can be done either of two ways: 1) generate efficiencies for each specific matrix from mono-isotopic sources (i.e., use a ^7Be standard for ^7Be efficiency in the matrix of choice), or 2) generate efficiencies for each specific matrix using a multi-isotopic standard (i.e., $^{152,154}\text{Eu}/^{125}\text{Sb}$ mixed solution, or QCY-48 multi-isotopic solution from IPL).

6.2.1 Solutions: mono- and multi-isotopic

- 6.2.1.1** A weighed (gravimetric) amount of radioactive standard solution should be added to the commonly used containers for the varying geometries and brought to volume with 0.1 M HCl. To minimize evaporation and prevent possible external contamination of other samples, the container should be capped tightly. The necessary information should be recorded and marked on the sample container itself.
- 6.2.1.2** Each matrix specific standard should be counted for the required counting time, as experimentally determined from adequate counting statistics. The spectral data should be reduced using any of a variety of commercially available gamma spectroscopy codes that will provide the necessary matrix specific calibration data.

6.2.2 Solids: mono- and multi-isotopic

- 6.2.2.1** A weighed amount of radioactive standard solution should be added to the matrix. The solution should be dried at room temperature and ball milled thoroughly to insure homogeneity.
- 6.2.2.2** Separate containers should be counted for each geometry to be calibrated and for each of the varying masses of the matrix (example: 25-, 50-, and 100-g).

- 6.2.2.3 Each matrix-specific standard should be counted for the required counting time, as experimentally determined from adequate counting statistics. The spectral data should be reduced using any of a variety of commercially available gamma spectroscopy codes that will provide the necessary matrix specific calibration data.

- 6.3 In instances where commercial products are not used and the calibration curve has to be determined empirically, the user should determine and record the efficiency of each energy as plotted. A mathematical algorithm should then be used (power or log function, 3rd or 4th order polynomial) to determine the best fitting line that will adequately characterize the line. A method of determining which line provides the “best fit” can be determined by examining the statistics of the line, such as the correlation coefficient. In expressing the function, the user will note that the calibration curve can be broken into two distinct parts, and should be calculated as such. An excellent example of a “typical” calibration curve can be seen in Crouthamel (1970).

7.0 Instrument Performance Criteria

- 7.1 Determining the systems’ “absolute” efficiencies for each detector and matrix is suggested on at least a monthly basis. This method maintains the absolute efficiency curves current with the systems’ present operational state. By sustaining timely calibration curves, the user is provided with a high degree of confidence in the samples being analyzed and the final data generated from the calibration set. This operation provides one point within the systems’ overall instrument performance assessment routine.
- 7.2 The “relative” efficiency of each detector should be monitored on a monthly basis through the use of NIST standards, or some form traceable to NIST. This can provide a secondary means of instrument performance assessment, independent of the sample size or matrix configuration. By examining the relative system performance over time, problem areas such as electronic component degradation, signal cable breakdown, cryostat failure, etc., can be more closely examined and either repaired or replaced to bring the system back to operational readiness.
- 7.3 Each week, the matrix specific backgrounds should be counted. This is necessary to provide an adequate record of the systems’ background performance for the data reduction process. The counting time should be determined from the users’ specific level of confidence, based on (among other factors) the counting statistics associated with the sample.

- 7.4 The detector energy calibrations should be maintained on a weekly basis. This will require the user to maintain adequate system resolution width limits; this increases the users'/programs' ability to distinguish and quantify closely spaced nuclides of interest. System resolution of approximately 1 keV/channel is usually recommended.

8.0 Procedure

- 8.1 **Sample Preparation.** In any of the following matrices, the sample size will depend upon such factors as the type of detector and specific configuration, along with the users' specific requirements for accuracy, precision, counting times (statistics), and minimum detection limits.

8.1.1 Water Samples

- 8.1.1.1 The sample should be filtered using the appropriate filter material (typically 0.45 μ m). This provides assurance that the activity is contained within the liquid sample itself, and not associated with the particulates.
- 8.1.1.2 An aliquot of the sample is measured into a graduated cylinder, poured into the polyethylene bottle, and sealed. The bottle should be appropriately marked with the necessary information so that the analyst can proceed with analyzing the sample.

8.1.2 Geological Samples

- 8.1.2.1 The samples should be dried (e.g., 48 h at 400°C) to drive off any incidental moisture that may remain.
- 8.1.2.2 Twice the normal sample volume is placed into a polyethylene bottle. Clean 1-in. ball bearings are added. The bottle should be capped and the sample ball milled for several hours to provide sample homogeneity.
- 8.1.2.3 An aliquot of the milled sample should be weighed into a new polyethylene bottle. The bottle should be appropriately marked with the necessary information so that the analyst can proceed with analyzing the sample.

8.1.3 Vegetation Samples

- 8.1.3.1 The samples are ashed to a constant weight.
- 8.1.3.2 The samples should be ground in a Wiley mill, Brinkman mill, or similar device.
- 8.1.3.3 An aliquot of the ground sample should be weighed into a new polyethylene bottle. The bottle should then be appropriately marked with the necessary information so that the analyst can proceed with the analysis of the sample.

8.1.4 Performance Evaluation Samples

The analysis of these samples provides the laboratory with a guide as to the accuracy, precision, and bias associated with each particular technique. This type of round-robin analysis also provides information concerning the laboratory's performance compared to other "outside" labs; it permits an inter-laboratory comparison.

8.1.4.1 "Open" performance evaluation samples

Samples of this type are run with regular sets to provide information concerning the system's performance during the counting process. The samples are usually blanks that have been spiked with the appropriate nuclide and are in the same configuration as the "real" samples. This type of performance evaluation gives the user system performance criteria, independent of the sample preparation process.

8.1.4.2 "Blind" performance evaluation samples

These samples are provided by either an in-house quality assurance (QA) section, or by programs such as the EML Study or the EPA Cross Check Inter-Laboratory Evaluation program. The purpose of programs such as this is to provide blind samples to the participating laboratories to run through the specific sample analysis protocols. This provides the laboratory with information concerning their performance to other laboratories and the level of specific biases and problems associated with each procedure.

9.0 Operation of Equipment

9.1 Nuclear Counting

- 9.1.1 The sample bottle is placed on the horizontal surface of the Ge(Li) or HPGe detector, and gamma-ray spectra for the users' specified counting time are accumulated. Average counting times (1000 to 5000 sec) are useful for most samples, long count times are effective for very low activity samples (>10,000 sec), and overnight counting (50,000 sec) is typically the practical statistical limit.
- 9.1.2 To provide adequate QA associated with each specific sample set, it is standard practice to count at least 10% "Open" QA samples with each set. This can provide the counting personnel with a high degree of confidence with the data sets being generated by the counting facility. Blind QA materials may also be run with the sample sets as an alternative method to determine other sources of error.
- 9.1.3 The acquisition process should begin per the specific data package instructions. The level of input that the user provides at the initial stages of this process is specific to each individual commercial or "home-grown" package that is available, and is at the discretion of the user. For more exact information, the specific system manual that accompanies each data reduction package should be referenced.
- 9.1.4 After the sample has been counted, the data are then processed to provide the user with a report listing what isotopes are present and in what amounts (activity of the sample per unit volume). This process is again specific to the data reduction package that is in use within the nuclear counting facility; the system manual may be referenced for the specific details in generating the sample reports.

10.0 Calculations

- 10.1 The activity for each nuclide is calculated using the following formula:

$$A = \frac{\left(\frac{C_s}{t_s} - \frac{C_b}{t_b} \right)}{\varepsilon \cdot BR \cdot Q \cdot D}$$

where

A	=	activity of nuclide (Bq/L or Bq/g)
C _s	=	net counts in the nuclide's gamma-ray peak
C _b	=	background counts in the same gamma region
ε	=	detector efficiency for the particular gamma-ray
t _s	=	sample count time (seconds)
t _b	=	background count time (seconds)
Q	=	sample quantity (g or L)
BR	=	isotopic branching ratio
D	=	decay correction from counting time to sampling time.

10.2 The decay correction, D, is calculated using one of the three following cases.

1. The half-life of the nuclide is extremely long compared with the counting time.

$$D = e^{-\lambda t}$$

where

λ	=	ln(2) / half-life
t	=	the elapsed time between start of counting and the sampling time.

2. The counting time is a few percent (or a significant fraction) of the nuclide's half-life; then decay must be considered significant throughout the counting period, and an integrated decay correction must be used:

$$D = \frac{1 - e^{-\lambda t_c}}{\lambda t_c e^{\lambda t}}$$

where

t _c	=	the length of the count
λ, t	=	same as the previous definitions.

3. If sampling does not occur instantaneously (air filter samples for example) and the nuclide's half-life is relatively short, then a further correction is necessary to account for decay during sampling.

$$D = \frac{(1 - e^{-\lambda t_c})(1 - e^{-\lambda t_s})}{\lambda^2 \cdot t_c \cdot t_s \cdot e^{\lambda t}}$$

10.2 The uncertainty in the nuclide result may be calculated using the formula:

$$\sigma_A = \frac{1}{(\epsilon \cdot BR \cdot Q \cdot D)} \sqrt{\left(\frac{\sigma_{C_s}^2}{t_s^2} + \frac{\sigma_{C_b}^2}{t_b^2} \right) + \left(\frac{C_s}{t_s} - \frac{C_b}{t_b} \right)^2 \cdot \left[\frac{\sigma_\epsilon^2}{\epsilon^2} + \frac{\sigma_Q^2}{Q^2} \right]} + R$$

where

- σ_{C_s} = uncertainty in the gross counts
- σ_{C_b} = uncertainty in the background counts
- σ_ϵ = uncertainty in the efficiency
- σ_Q = uncertainty in the sample quantity
- R = random errors
- others = same as previous definitions.

Note: All terms under the quadrature are considered systematic errors, while the R includes the random errors associated with the process. The two should be treated independently within the source term while providing an overall additive effect on the total error (uncertainty) associated with the sample.

11.0 Method Performance

Table 2 summarizes single-laboratory performance data obtained on triplicate analyses with aqueous performance evaluation samples from the EPA. The samples were 500 mL in volume and were counted in Marinelli beakers for 1000 min.

DRAFT

12.0

Reference

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12.0

Further Reading

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Knoll, G. F. 1989. *Radiation Detection and Measurement*. Second edition. John Wiley & Sons, New York.

Lawrence Berkeley Laboratory. 1983. *Instrumentation for Environmental Monitoring*, Vol. 1, Radiation, Environmental Instrumentation Survey. John Wiley & Sons, New York.

RI100^(a)

Liquid Scintillation Instrumentation Method

Note:

This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This procedure describes guidelines for operating a general liquid scintillation counting (LSC) system. In general, most LSC systems have an operating range from 0 to 2000 keV; however, 2000 keV is not a physical limitation of the instrument. For specific details, the operation manual supplied with the instrument should be referenced.

The basic detection process in liquid scintillation relies on adding an aqueous radioactive sample to a scintillation cocktail to create a homogeneous mixture. As the sample undergoes radioactive decay, the fluor (scintillator) molecules in the scintillation cocktail are excited by collisions with the emitted (beta) particles and emit light pulses through a molecular de-excitation process. Multiple solutes are used in the scintillator to provide the best combination of wavelength and pulse height for this application. The number of pulses per unit time is proportional to the quantity of activity present and are detected by two photomultiplier tubes connected in coincidence and converted into electrical pulses. These pulses are amplified and recorded, and the count rate is measured.

The scintillation cocktail completely surrounds the radioactive sample, which results in an optimal 4π counting geometry, and counting efficiencies can approach 100%. This is a major advantage of LSC over low background gas-flow proportional counting. The latter has a planar, 2π counting geometry, and detection efficiencies have a theoretical maximum of only 50%. Thus, LSC can drastically reduce counting times and increase sample throughput.

The efficiency of the system is determined by using prepared standards having the same density and color as the sample. Detection limits for this method depend on instrument background, detector efficiency, count time, aliquot size and scintillation cocktail used.

(a) This method was supplied by W. P. Brug (Los Alamos National Laboratory, Los Alamos, New Mexico).

2.0 Summary of Method

After initial efficiency calibration (i.e., quench correction), blanks, standards and samples are counted in batches on a liquid scintillation counter. Blanks allow for correct background subtraction and check for cross-contamination in sample preparation; standards ensure the instrument is operating within specified guidelines; and samples contain analytes of interest. By determining the net counting rate and the sample dependent efficiency (quenching), sample activities can be determined. While the preceding statements are seemingly general and rather straightforward, the term “blank” has been defined several different ways across the DOE complex, and to avoid confusion, the following definitions are offered:

<i>Dark Blank</i>	A scintillation vial is filled with lead shot and wrapped with black tape, and is used to verify the stability of the photomultiplier and thus is the lowest background obtainable. <i>Note: only a very small number of DOE laboratories use this type of blank.</i>
<i>Method or Preparation Blank</i>	A natural or purified (i.e., Milli-Q) low-emission water “sample” that is prepared in exactly the same manner as the analyte samples — including the same ratio of scintillation cocktail to sample volumes. These blanks are used to verify the reagents and as a check for cross-contamination (i.e., the observed uncertainty of the measurement is considered).
<i>Calibration Blank</i>	The water used to prepare the calibration standards is mixed with the scintillation cocktail in the same ratio as the samples. This blank is used to check the purity and background level of water, scintillation fluid, and vials. <i>Note: only a very small number of DOE laboratories use this type of blank.</i>
<i>Background or Instrument Blank</i>	This is used to determine instrument background and consists of adding low-emission (Milli-Q) water to the cocktail in the same water/cocktail ratio as the samples are prepared.

3.0 Interferences and Limitations

- 3.1 Quenching.** Quenching is probably the most common interference in LSC. Quenching is defined as all means that reduce the light output from sample/cocktail mixture as opposed to the pure cocktail (i.e., all radiationless de-excitation modes for the excited scintillation molecules). The primary visible manifestation of quenching is to shift the detected energy spectrum to lower energies. The three basic types of quenching are color, chemical, and impurity. Generally, quenching either de-excites the solute molecules or atoms before they can excite the solvent molecules or absorbs the emitted

light before it reaches the phototubes. Quenching species that are particularly effective are oxygen and molecules that contain heavy atoms, such as bromine and iodine. Thus, water is an effective quenching agent. In addition, using an oxidizing agent (such as potassium permanganate) in sample preparation can oxidize trace organic constituents. If these oxidized organics are present during counting, they can cause chemical quenching. Therefore, quenching can very well differ from sample to sample, and increasing quenching causes an overall reduction in detection efficiency. To correct for this effect, tremendous efforts have been undertaken to independently measure the degree of quenching for each sample. This measurement is then correlated to a matrix-specific calibrated quench curve to determine the counting efficiency for each sample.

Quench Correction

- *External (Instrumental) Standardization.* This technique places a high-energy gamma source (i.e., ^{137}Cs or ^{226}Ra) near the sample vial to produce a continuum of Compton recoil electrons that can excite solvent molecules. These excited molecules will collisionally transfer the excitation energy to solute (scintillation) molecules, which in turn will produce their characteristic photons. If quenching is present in the sample, the resulting Compton pulse height distribution is affected in the same manner as the light distribution of the radioactive sample. The true quench level of the sample is expressed as a shift in the Compton edge of the sample relative to an unquenched sample, and the difference in the channel setting represents the extent quenching has affected the light output. Different manufacturers have several names to describe this process (H-number, Spectral Index of Sample, Automatic Quench Compensation...), but they all work on the same basic principal. By relating the measured Compton edge shift to a matrix-specific calibration curve, the degree of quenching in each sample can be independently measured, and thus the counting efficiency for each sample is then determined.
- *Internal Standardization.* This technique is simply the method of standard additions. An aliquot of sample is counted directly; then an identical aliquot is counted after spiking with a known amount of radionuclide of interest. The activity of the original sample can then be calculated irrespective of the degree of quenching in the sample. This technique assumes that sample spiking does not affect the degree of quenching and has the advantage that a calibration quench curve need not be determined. However, sample throughput is reduced drastically.

- 3.2 Thermal Noise.** Thermal luminescence and thermally generated electrons from the photocathode of the photomultiplier tubes can provide significant contributions to noise. Refrigeration options on many instruments allow samples to be cooled to minimize

thermal noise, and signal discriminators can be set at appropriate levels to all but eliminate single-event noise. *Note: Not all scintillation cocktails retain their characteristic properties when cooled. Manufacturers' specifications should be checked before cooling samples.*

- 3.3 Luminescence.** Three general de-excitation modes exist (fluorescence, delayed fluorescence, and phosphorescence) for excited scintillation molecules to produce photons. Two of these (delayed fluorescence and phosphorescence) generally are produced by other processes (chemi-luminescence, etc.) rather than interaction with radioisotope emissions, and thus are interferences. Both of these interferences are characterized by having a much longer decay time than the desired fluorescence. Therefore, it is possible to discriminate against these unwanted photons by using timing circuitry. Many manufacturers offer luminescence interference correction options for their counting systems.
- 3.4 Electrostatic Charge.** Electrostatic charge can accumulate on plastic sample vials. Instrument manufacturers offer electrostatic controllers to virtually eliminate this problem.
- 3.5 High Background Water.** Tritium is a very common radioactive isotope and is the major contributor to elevated beta background levels in water. Since the background level will restrict the overall sensitivity of the measurement, low-tritium water should be used for environmental measurements. Low-tritium water can often be found in very deep wells.

4.0 Safety

General good laboratory operating procedures need to be applied whenever operating any electrical and computerized equipment. Also, the same care needs to be applied to handling any low-level radioactive materials.

5.0 Apparatus and Materials

- Liquid scintillation counting instrument from any manufacturer
- Sample vials. Sample vials can either be made from glass or from polyethylene.
 - Glass vials. If glass vials are chosen, they must be made from low-potassium glass to minimize ^{40}K emissions, which would elevate backgrounds in a non-uniform fashion among different vials.

- Polyethylene vials. Plastic scintillation vials generally give a lower background than glass. However, some plastic vials must be counted within relatively short times of preparation since some cocktails can diffuse through the plastic. These types of vials are usually chosen because of the following characteristics: low background, consistent construction materials, and sample geometry reproducibility.

6.0 Reagents

Scintillation Cocktail. The scintillation cocktail depends on the nature of the particular analysis. For example, if the sample readily forms a miscible, homogeneous mixture with the scintillation cocktail, one of the more traditional cocktails can be chosen. On the other hand, if the sample is not miscible with the cocktail, relatively homogeneous suspensions can be formed by using one of the available "gelling" cocktails. In either case, cocktails should be chosen so that they exhibit very little diffusion loss through polyethylene container walls. Additionally, many scintillators contain components that do not generate hazardous waste streams.

7.0 Sample Collection, Preservation, and Storage

Not applicable for this method.

8.0 Procedure

8.1 General Operation Principles

- 8.1.1 **Sample Vial Handling.** Sample vials should be wiped free of hand prints and scintillation cocktail (e.g., with methanol or ethanol). This allows consistent light emission and prevents buildup of cocktail residues on the counter tray floor. Residues can attract dirt, which can cause interfering static charge buildup.
- 8.1.2 **Dark Adaptation.** After the samples are mixed with the scintillation cocktail, constituents of the sample can react with the sample causing either chemiluminescence, phosphorescence, or both. Samples are usually placed in the dark (inside the counter with the lid closed) so that these interferences are allowed to minimize. The time necessary for dark adaptation varies with the nature of the sample as well as the specific scintillation cocktail used. Specific times range from 15 min to 12 h with the median being approximately 30 min. **Note:** The use of a refrigeration option can also lessen the dark adaptation time.

8.2 Calibration

- 8.2.1 **Instrument Calibration.** A quench curve or efficiency curve should be generated when the instrument is first put into service; also any mechanical or electronic repairs that are performed on the counter may invalidate the quench curve. Once this curve is generated, a calibration is performed several times per year (twice generally serves as a good guideline) as verification. Quench standards used for calibration can be purchased commercially; however, quenching is matrix specific. If no matrix specific standards are available, quench standards for a matrix of similar characteristics can be substituted; however, the method of standard additions is preferred. If standards are made from a dissimilar matrix, the instrument quench correction should be verified by spiking several samples with differing activities of the radionuclide of interest (method of standard additions). This allows the sample activity to be calculated irrespective of the quench level. The activities of the two different methods should be comparable for automatic quench correction to be used.
- 8.2.2 **Calibration Standards.** Calibration standards of the isotope being counted are prepared in a matrix as nearly identical as possible to that of the sample. When no standards are available for an isotope, an alternate standard isotope of similar maximum and average beta energy may be used.
- 8.2.3 **Quench Curve Preparation.** Note: If the method of standard additions is being used, no quench curve is necessary.
- 8.2.3.1 A volume of an appropriate matrix is added, consistent with the samples to be analyzed, to each vial.
- 8.2.3.2 A known amount of National Institute of Standards and Testing (NIST) traceable standard is added to each vial. The standard should be the same isotope or, if the isotope is not available, one with similar energy characteristics as that to be measured.
- 8.2.3.3 The appropriate amount of scintillation cocktail is added (consistent with the analytical samples) to each vial.
- 8.2.3.4 Chemical and color quenching agents are added to vary the amount of quench. For example, acetone is a good chemical quencher, and food color is a good color quenching agent.

8.2.3.5 Samples are loaded into the liquid scintillation counter and allowed to dark adapt and reach equilibrium with the cooling unit, if necessary. Then samples are counted for an appropriate length of time.

8.2.3.6 The instrument will generally store the quench curve data and automatically calculate the counting efficiency from the stored data.

When preparing a quench curve, a minimum of three and a maximum of ten points are recommended. Keeping with good laboratory practices, the quench curve should be verified with the method of standard additions.

8.2.4 **Method of Standard Additions.** A sample is split into several aliquots, and each aliquot is placed into a separate scintillation vial. One vial will contain the analyte activity of interest and is set aside. The remaining vials are spiked with differing amounts of the radioisotope of interest. *Note: the spike solution should be prepared so that it does not affect the quenching characteristics of the sample.* All the vials are placed sequentially in the counter, and the sample activity is calculated via the method of standard additions.

8.3 **Instrument (Batch) Loading.** Samples are generally analyzed in batches that normally contain replicate sample analyses, control samples, method blanks, background blanks, and sometimes spiked samples.

9.0 Calculations

Calculations often depend on the sample preparation method being used. However, general calculations can be given for both the external quench correction method as well as the method of standard additions.

9.1 **External Quench Correction.** This calculation is very similar to any gross counting method with the exception that the counting efficiency can very well differ between the background blanks and sample. This generalized equation can be written as

$$A = \frac{D}{K \cdot V} \text{ where } D = \frac{C_s}{t_s \cdot \epsilon_s} - \frac{C_b}{t_b \cdot \epsilon_b}$$

A = sample activity
D = measured sample disintegration rate
C_s, C_b = sample and background counts
t_s, t_b = sample and background count times

- $\varepsilon_s, \varepsilon_b$ = sample and background counting efficiencies
 K = factor to convert to the desired reporting units
 V = sample volume (with dilution corrections).

The error for the measured sample disintegration rate is calculated as

$$\sigma_D = \sqrt{\left(\frac{1}{\varepsilon_s \cdot t_s}\right) \left[\sigma_{C_s}^2 + \left(\frac{C_s}{\varepsilon_s}\right)^2 \sigma_{\varepsilon_s}^2 \right] + \left(\frac{1}{\varepsilon_b \cdot t_b}\right) \left[\sigma_{C_b}^2 + \left(\frac{C_b}{\varepsilon_b}\right)^2 \sigma_{\varepsilon_b}^2 \right]}$$

If Poisson counting statistics are assumed, the previous equation can be rewritten as

$$\sigma_D = \sqrt{\left(\frac{1}{\varepsilon_s \cdot t_s}\right) \left[C_s + \left(\frac{C_s}{\varepsilon_s}\right)^2 \sigma_{\varepsilon_s}^2 \right] + \left(\frac{1}{\varepsilon_b \cdot t_b}\right) \left[C_b + \left(\frac{C_b}{\varepsilon_b}\right)^2 \sigma_{\varepsilon_b}^2 \right]}$$

- σ_D = error in the measured disintegration rate
 $\sigma_{C_s}, \sigma_{C_b}$ = counting errors for the sample and the background
 $\sigma_{\varepsilon_s}, \sigma_{\varepsilon_b}$ = uncertainties in the sample and background counting efficiencies.

The activity error is expressed as

$$\sigma_A = \left(\frac{1}{K \cdot V}\right) \sqrt{\sigma_D^2 + \left(\frac{D}{V}\right) \sigma_V^2}$$

- σ_A = error in the measured activity
 σ_V = uncertainty in the sample volume measurement.

9.2 Method of Standard Additions. For the method of standard additions, the measured count rate of the sample to be determined can be expressed as

$$R_s = q \cdot A_s$$

where

- R_s = measured count rate of the sample
 A_s = activity of the sample
 q = quench (efficiency) factor for the sample.

The measured count rate for the spiked sample is given by

$$R_{s+x} = q \cdot A_{s+x} = \frac{q \cdot (A_s V_s + A_x V_x)}{V_x + V_s}$$

where

- R_{s+x} = measured count rate of the spiked sample
- A_{s+x} = activity of the spiked sample
- A_x = activity of the spike solution
- V_s = volume of sample solution before spiking
- V_x = volume of the spike solution added.

Note: activity is defined as a disintegration rate per unit volume. Thus $A_x V_x$ is simply the amount of Bq (dpm) of the spike added.

The q factor from the previous two equations can be eliminated, and the desired sample activity can be calculated as

$$A_s = \frac{R_s (A_x V_x)}{R_{s+x} (V_x + V_s) - R_s V_s}$$

Notice: The calculated activity is independent of the particular quenching activity and the background (which is assumed constant for the sample batch).

Multiple aliquots of the sample can be spiked if more precise measurements are required. In this case, the original sample activity is calculated using the previous equation and the traditional least-squares calculation.

The activity error is rather complicated and is calculated as follows:

$$\sigma_{A_s} = \frac{R_s (A_x V_x)}{d} \sqrt{\left(d \cdot \frac{\sigma_{A_x}}{A_x}\right)^2 + (V_s + V_x)^2 \left[\left(\frac{R_{s+x}}{R_s} \cdot \sigma_{R_s}\right)^2 + \sigma_{R_{s+x}}^2\right] + (R_{s+x} - R_s)^2 \left[\left(\frac{V_s}{V_x} \cdot \sigma_{V_x}\right)^2 + \sigma_{V_s}^2\right]}$$

If Poisson counting statistics are assumed, the previous equation simplifies to

$$\sigma_{A_s} = \frac{R_s (A_x V_x)}{d} \sqrt{\left(d \cdot \frac{\sigma_{A_x}}{A_x}\right)^2 + (V_s + V_x)^2 [R_{s+x} (R_{s+x} + 1)] + (R_{s+x} - R_s)^2 \left[\left(\frac{V_s}{V_x} \cdot \sigma_{V_x}\right)^2 + \sigma_{V_s}^2\right]}$$

where

- σ_{A_s} = method of standard addition activity error
 σ_{A_x} = uncertainty in the activity of the spiking solution
 d = $R_{s+x}(V_x + V_s) - R_s V_s$
 $\sigma_{V_s}, \sigma_{V_x}$ = uncertainty in the volume measurements of sample and the spike aliquots.

9.3 Volume Uncertainties. In many cases, the uncertainties in the volume measurements, σ_v , are insignificant compared with the other uncertainties, and thus can be considered essentially equal to zero. This assumption will greatly simplify the preceding error calculations.

10.0 Quality Control

10.1 Instrumentation Controls. General good laboratory practices should be followed to ensure the liquid scintillation counter is in calibration and operating properly. These include control charts, control limits for quality control (QC) instrument check samples, instrumental drift checks, and possibly running dark blanks to check photomultiplier tube noise.

10.2 Sample Controls. Control samples are generally counted with each sample batch to ensure proper operation. Additionally, preparation blanks are also counted with each sample batch to detect any cross-contamination that might have occurred. Finally some laboratories state that QC samples with sufficient activity {i.e., greater than 7.4 Bq/mL (200 pCi/mL)} should be analyzed with a precision of 5% at the 95% confidence level for the entire sample batch to be in control.

11.0 Method Performance

Not applicable for this method.

RA010^(a)**Method for Utilization of Electret Ionization Chambers for Characterization of Gross Alpha Emission from Indoor Surfaces**

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This is a technique for measuring gross-alpha-particle emission from interior contaminated surfaces (e.g., concrete, metal, wood, and vinyl floors). The technique uses electret ionization chambers (EICs), which are simple, inexpensive detectors that consist of a charged electret (Teflon) plate and a conductive plastic housing of 145 mL volume. The electret is screwed into the housing, and the housing is placed in contact with the contaminated surface to be characterized. Alpha particles entering the housing volume generate ions, which are collected on the electret surface, reducing its surface charge. The change in surface charge is measured with a hand-held voltmeter, and the charge's rate of change is converted into an activity using an appropriate calibration factor. The electrets are pre-charged by the vendor.

The method detection limit (MDL) is 4300 disintegrations/ 4π (all activity references in this method refer to the total emission into a 4π geometry). For high activity levels (20,000 dpm/100 cm²), an exposure time of 2.1 min is sufficient to yield a measurement at ten times the MDL. At low levels (100 dpm/100 cm²), an exposure time of 7.2 h is required for the same signal/noise ratio.

Laboratory measurements have been carried out for the following alpha-emitters: ²⁴¹Am, ²³⁹Pu, ²³⁰Th, ²⁴⁴Cm, ²³⁸U, ²³⁵U/²³⁴U, and ²⁵²Cf. The method has been calibrated in the laboratory for activities in the range of 462 to 27,000 dpm/ 4π .

(a) This method was provided by K. E. Meyer, R. B. Gammage, C. S. Dudney, and I. M. Angelini (Oak Ridge National Laboratory, Oak Ridge, Tennessee), and P. Kotrappa (Rad Elec, Inc., Frederick, Maryland).

2.0 Summary of Method

A baseline voltage for the electret is recorded. The electret is then deployed and exposed for a specific exposure time on the sample surface. The final voltage is determined. The background is determined by placing a Tyvek[®]-paper screen over the electret holder, and the procedure is repeated. Mylar screen can be used to protect the electret from dust and dirt. The alpha activity at the sample surface is calculated based on the difference in voltage and the time of exposure. Mylar attenuation correction factors are provided along with isotope calibration factors and geometrical correction factors.

3.0 Interferences

- 3.1 The surface being measured should be relatively free of dust, dirt, water, oil, or other materials that absorb alpha particles. Measurements on dirty surfaces will yield activity levels that are erroneously low. To minimize this interference, the surface should be brushed or wiped clean as appropriate, as dictated by the degree of accuracy required for the measurement.
- 3.2 The Teflon[®] surface of the electret will discharge if it comes into contact with any material. Such a spurious discharge will lead to erroneously high activity values. Care should be taken not to touch the Teflon[®] surface or to allow it to be contaminated with dust or fibers. If the surface does become contaminated with a small amount of dust, it may be cleaned by blowing off the surface with a jet of clean dry air or nitrogen (see section 8.5). In situations where dust cannot be avoided, it is recommended that a mylar screen be used. Correction factors for mylar attenuation are given in section 11.7.
- 3.3 The detectors are sensitive to beta and gamma radiation and to radon. For measurements in mixed fields, two parallel measurements are necessary, one with a bare electret and the other using a Tyvek[®]-paper screen. The bare electret response is the sum of its response to alphas, betas, gammas, and radon. The Tyvek[®]-paper screen passes gamma radiation, radon, and a significant degree of the incident beta radiation. Therefore, the difference in the two responses yields the response due to alpha particles alone.

The radon response for a bare electret in a 145 mL chamber is 7.4 V/day at a radon level of 5 pCi/L. The gamma response for a bare electret is 1.5 V/day in a gamma field of 10 μ R/h (E-PERM System Manual, published by Rad Elec, Inc., Frederick, Maryland, 1992).

- 3.4 The EIC has been designed for use on surfaces that are flat on the scale of the EIC footprint (3 in. diameter). Usage on highly irregular or curved surfaces will yield erroneous results.

3.5 Calibrations have been carried out assuming a uniformly contaminated large surface area ($> 48.7 \text{ cm}^2$). A geometrical correction is necessary for measurements on smaller surface areas (see section 11.6).

4.0 Safety

No special safety precautions are indicated for this method.

5.0 Apparatus and Materials

- High-sensitivity electrets (type ST, Rad Elec, Inc., Richmond, Virginia)
- Molded conducting plastic electret holder (Rad Elec, Inc., Richmond, Virginia)
- Electret voltage reader (model SPER-1, Rad Elec, Inc., Richmond, Virginia)
- Set of two reference electrets (Rad Elec, Inc., Richmond, Virginia)
- Mylar screens (aluminized Mylar is available from Alexander Vacuum Research, Greenfield, Massachusetts)
- Paper screen (6.0 mg/cm^2 Tyvek[®] paper, stock # R1460, International Envelope Company, Aston, Pennsylvania)
- Collars for holding screens (Rad Elec, Inc, Richmond, Virginia)

6.0 Reagents

None

7.0 Sample Collection, Preservation, and Handling

The sample surface should be wiped clean of dirt and removable residues before analysis.

8.0 Procedure

8.1 Basic Electret Exposure/Readout Procedure

8.1.1 **Initial Voltage Reading.** The electret voltage is read out using the following steps:

1. The protective cap is removed from the electret and placed, Teflon® side down, into the circular receptacle on top of the SPER-1 reader.
2. The electret is rotated so that its serial number is parallel with the label "Rad Elec Inc." on the reader.
3. The electret must be resting against the lower edge of the receptacle (i.e., the edge closest to the operator when reading the meter).
4. The shutter knob is drawn slowly to its downward limit, then allowed to return slowly to its top ("shutter closed") position. This turns on the reader. The reading that appears on the panel at this time should be ignored.
5. The shutter knob is drawn down slowly to its open position, held open for 5 sec, then returned slowly to its closed position. The reader is now reading the electret voltage.
6. After the shutter is left in its closed position for at least 5 sec, step four is repeated and the voltage is read again. The second reading should be the same as the first. If different, the procedure is repeated until the same voltage reading occurs at least twice in succession.
7. This voltage is recorded as V_i ; the electret serial number is also recorded.

8.1.2 Electret Exposure

1. The electret is placed, without touching the electret surface, in a conducting plastic holder and screwed in finger-tight.
2. The electret and holder are placed on the surface to be characterized, and this time is recorded as T_i .

3. The electret and holder are picked up after the desired exposure time. This time is recorded as T_f .

8.1.3 Final Voltage Reading

1. The electret is unscrewed from its holder, and its voltage is read out following the procedure described above in 8.1.1 (steps 2 through 6). This voltage is recorded as V_f .
2. The storage cap is replaced onto the electret by screwing the electret into its cap.
3. The capped electret and chamber are placed in a sealed plastic bag for storage.

8.2 Mixed Radiological Field Procedure. If it is known or suspected that significant gamma, beta, or radon fields are present where the EIC is being exposed, then a background measurement should be taken. This is particularly important when low-activity measurements are being undertaken. The procedure is the same as above with the exception that a Tyvek[®]-paper screen is used over the electret holder. This blocks alpha particles and transmits gamma, radon, and most beta. This measurement is most easily done in parallel with the measurement using the open electret. Following steps 8.1.1 (steps 2 through 6), the initial voltage of a second electret should be read out. Then it is placed in a holder with a Tyvek[®]-paper screen and placed next to the open electret. The screened electret is exposed for the same period of time as the open electret. The final voltage and the elapsed time are recorded separately from the data for the open electret.

8.3 Mylar Screen Procedure for Dusty/Dirty Surfaces and Prevention of Electret Contamination. The accuracy of the EIC measurement will be degraded if a significant amount of dust, oil, water, or other potential alpha absorber is present on the surface being characterized. Every effort should be made to remove such interfering layers before proceeding with a measurement, i.e., by brushing off the surface or mopping up any liquids on the surface. In situations where a significant amount of dust or dirt is unavoidable, a mylar screen should be used to prevent the sensitive surface of the electret from becoming contaminated with dust. In addition, in situations where transferable contamination exists, a mylar screen should be used to prevent contamination of the electret and holder. An appropriate mylar thickness must be chosen; thicker screens are more robust and rugged, but they absorb more alpha particles and therefore degrade the sensitivity more than thinner screens. In each case, the thinnest possible screen should be used for the application at hand.

The exposure and measurement procedures are exactly as in section 8.1, with these additional steps:

- The electret is screwed into an electret holder/mylar screen combination after the initial electret voltage measurement.
- After exposure, the electret is unscrewed from the holder/screen combination, and the electret voltage is read. If the mylar screen has not become damaged, dirty, or contaminated, it may be reused; otherwise, it should be discarded.

8.4 Cleaning of Electret Surface. It is important to maintain the interior of the electret cap, the electret surface, and the interior of the chamber as dust free as possible. Any dust or fibers present on the surface of the electret can cause accelerated discharge of the electret, which will lead to an erroneously high reading. If some dust or fibers are observed on the electret surface, they can be blown off. Clean compressed air or nitrogen is best for this. A puff of air blown by mouth can be used if compressed air or nitrogen is unavailable. Any dust or dirt observed on the electret holder should be removed before a measurement is undertaken.

8.5 Voltage Reader Calibration Check. A check of the voltage reader calibration should be carried out once a week and whenever it is suspected that the reader is not responding correctly. Two reference electrets are provided for this purpose, together with voltage readings obtained at the factory for each electret. The voltage on each reference electret should be measured using the procedure described in section 8.1, and the readings should be recorded in a calibration log. If both of the readings are within $\pm 2V$ of their corresponding factory values, the voltage reader is within calibration. If one of the readings has a larger discrepancy than this, it is probable that the reference electret has become contaminated, and it should be returned to the factory. If both readings show a discrepancy larger than $\pm 2V$, the voltage reader is out of calibration and should be returned to the factory for recertification.

9.0 Calculations

9.1 Conversion of Electret Voltage Readings to Activity Measurements. The expression for the relationship between the electret voltage readings and the source activity is

$$\left(\left[\frac{V_f - V_i}{T_f - T_i} \right]_{\text{open}} - \left[\frac{V_f - V_i}{T_f - T_i} \right]_{\text{fp}} \right) \cdot \frac{NL \cdot G \cdot MY \cdot (2.053)}{CAL} = (\text{dpm}/100 \text{ cm}^2) \quad (1)$$

where

- open = open electret measurement
- fp = electret/Tyvek[®]-paper measurement
- NL = nonlinearity correction factor (see Table 1)
- G = geometrical correction factor (for sources with area <48.7 cm², see Table 2)
- MY = mylar attenuation factor, if mylar is used (see Table 3)
- CAL = isotope calibration factor in V/disintegration (see Table 4)
- 2.053 = area conversion factor (to covert from 48.7 cm² to 100 cm²).

The mid-point voltage (V_{MPV}) that is used in the nonlinearity correction factor reference table (Table 1) is given by

$$V_{MPV} = \frac{V_f + V_i}{2} \quad (2)$$

Table 1. Nonlinearity Correction Factors (Abridged, see section 11.8)					
Mid-Point Voltage V_{MPV} (volts)	NL	V_{MPV} (volts)	NL	V_{MPV} (volts)	NL
100	1.3176	325	1.0331	550	0.9739
125	1.2387	350	1.0250	575	0.9704
150	1.1798	375	1.0172	600	0.9670
175	1.1366	400	1.0097	625	0.9636
200	1.1050	425	1.0025	650	0.9573
225	1.0820	450	0.9955	675	0.9482
250	1.0652	475	0.9888	700	0.9336
275	1.0523	500	0.9830	725	0.9110
300	1.0419	525	0.9781	750	0.8769

Table 2. Geometrical Correction
(Abridged, see section 11.6)

Source Area (cm ²)	Curve-Fit Values	Source Area (cm ²)	Curve-Fit Values	Source Area (cm ²)	Curve-Fit Values	Source Area (cm ²)	Curve-Fit Values
0	0	13	0.7704	26	0.8691	39	0.9630
1	0.7250	14	0.7769	27	0.8773	40	0.9683
2	0.7260	15	0.7836	28	0.8853	41	0.9733
3	0.7275	16	0.7906	29	0.8933	42	0.9778
4	0.7296	17	0.7979	30	0.9012	43	0.9819
5	0.7323	18	0.8053	31	0.9090	44	0.9855
6	0.7355	19	0.8129	32	0.9166	45	0.9886
7	0.7392	20	0.8207	33	0.9240	46	0.9912
8	0.7434	21	0.8286	34	0.9311	47	0.9932
9	0.7480	22	0.8366	35	0.9381	48	0.9946
10	0.7531	23	0.8447	36	0.9448	49	0.9955
11	0.7585	24	0.8528	37	0.9512		
12	0.7643	25	0.8610	38	0.9572		

Table 3. Mylar Attenuation Correction Factors
(Abridged, see section 11.7)

Source	Alpha Energy (MeV)	Mylar Thickness (mg/cm ²)	Correction Factor
²⁴⁴ Cm	5.795	0.29	1.114 ± 3.23%
		0.53	1.358 ± 3.49%
		0.85	1.456 ± 7.21%
		1.8	2.361 ± 2.75%
²³⁹ Pu	5.09	0.29	1.238 ± 3.27%
		0.53	1.465 ± 1.15%
		0.85	1.764 ± 1.85%
		1.8	3.586 ± 4.51%
²⁴¹ Am	5.479	0.29	1.209 ± 3.60%
		0.53	1.451 ± 1.73%
		0.85	1.642 ± 1.94%
		1.8	2.976 ± 6.62%
²³⁰ Th	4.673	0.29	1.410 ± 3.23%
		0.53	1.691 ± 3.62%
		0.85	2.315 ± 1.83%
		1.8	5.391 ± 2.24%
Average of Four Sources		0.29	1.243 ± 12.43%
		0.53	1.491 ± 14.35%
		0.85	1.794 ± 37.05%
		1.8	3.579 ± 130.78%

Table 4. Isotope Calibration Factors
(Abridged, see section 11.5)

Source	CAL (V/disintegration)
ALL	7.4e-4
²⁴¹ Am	8.04e-4
²³⁸ Th	8.09e-4
²⁴⁴ Cm	7.01e-4
²⁵² Cf	5.09e-4
²³⁷ Np	8.24e-4
²³⁵ U	7.17e-4
²³⁸ U	7.14e-4
²³⁹ Pu	8.18e-4
	± 3.9%
	± 2.2%
	± 4.9%
	± 7.6%
	± 5.7%
	± 5.9%
	± 4.4%
	± 5.2%
	± 4.3%

9.2

Error Analysis. The fundamental relationship between EIC response and measured surface activity is equation (1). In this section, the total uncertainty in such a measurement is estimated using a sum-of-squares approach, and two examples are given for typical applications. If the uncertainty in each factor in eq. (1) is stated as a percentage error, then the uncertainties can be combined in a simple expression:

$$\Delta(\text{dpm}/100 \text{ cm}^2) = [\Delta_{V_i}^2 - V_i^2 + \Delta_{T_i}^2 - T_i^2 + \Delta_{NL}^2 + \Delta_G^2 + \Delta_{MY}^2 + \Delta_{CAL}^2]^{1/2} \quad (3)$$

where each Δ is the percentage error in that factor.

Example 1: Bare electret, no background correction, on a ²³⁰Th contaminated surface: Suppose that the initial voltage $V_i = 700$ V, the final voltage $V_f = 650$ V, and the exposure time is 2 h. The uncertainty in the voltage measurement is ± 1 V, and the timing uncertainty is ± 2 min. If the uncertainty in the initial and final voltage measurements is ± 1 V, then the uncertainty in the difference in the two is ± 1.4 V. Then according to eq. (1) and Tables 1 and 4,

$$(\text{dpm}/100 \text{ cm}^2) = \frac{50 \text{ V}}{120 \text{ min}} \cdot \frac{8.09e-4 \text{ V/disintegration}}{(0.9482) \cdot 2.053} = 1003 \text{ dpm}/100 \text{ cm}^2 \quad (4)$$

Next, using eq. (3), the stated uncertainties, and the errors tabulated in Tables 4 and 1, the total estimated uncertainty is

$$\Delta(\text{dpm}/100 \text{ cm}^2) = \left[\left(\frac{1.4\text{V}}{50\text{V}} \right)^2 + \left(\frac{2 \text{ min}}{120 \text{ min}} \right)^2 + (0.0085)^2 + (0.049)^2 \right]^{1/2} = 5.9\% (5)$$

Example 2: Electret covered with 0.53 mg/cm^2 mylar screen, background correction, on a surface contaminated with ^{244}Cm : Suppose that the initial voltage $V_i = 500\text{V}$, the final voltage $V_f = 425\text{V}$, the exposure time is 24 h, and a parallel background measurement with a Tyvek[®]-paper screen yields a voltage drop of 3V. The uncertainty in the voltage measurements is $\pm 1\text{V}$, and the timing uncertainty is $\pm 10 \text{ min}$. Then according to eq. (1) and Tables 1, 3, and 4.

$$\left(\text{dpm}/100 \text{ cm}^2 \right) = \left[\frac{75\text{V}}{1440 \text{ min}} - \frac{3\text{V}}{1440 \text{ min}} \right] \cdot \frac{(0.9953) \cdot (1.358) \cdot 2.053}{7.01\text{e-}4\text{V/disintegration}} = 198 \text{ dpm}/100 \text{ cm}^2 \quad (6)$$

Next, using eq. (3), the stated uncertainties, and the errors tabulated in Tables 4, 3, and 1, the total estimated uncertainty is

$$\Delta(\text{dpm}/100 \text{ cm}^2) = \left[\left(\frac{1.4\text{V}}{75\text{V}} \right)^2 + \left(\frac{10 \text{ min}}{1440 \text{ min}} \right)^2 + (0.0085)^2 + (0.035)^2 + (0.076)^2 \right]^{1/2} = 8.6\% \quad (7)$$

9.3 Method Detection Limit. The minimum detectable activity depends on the exposure time used for the measurement. The total number of disintegrations, N_{dis} , does not depend on exposure time and therefore is a more appropriate parameter to use for the method detection limit (MDL).

As will be discussed in section 11.4, when the exposure time was reduced to 1 min, the standard deviation in the measurement increased above 10%. This standard deviation will be used to calculate the MDL, defined as

$$\text{MDL} = t(n-1, 99\%) \cdot s \quad (8)$$

where t is the one-sided t -statistic appropriate for the number of samples used to determine s , the standard deviation, at the 99% confidence level. For this case, the number of samples is 5, and the t -statistic is 3.75; therefore,

$$\text{MDL} = (3.75) \cdot (0.901\text{V/min}) = 3.38\text{V/min} \quad (9)$$

This can now be converted to the number of disintegrations, N_{dis} , which is independent of exposure time:

$$\text{MDL}_{\text{NDIS}} = \text{MDL(V/min)} \cdot \frac{(\text{source activity}) \cdot (\text{exposure time})}{(\text{detector response})} \quad (10)$$

where the source activity is in dpm/4 π , the exposure time is in min, and the detector response is in V/min. For this case,

$$\text{MDL}_{\text{NDIS}} = (3.38\text{V/min}) \cdot \frac{(21887 \text{ dpm}) \cdot (1 \text{ min})}{(17.2\text{V/min})} = 4301 \text{ disintegrations} \quad (11)$$

10.0 Quality Control

As long as the electrometer remains in calibration, as described in section 8.5, the measurement system is considered in control. No further control-check procedures are necessary.

11.0 Method Performance

The reference sources used for the measurements described in this section are listed in Table 5. The source activities range from 460 to 27,000 dpm/4 π .

Radionuclide	Reference Number	Activity (dpm/4 π)	Activity Uncertainty (%)	Active Area (cm ²)
²⁴⁴ Cm	93CM4701959	462	±9.7	15.5
²³⁰ Th	10943	3810	±5.0	3.90
²³⁹ Pu	1399/89	7640	±5.0	7.79
²⁴¹ Am	DL124	21887	±10	48.7
²⁴¹ Am	M2020	11829	±0.8	2.85
²⁴¹ Am	M1040	10967	±5.0	2.85
²⁴¹ Am	170-86-1	10400	±3.2	0.196
²³⁷ Np	180-21-1	12400	±2.7	0.196
²³⁰ Th	180-21-4	11100	±3.0	0.196
²⁴⁴ Cm	170-86-3	8700	±3.3	0.196
²⁵² Cf	180-21-3	1710	±3.0	0.196
²³⁵ U	177-30-1	27000	±3.8	1.27
²³⁸ U	177-30-2	496	±3.8	1.27

11.1 Detector Response vs. Source Activity. Thirteen reference sources were used to measure detector response versus source activity. Electret ionization chambers were exposed to each source for a standard 30 min, and each measurement was repeated five times. Each measurement was then corrected for background, nonlinearity, and source area. These corrected data were then used to calculate the average EIC response to each reference source. The data are tabulated in Table 6 and plotted in Figure 1.

Figure 1. EIC Detector Response vs. Reference Source Activity (corrected for background, nonlinearity, and source area)

Table 6. Detector Response vs. Activity			
Source	Activity (dpm/yr)	Ave. Corrected (dV/dT)	Response (V/min)
244Cm	462	0.369	0.369
238U	496	0.354	0.354
252Cf	1719	0.869	0.869
230Th	3810	3.192	3.192
239Pu	7640	6.303	6.303
244Cm	8700	6.095	6.095
241Am	10967	9.106	9.106
241Am	11829	10.206	10.206
241Am	10400	8.117	8.117
230Th	11100	8.914	8.914
237Np	12400	10.219	10.219
241Am	21887	17.164	17.164
235U	27000	19.364	19.364
#93cm4701959	462	0.369	0.369
#177-30-2	496	0.354	0.354
#180-21-3	1719	0.869	0.869
#10943	3810	3.192	3.192
#1399/89	7640	6.303	6.303
#170-86-3	8700	6.095	6.095
#M1040	10967	9.106	9.106
#M2020	11829	10.206	10.206
#170-86-1	10400	8.117	8.117
#180-21-4	11100	8.914	8.914
#180-21-1	12400	10.219	10.219
#DL124	21887	17.164	17.164
#177-30-1	27000	19.364	19.364

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11.2 Measurement Uncertainty vs. Source Activity. Measurements for uncertainty versus activity were taken with 13 traceable reference sources. Then EICs were exposed for a standard exposure time of 30 min, and each exposure was repeated five times. For each exposure, the electret voltage response (dV/dt) was calculated. Each response was then corrected for background response due to possible gamma and beta radiation and radon response from both the source and the room, following the procedure described in section 8.2. A single 24-h background measurement using an EIC screened with Tyvek® paper was performed for each reference source. Next, the data were corrected for response nonlinearity using the correction factors tabulated in Table 1. Using the corrected response, the standard deviation and the standard deviation of the mean were calculated for each source used. As seen from Table 7 and Figure 2, no correlation exists between the experimental uncertainty and the source activity over the range of 462 to 27,000 dpm/4 π . The average uncertainty is 2.9% with a maximum of 5.2% and a minimum of 1.5%.

Source		Activity dpm/4 π	Standard Deviation (V/min)	% Standard Deviation of the Mean
²⁴⁴ Cm	#93CM4701959	462	0.023	4.9
²³⁸ U	#177-30-2	496	0.0173	3.5
²⁵² Cf	#180-21-3	1710	0.0251	2.1
²³⁰ Th	#10943	3810	0.067	1.5
²³⁹ Pu	#1399/89	7640	0.18	2.1
²⁴⁴ Cm	#170-86-3	8700	0.237	2.8
²⁴¹ Am	#170-86-1	10400	0.372	3.3
²⁴¹ Am	#DL124	21887	0.262	1.5
²⁴¹ Am	#M2020	11829	0.46	3.3
²³⁰ Th	#180-21-4	11100	0.439	3.5
²⁴¹ Am	#M1040	10967	0.249	2.0
²³⁷ Np	#180-21-1	12400	0.740	5.2
²³⁵ U	#177-30-1	27000	0.594	2.2

Figure 2. EIC Measurement Uncertainty vs. Reference Source Activity

- 11.3 Detector Response vs. Alpha Energy.** Thirteen reference sources were used to measure detector response versus weighted source activity. Electret ionization chambers were exposed to each source for a standard 30 min, and each measurement was repeated five times. Each measurement was then corrected for background, nonlinearity, and source area. These corrected data were then used to calculate the average EIC response to each reference source. The average corrected EIC response (dV/dt) was then normalized to the source activity ($dpm/4\pi$) to arrive at the fundamental detector response ($dV/disintegration$). The alpha-particle energies used in Table 8 are the weighted averages of the three most prominent peaks in the source's alpha-particle emission spectrum. These data are tabulated in Table 8 and plotted in Figure 3. The dotted line in Figure 3 corresponds to a linear regression fit for the entire data set. The slope of the line corresponds to an average fundamental detector response of 0.75 mV/disintegration.

Source	Weighted Alpha-Particle Energy (MeV)	Fundamental Detector Response (mV/disintegration)
^{238}U	#177-30-2	4.18
$^{235}\text{U}/^{234}\text{U}$	#177-30-1	4.54
^{230}Th	#10943	4.67
^{230}Th	#180-21-4	4.67
^{237}Np	#180-21-1	4.74
^{239}Pu	#1399/89	5.09
^{241}Am	#DL124	5.47
^{241}Am	#M1040	5.47
^{241}Am	#M2020	5.47
^{241}Am	#170-86-1	5.47
^{244}Cm	#93cm4701959	5.79
^{244}Cm	#170-86-3	5.79
^{252}Cf	#180-21-3	6.11

Figure 3. EIC Detector Response vs. Alpha Energy (corrected for background, nonlinearity, and source area)

- 11.4 Measurement Uncertainty vs. Exposure Time.** Measurements for uncertainty versus exposure time were taken with a single reference source, ^{241}Am #DL124 (activity = 21887 dpm/4 π). The EICs were exposed for times ranging from 0.5 min to 70 min. Each measurement was repeated five times. The measurements were then corrected for background contribution and nonlinearity. The corrected measurements were then used to calculate the average response, standard deviation, and standard deviation of the mean for each exposure time. These data are tabulated in Table 9 and graphed in Figure 4. For exposure times of 2 min and longer, the average uncertainty is 2.5% with a maximum of 3.7% and a minimum of 1.4%. For exposure times less than 2 min, the voltage readout uncertainty ($\pm 1\text{V}$) becomes a significant proportion of the voltage drop (17.2V/min), and the uncertainty increases to >10%.

Table 9. Uncertainty vs. Exposure Time

Exposure Time (min)	Total Disintegrations (4 π)	Standard Deviation (V/min)	Standard Deviation of the Mean
70	1.53e6	0.297	0.035
60	1.31e6	0.243	0.029
50	1.09e6	0.310	0.037
40	8.75e5	0.163	0.019
30	6.57e5	0.224	0.026
20	4.38e5	0.263	0.031
10	2.19e5	0.0115	0.014
5	1.09e5	0.157	0.019
2	4.38e4	0.144	0.017
1	2.18e4	0.901	0.10
0.5	1.09e4	0.998	0.10

Figure 4. EIC Measurement Uncertainty vs. Experimental Exposure Time

- 11.5 Isotope Calibration Factor.** The EIC response data in Tables 7 and 8 constitute the fundamental calibration factor, CAL, for relating the EIC response to the source activity. For those cases where more than one reference source for a given radionuclide was available, a linear regression analysis of the data has been carried out. The regression results and corresponding statistics are shown in Table 10 (reproduced from Table 4). For those cases where only a single radionuclide source was available, the calibration factor shown in the table corresponds to the average corrected EIC response for that reference source divided by the source activity.

The errors were estimated by the standard deviation of the slope, calculated from the error sum of squares, for the two cases in the table where more than two data points were in the regression analysis. For the other cases, the average of the sum-of-squares uncertainty for each source, taking into account both the experimental error and the error in the source activity, has been estimated.

Table 10: Isotope Calibration Factors

Source	CAL (V/disintegration)	r^2	F	degrees of freedom	SS _{reg}	SS _{residual}
ALL	7.4e-4 ± 3.9%	.9676	358.9	12	407.4	13.6
²⁴¹ Am	8.04e-4 ± 22%	.9289	39.24	3	46.85	3.58
²³⁰ Th	8.09e-4 ± 4.9%	.9977	435.35	1	16.33	0.037
²⁴⁴ Cm	7.01e-4 ± 7.6%	.9998	7749	1	16.39	0.0021
²⁵² Cf	5.09e-4 ± 5.7%					
²³⁷ Np	8.24e-4 ± 5.9%					
²³⁵ U	7.17e-4 ± 4.4%					
²³⁸ U	7.14e-4 ± 5.2%					
²³⁹ Pu	8.18e-4 ± 4.3%					

r^2 = correlation coefficient
F = F statistic
SS_{reg} = regression sum of squares
SS_{residual} = residual sum of squares

11.6 Geometrical Correction for Variation in Source Area. The objective of a geometrical correction is to allow the detector response to be predicted on large area sources (= 48.7 cm², the footprint of the electret holder) based on measurements and calibrations using small-area (<48.7 cm²) reference sources. A secondary objective is to allow measurements on sources or surfaces with different active areas to be compared. For these measurements, a large-area (150 cm²) ²⁴¹Am reference source was used. A set of paper masks was fabricated with concentric holes ranging in area from 5 to 40 cm². For each measurement, the mask was placed on the source, and the EIC was placed symmetrically over the hole in the mask and exposed for 30 min. For each mask area, the measurement was repeated five times. The data were then corrected for background and nonlinearity, and the average corrected response was calculated. These data formed the basis for determining the correction factor, which is defined as the ratio of the large-area (48.7 cm²) response relative to the small-area (<48.7 cm²) response for sources of the same activity:

$$G = \frac{\text{large - area source response}}{\text{small - area source response}} \quad (12)$$

The correction factor G was calculated as a function of mask area for the eight different areas used, and these data were then fit with a polynomial of the form

$$G = a + bx^2 + cx^3 \quad (13)$$

where

x = source area (cm²)

a = 0.7247

b = 3.278e-4

c = -4.3882e-6

This functional fit is tabulated in Table 11, and both the experimental data and the empirical fit are plotted in Figure 5. The average residual is 0.0103, which yields an average error for the fit of 1.2%.

Source Area (cm ²)	Curve-Fit Values	Source Area (cm ²)	Curve-Fit Values	Source Area (cm ²)	Curve-Fit Values	Source Area (cm ²)	Curve-Fit Values
0	0	13	0.7704	26	0.8691	39	0.9630
1	0.7250	14	0.7769	27	0.8773	40	0.9683
2	0.7260	15	0.7836	28	0.8853	41	0.9733
3	0.7275	16	0.7906	29	0.8933	42	0.9778
4	0.7296	17	0.7979	30	0.9012	43	0.9819
5	0.7323	18	0.8053	31	0.9090	44	0.9855
6	0.7355	19	0.8129	32	0.9166	45	0.9886
7	0.7392	20	0.8207	33	0.9240	46	0.9912
8	0.7434	21	0.8286	34	0.9311	47	0.9932
9	0.7480	22	0.8366	35	0.9381	48	0.9946
10	0.7531	23	0.8447	36	0.9448	49	0.9955
11	0.7585	24	0.8528	37	0.9512		
12	0.7643	25	0.8610	38	0.9572		
		F =	196.4				
regression sum of squares (SS _{reg})		=	0.07198				
residual sum of squares (SS _{residual})		=	0.001099

Figure 5. Electret Geometrical Correction Factors for Variations in Source Area

- 11.7 Mylar Attenuation Correction.** The correction for alpha-particle attenuation in mylar films has been measured with four different reference sources, ^{244}Cm , ^{239}Pu , ^{241}Am , and ^{230}Th . For each source, 30-min exposures were carried out with an open electret and with electrets screened with mylar shields of density 0.29, 0.53, 0.85, and 1.8 mg/cm^3 . Each of these measurements was repeated three times. The correction factor was then defined as the ratio of the average open EIC response to the average screened EIC response:

$$\text{MY} = \frac{(\text{average open EIC response})}{(\text{average screened EIC response})} \quad (14)$$

The data are tabulated in Table 12 and plotted in Figure 6. It is apparent from the figure that the alpha-particle attenuation in mylar films is a strong function of the mylar density and a weaker function of the alpha-particle energy.

Table 12. Mylar Attenuation Correction Factors

Source	Alpha Energy (MeV)	Activity (dpm/4 π)	Mylar Thickness (mg/cm ²)	Correction Factor
²⁴⁴ Cm #93cm4701959	5.795	462	0.29	1.114 $\pm$ 3.23%
			0.53	1.358 $\pm$ 3.49%
			0.85	1.456 $\pm$ 7.21%
			1.8	2.361 $\pm$ 2.75%
²³⁹ Pu #1399/89	5.09	7640	0.29	1.238 $\pm$ 3.27%
			0.53	1.465 $\pm$ 1.15%
			0.85	1.764 $\pm$ 1.85%
			1.8	3.586 $\pm$ 4.51%
²⁴¹ Am #M2020	5.479	11829	0.29	1.209 $\pm$ 3.60%
			0.53	1.451 $\pm$ 1.73%
			0.85	1.642 $\pm$ 1.94%
			1.8	2.976 $\pm$ 6.62%
²³⁰ Th #10943	4.673	3810	0.29	1.410 $\pm$ 3.23%
			0.53	1.691 $\pm$ 3.62%
			0.85	2.315 $\pm$ 1.83%
			1.8	5.391 $\pm$ 2.24%
Average of Four Sources			0.29	1.243 $\pm$ 12.43%
			0.53	1.491 $\pm$ 14.35%
			0.85	1.794 $\pm$ 37.05%
			1.8	3.579 $\pm$ 130.78%

Figure 6. Mylar Attenuation Correction Factor for Different Mylar Thicknesses and Reference Sources

- 11.8 Nonlinearity Correction.** The source used was ^{239}Pu (#139989), with an activity of 7700 dpm (4π). The correction derived here can be applied for any source. Thirteen electret voltage measurements were made at exposure time intervals of 5.5 min. The voltage drop for each time interval was plotted versus the mid-point voltage for each measurement. The measurements were then normalized to the measurement at $V_{\text{MPV}} = 400\text{V}$. These data were then fit with a polynomial curve of the form

$$y = a + bx + cx^2 + dx^3 + ex^4 + fx^5 \quad (15)$$

where

$y = \text{NL}$	$c = 4.487317\text{e-}5$
$x = V_{\text{MPV}}$	$d = 1.03644\text{e-}7$
$a = 1.9555$	$e = 1.18166\text{e-}10$
$b = -0.0099419$	$f = -5.27881\text{e-}14$

The average residual for the curve fit is 0.0085, which yields an average fit error of 0.85%. The curve-fit correction factors (NL) data are tabulated in Table 13 (reproduced from Table 1), and both the experimental data and the empirical fit are plotted in Figure 7.

Mid-Point Voltage V_{MPV} (volts)	NL	V_{MPV} (volts)	NL	V_{MPV} (volts)	NL
100	1.3176	325	1.0331	550	0.9739
125	1.2387	350	1.0250	575	0.9704
150	1.1798	375	1.0172	600	0.9670
175	1.1366	400	1.0097	625	0.9360
200	1.1050	425	1.0025	650	0.9573
225	1.0820	450	0.9953	675	0.9482
250	1.0652	475	0.9888	700	0.9336
275	1.0523	500	0.9830	725	0.9110
300	1.0419	525	0.9781	750	0.8769
F = 161.15					
regression sum of squares (SS_{reg}) = 0.0537					
residual sum of squares ($SS_{residual}$) = 0.00047

Figure 7. Electret Nonlinearity Correction Factors vs Mid-Point Voltage

RA020(a)

Method for Utilization of Alpha Track Detectors for Characterization of Gross Alpha Emission from Indoor Surfaces

Note: This is a draft method and is made available for use at your discretion. The method has been used in at least one laboratory, but has not been extensively reviewed. Performance parameters, such as precision and bias, may not be available. If you use this method, please provide the editors of *DOE Methods* with comments. Please also provide any performance data you may generate. Your input will assist us in verifying this method.

1.0 Scope and Application

This is a technique for measuring gross alpha-particle emission from indoor contaminated surfaces (i.e., concrete, metal, wood, and vinyl floors) (Gammage and Wheeler 1993). This technique uses alpha track detectors (ATDs), which are simple, inexpensive detectors that were originally developed for indoor radon measurements (Espinosa and Gammage 1993). The ATD consists of a plastic sheet made from allyl diglycol carbonate monomer, commonly known as CR-39 (the particular form of CR-39 that has been evaluated in these measurements is Lantrack[®], which is cast using proprietary methods and is used extensively by Landauer, Inc. in radon measurements). This plastic may be easily cut to any shape or size for a given application using simple machining techniques. The work described here has used detectors fabricated in a particular format, chips approximately 1 cm x 2 cm in dimension with a number laser-scribed on one surface to facilitate detector tracking. When the plastic material is exposed to a source, the alpha particles passing through the medium cause localized damage in the molecular structure. These "damage tracks" can then be made visible to the eye by etching the material in a caustic solution (KOH) that preferentially attacks the damage centers. After etching, the damage tracks appear as microscopic pits (on the surface) that may be counted with an optical scanner. The resulting "track density" may then be related to the source activity through an appropriate calibration.

At this time, the etching and counting are carried out by the vendor, requiring that the exposed material be shipped to the vendor in a timely manner. It is anticipated that for those using a large amount of material and requiring fast turn-around times between exposure and analysis, the necessary etching and counting equipment could be established in an on-site mobile laboratory.

- (a) This method was supplied by K. E. Meyer, R. B. Gammage, C. S. Dudney, and I. M. Angelini (Oak Ridge National Laboratory, Oak Ridge, Tennessee); G. Espinosa (University of Mexico, Mexico City, Mexico); and R. V. Wheeler and M. Salasky (Landauer, Inc., Glenwood, Illinois).

Laboratory analysis has been carried out for the following alpha-emitters: ^{241}Am , ^{239}Pu , ^{230}Th , ^{244}Cm , ^{238}U , and ^{237}Np . The method has been calibrated in the laboratory for activities in the range of 7.7 to 450 Bq/4 π (462 to 27,000 dpm/4 π) and alpha-particle energies in the range of 4.2 to 5.8 MeV.

2.0 Summary of Method

This method simply entails placing ATDs on a surface to be analyzed for a given length of time. After exposure, the ATDs are packaged and returned to the vendor for a track-density analysis. The alpha emission rate is then calculated based on the alpha-track density.

3.0 Interferences

- 3.1 The surface being measured must be as free as possible of dust, dirt, water, oil, or other materials that may absorb alpha particles. Measurements on dirty surfaces will yield alpha activities that are erroneously low. To minimize this interference, the surface should be brushed or wiped clean as appropriate, depending on the accuracy required for a given measurement.
- 3.2 The ATD surfaces are sensitive to scratching and abrasion. The detectors should be handled carefully, preferably with plastic tweezers or gloved hands.
- 3.3 The detectors are sensitive to oil and perspiration present on the skin. The detectors should be handled with gloved hands.
- 3.4 The detectors are sensitive to radon. Since most ambient air environments contain small amounts of radon, a small radon exposure cannot be avoided, but can be minimized. The detectors are delivered from the vendor in a sealed aluminized mylar bag. To minimize radon exposure, the bag should not be opened until just before deploying the ATD. After deployment, the chip(s) should be returned to the bag and the bag resealed as soon as possible.
- 3.5 The ATD has been designed for use on relatively flat surfaces (on the scale of the detector, ~1 cm). Usage on very irregular or highly curved surfaces will yield erroneous results.

4.0 Safety

No safety issues are involved with this method.

5.0 Apparatus and Materials

- Laser-scribed CR-39 ATD chips (Landauer, Inc, Glenwood, Illinois)
- Tweezers, preferably plastic, for handling the chips
- Plastic or cotton gloves for handling the chips
- Extra aluminized mylar bags for shipping, as required (Landauer, Inc, Glenwood, Illinois)
- Portable heat sealer, for resealing the mylar bags (Rennco Lift Seal Model LS, Rennco Inc, Homer, Michigan), or equivalent

6.0 Reagents

None

7.0 Sample Collection, Preservation, and Handling

Not applicable.

8.0 Procedure

8.1 Sample Surface Exposure. To expose a set of chips to a contaminated surface, the following procedure should be used.

8.1.1 The analytical surface should be cleaned so that it is as free of dust, dirt, water, oil, or other interferents as possible.

8.1.2 The sealed mylar bag containing ATDs is then opened.

Plastic or cotton gloves should be worn to prevent detector contamination with oil and perspiration.

8.1.3 The number on the first chip to be deployed and the location of its deployment are recorded.

8.1.4 The protective polyethylene film *on the side of the chip that has been laser-scribed* is stripped off with tweezers.

- 8.1.5 The chip is deployed on the surface to be characterized *with the laser-scribed face in contact with the surface*. The time is recorded as T_1 .
- 8.1.6 Steps 8.1.3 through 8.1.5 are repeated for all chips to be deployed.
- 8.1.7 Chips are left undisturbed in place for the duration of the chosen exposure time.
- 8.1.8 The first deployed chip is picked up, and the time is recorded as T_2 ; the process is repeated for all the chips.
- 8.1.9 The chips are placed in the mylar bag, and the bag is resealed, using the portable heat sealer.
- 8.1.10 The chips should be shipped to the vendor as soon as possible for subsequent processing and track-density measurement.

- 8.2 Exposure for Measurement of Background.** The ATDs are sensitive to radon. Radon present in the ambient air or emanating from the surface being characterized will contribute a low background track density. A good estimate of this background contribution can be obtained by exposing the back side of the ATD chip to ambient air while the front side is being exposed to the contaminated surface. This step is recommended in situations where a low level of activity is being measured and simply involves stripping off the polyethylene films on *both* sides of the chip with tweezers, in step 8.1.4.

The vendor should be informed of which chips have been exposed to both the contaminated surface (front surface) and ambient air (back surface). The vendor will count the track densities on both surfaces separately.

- 8.3 Track-Density Measurement.** All of the ATD chips will be processed and counted in the same way by the vendor. The vendor will provide the detector response in the form of track density, D , in tracks/mm² averaged over the face of each chip. The track density for the front surface of the chips (the side exposed to the contaminated surface) constitutes the measurement track density. The track density for the back surface of the chips (the side exposed to ambient air) constitutes the background track density D_{back} . Two methods of track-density analysis may be used. The optical scanner for "Method 1" uses transmitted light for counting the tracks. This scanner is used primarily for counting low track densities. The optical scanner for "Method 2" relies on reflected-light illumination of the tracks and is generally more useful at moderate to high track densities.

- 8.4 Prevention of Transferred Contamination.** This technique requires that detectors be placed in contact or very close proximity to contaminated surfaces. In this situation, the possibility exists that the detector will pick up transferable contamination in the form of dust, dirt, or other material. If this occurs, the detector should be gently rinsed with clean water or alcohol. This will remove the contaminated material in most cases. If material is still attached to the detector after this step, the ATD may be wiped *very gently* with a soft cloth or tissue that has been moistened with clean water or alcohol. Detectors should be allowed to dry completely before being sealed in the mylar shipping bags.

9.0 Calculations

- 9.1 Conversion of Track Density to Surface Activity.** The expression for the relationship between the ATD track-density measurements and the source activity is

$$\frac{D - D_{\text{back}}}{T_2 - T_1} \cdot \text{CAL} \cdot 10^4 = (\text{dpm}/100 \text{ cm}^2) \quad (1)$$

where

- D = measurement track density (tr/mm²)
 D_{back} = background track density (tr/mm²)
 T₂ - T₁ = exposure time (min)
 CAL = isotope calibration factor (disintegrations/track); see Table 1
 10⁴ = conversion from mm² to 100 cm²
 dpm = activity in 4π geometry (Divide by 60 to obtain Bq/100 cm²)

Table 1. Isotope Calibration Factors	
Source	CAL (disintegrations/track)
ALL	3.69 ± 8.6%
²⁴¹ Am	3.78 ± 0.8%
²⁴⁴ Cm	5.10 ± 19.7%
²³⁸ U	3.50 ± 2.5%
²³⁰ Th	3.68 ± 8.3%
²³⁷ Np	3.37 ± 13.5%
²³⁹ Pu	2.75 ± 6.9%

- 9.2 Error Analysis.** The total uncertainty in the surface activity measurement is estimated using a sum-of-squares approach, and two examples are given for typical applications.

If the uncertainty in each factor in eq. (1) is stated as a percentage error, then the uncertainties can be combined in a simple expression:

$$\Delta(\text{dpm}/100 \text{ cm}^2) = [\Delta_D^2 + \Delta_T^2 + \Delta_{\text{CAL}}^2]^{1/2} \quad (2)$$

where each Δ is the percentage error in that factor.

Example 1: Set of five ATD chips, no background correction, on an ^{241}Am contaminated surface: Suppose that the average track density for all five chips is 120 tracks/mm^2 , the standard deviation of the track density for all the chips is 7 tracks/mm^2 , the exposure time is 6 h, and the uncertainty in the exposure time is $\pm 10 \text{ min}$. Then according to eq. (1) and Table 1, the surface activity is

$$\begin{aligned} (\text{dpm}/100 \text{ cm}^2) &= \frac{120 \text{ tracks/mm}^2}{360 \text{ min}} \cdot 3.78 (\text{disintegrations/track}) \cdot 10^4 \\ &= 12,600 \text{ dpm}/100 \text{ cm}^2 = 210 \text{ Bq}/100 \text{ cm}^2 \end{aligned} \quad (3)$$

Next, using eq. (2), the stated uncertainties, and the uncertainty in the isotope calibration factor (Table 1), the total estimated uncertainty is

$$\Delta(\text{dpm}/100 \text{ cm}^2) = \left[\left(\frac{7 \text{ tr/mm}^2}{120 \text{ tr/mm}^2} \right)^2 + \left(\frac{10 \text{ min}}{360 \text{ min}} \right)^2 + (0.008)^2 \right]^{1/2} = 2.9\% \quad (4)$$

Example 2: One ATD chip, with background correction, on a surface contaminated with an unknown radionuclide: In this case, let the average track density for the chip be 45 tr/mm^2 , the background track density is 2 tr/mm^2 , the standard deviation of the track density for all fields counted on the chip is 9 tr/mm^2 , the exposure time is 24 h, and the uncertainty in the exposure time is $\pm 15 \text{ min}$. For the case of an unknown radionuclide, the best estimate of the calibration factor is given by that obtained using all sources in this protocol. Then according to eq. (1) and Table 1, the surface activity is

$$\begin{aligned}
 & \left(\text{dpm}/100 \text{ cm}^2 \right) = \\
 & \frac{(45 - 2) \text{ tracks}/\text{mm}^2}{1440 \text{ min}} \bullet 3.69 \text{ (disintegrations/track)} \bullet 10^4 = 1102 \text{ dpm}/100 \text{ cm}^2 \quad (5) \\
 & = 18 \text{ Bq}/100 \text{ cm}^2
 \end{aligned}$$

Using eq. (2), the stated uncertainties, and the uncertainty in the isotope calibration factor (Table 1), the total uncertainty is then estimated to be

$$\Delta(\text{dpm}/100 \text{ cm}^2) = \left[\left(\frac{9 \text{ tr}/\text{mm}^2}{45 \text{ tr}/\text{mm}^2} \right)^2 + \left(\frac{15 \text{ min}}{1440 \text{ min}} \right)^2 + (0.086)^2 \right]^{1/2} = 22\% \quad (6)$$

9.3 Minimum Detection Limits. The minimum detectable activity depends on the exposure time used for the measurement. The total number of disintegrations, N_{dis} , does not depend on exposure time and therefore is a more appropriate parameter to use for the minimum detection limits (MDL).

The standard deviation will be used to calculate the MDL, defined as

$$\text{MDL} = t(n-1, 99\%) \bullet s \quad (7)$$

where t is the one-sided t -statistic appropriate for the number of samples used to determine s , the standard deviation, at the 99% confidence level. For this case, the number of samples is 10, the t -statistic is 2.81, the exposure time is 80 sec, and the track density is $0.75 \text{ tr}/\text{mm}^2/\text{min}$; therefore

$$\text{MDL} = (2.81) \bullet (0.70 \text{ tracks}/\text{mm}^2/\text{min}) = 1.96 \text{ tracks}/\text{mm}^2/\text{min} \quad (8)$$

This can now be converted to number of disintegrations, N_{dis} , which is independent of exposure time:

$$\text{MDL}_{\text{NDIS}} = \text{MDL}(\text{tr}/\text{mm}^2/\text{min}) \bullet \frac{(\text{source activity}) \bullet (\text{exposure time})}{(\text{detector response})} \quad (9)$$

where the source activity is in $\text{dpm}/\text{mm}^2/4\pi$, the exposure time is in min, and the detector response is in $\text{tracks}/\text{mm}^2/\text{min}$.

For this case,

$$\begin{aligned} \text{MDL}_{\text{NDIS}} &= \left[1.96 \left(\text{tr/mm}^2/\text{min} \right) \right] \cdot \frac{(4.49 \text{ dpm/mm}^2) \cdot (1.33 \text{ min})}{(0.75 \text{ tr/mm}^2/\text{min})} \\ &= 15.5 \text{ disintegrations/mm}^2 \end{aligned} \quad (10)$$

A further discussion of measurement uncertainty is presented in Section 11.1.

- 9.4 Upper Detection Limit.** As discussed above, the detectable activity depends on the exposure time used and therefore is not a good parameter for specifying detection limits. The parameter to be used here, which is independent of exposure time, is the disintegration density, calculated from the track density:

$$\frac{\text{disintegrations}}{\text{mm}^2} = \frac{\text{tracks/mm}^2}{\text{efficiency (tracks/disintegration)}} \quad (11)$$

The upper limit of detectability for this technique is determined by the saturation effect discussed in section 11.1^(a). The Method 2 counting technique is linear up to track densities of the order of 340 tr/mm² and is sublinear above this density. This track density, and the corresponding detector efficiency, will be used to calculate the maximum (MAX) detectable disintegration density:

$$\begin{aligned} \text{MAX detectable disintegration density} &= \\ \frac{338 \text{ tracks/mm}^2}{0.25 \text{ tracks/disintegration}} &= 1352 \text{ disintegrations/mm}^2 \end{aligned} \quad (12)$$

10.0 Quality Control

A fixed alpha source standard should be prepared and tested periodically to evaluate the accuracy of the overall process (reproducibility of ATD lot materials and alpha-track density measurements).

11.0 Method Performance

The reference sources used in these measurements are described in Table 2. The source activities range from 460 to 27,000 dpm/4π.

- (a) If a correction is applied for the saturation effect, then the upper detection limit can be considerably higher than this.

Table 2. Reference Sources

Source	Reference Number	Activity (dpm/4 π)	Activity Uncertainty	Area (cm ²)	dpm/mm ²
²⁴⁴ Cm	93CM4701959	462	± 9.7	15.5	298
²³⁸ U	177-30-2	496	± 3.8	1.27	3.91
²⁵² Cf	180-21-3	1710	± 3.0	0.196	87.2
²³⁰ Th	10943	3810	± 3.0	3.90	9.77
²³⁹ Pu	1399/89	7640	± 3.0	7.79	9.80
²⁴⁴ Cm	170-86-3	8700	± 3.3	0.196	443.9
²⁴¹ Am	170-86-1	10400	± 3.2	0.196	530.6
²⁴¹ Am	DL124	21887	± 10.0	48.7	4.49
²⁴¹ Am	M2020	11829	± 3.0	2.85	41.5
²³⁰ Th	180-21-4	11100	± 3.0	0.196	566.3
²⁴¹ Am	M1040	10967	± 3.0	2.85	38.5
²³⁷ Np	180-21-1	12400	± 2.7	0.196	632.7
²³⁵ U	177-30-2	27000	± 3.8	1.27	212.6

11.1 Measurement Uncertainty vs. Track Density

To establish the applicable range of exposure times and track densities for this measurement technique, experiments were carried out with a single reference source, ²⁴¹Am #DL124 (activity = 4.49 dpm/mm² in 4 π) and a variety of exposure times. The reference source was a large-area planar source with high uniformity, which allowed sets of ten ATD chips to be exposed at a time. Exposure times ranged from 6 sec to 10 h. For each set of ten chips, a single chip was deployed with the polyethylene films stripped from both faces of the chip to measure the background track density accumulated during handling, exposure, and shipment. After exposure, the chips were immediately sealed into mylar bags and shipped to the vendor for analysis.

The vendor etched all 187 chips in one batch and proceeded to count the track densities. The optical scanner for Method 1 was used to analyze chips exposed for times ranging from 6 sec to 1.3 h. For each chip, the track density was averaged over twelve fields of view uniformly spaced over the chip. The area of each field of view was 2.43 mm². The optical scanner, from Method 2, was used to count track densities on chips exposed in the range of 20 min to 10 h. For each chip, the track density was averaged over 24 fields of view uniformly spaced over the chip. The area of each field of view was 0.67 mm².

The measurement uncertainties, in the form of standard deviations of the mean, are tabulated in Table 3 and plotted in Figures 1 (for Method 1) and 2 (for Method 2). For Method 1, the measurement uncertainties are approximately independent of net track density above 2 tracks/mm². For this set of measurements, the background track densities were in the range of 0.5 to 1.0 tracks/mm². When the background track density begins to become a significant fraction of the measurement track density, the net difference becomes small, and the associated uncertainty increases sharply, as can be seen in Figure 1. Another contribution to the uncertainty in this case is the short exposure times of 6 and 10 sec. It is difficult to control exposure times in this limit with a high degree of accuracy.

Table 3. Measurement Uncertainty vs. Track Density

Exposure Time (seconds)	Net track density ^(a) (tracks/mm ²)	Detector Response (tracks/mm ² /min)	Standard Deviation of the Mean	Counting Method
6	0.11	1.13	1.478	1
10	0.19	1.15	1.141	1
20	0.25	0.75	0.936	1
40	0.43	0.64	0.532	1
80	1.00	0.75	0.207	1
160	2.19	0.82	0.0683	1
300	4.12	0.82	0.0759	1
600	8.36	0.84	0.0478	1
1200	17.6	0.88	0.0604	1
2400	31.5	0.78	0.106	1
4800	48.9	0.61	0.124	1
1200	26.7	1.34	0.175	2
2400	53.1	1.33	0.0966	2
4800	75.4	0.94	0.0428	2
10800	209.1	1.16	0.0421	2
18000	335.8	1.12	0.0573	2
36000	295.0	0.49	0.0439	2

(a) Measurement Track Density - Background Track Density

Figure 1. Measurement Uncertainty vs. Net Track Density for Track Counting Using Method 1.

For Method 2, it was observed that the measurement uncertainty was independent of track density above densities of the order of 80 tr/mm^2 . Below this density, the measurement uncertainty increased with decreasing track density (cf. Figure 2). The reason for this increase is that the uncertainty in the track-density measurement is

approximately independent of track density in this regime. Therefore, the percentage increase in the uncertainty, relative to the mean value, increases as the mean track density decreases.

Figure 2. Measurement Uncertainty vs. Net Track Density for Track Counting Using Method 2.

11.2 Detector Response vs. Exposure Time

For any particular automated method for counting track densities, some errors will be introduced at "high" track densities due to the overlap of tracks that cannot be distinguished from one another. This appears as a saturation effect, in which the measured track density deviates from the real track density as the exposure time is increased for a given source. This effect is readily visualized in a plot of measured track density vs. exposure time. The data from Table 3 have been plotted in Figures 3 (Method 1) and 4 (Method 2). For track densities in the sublinear regime, an appropriate correction may be applied to arrive at the true track density.

It is apparent from Figure 3 that when track-counting Method 1 is used, the track density is highly linear with exposure time up to an exposure of 1200 sec (20 min), and for longer exposures, the track density increases with a sub-linear response. The dotted line in the figure is a linear-regression fit of the first nine data points. The slope of the line yields an alpha-to-track conversion efficiency of 40.2%. It may be concluded that for track densities above approximately 20 tracks/mm², this counting method will underestimate the real track density and hence the calculated source activity.

Figure 4 illustrates the same phenomenon for counting Method 2. In this case, the linear regime extends to exposure times of 5 h and corresponding track densities of approximately 340 tracks/mm². For track densities above 340 tracks/mm², this method will underestimate the real track density and the inferred surface activity. The dotted line in the figure is a linear-regression fit for the first five data points ranging from exposure times of 1200 sec to 18,000 sec (20 min to 300 min). The slope of this line yields an alpha-to-track conversion efficiency of 51.6%.

Figure 3. Measured Track Density vs. Exposure Time for Track Counting Using Method 1.

Figure 4. Measured Track Density vs. Exposure Time for Track Counting Method 2.

11.3 Detector Response vs. Reference Source Activity. To characterize the detector linearity versus reference source activity, measurements were carried out with ten different certified reference sources ranging in activity from 460 to 27,000 dpm/4 π . For each measurement, five chips were exposed in identical fashion to a particular reference source. The exposure time was chosen in each case to produce a track density in the "optimum" range of 200 to 250 tr/mm². For each set of five chips, one chip was deployed with the polyethylene films removed from both sides of the chip to measure the accumulated background track density. For all of the measurements discussed below, Method 2 was used to count the track densities. The data are tabulated in Table 4 and plotted in Figure 5.

As can be seen in Figure 5, the detector response is linear in source activity, independent of the source alpha energy, to first order (the energy dependence of the detector response will be specifically addressed in the next section). The slope of the response yields a detector calibration factor of 0.27 tracks/disintegration ($\pm 4.3\%$), which corresponds to an alpha-to-track conversion efficiency of $54\% \pm 4.3\%$. For this regression analysis, the correlation coefficient $r^2 = 0.9857$, the F-statistic is $F = 618.9$, the regression sum-of-squares is $ss_{\text{reg}} = 43,758$, and the residual sum-of-squares is $ss_{\text{residual}} = 636.3$.

Table 4. Detector Response vs. Reference Source Activity

Source	Activity (dpm/mm ²)	Net Average Track Density (tr/mm ²)	Exposure Time (min)	Detector Response (tr/mm ² /min)
²⁴⁴ Cm #93-Cm-470	0.297	157.3	3078	0.0511
²³⁸ U #177-30-2	2.9	193.6	233	0.829
²⁴¹ Am #DL124	4.49	232.2	200	1.161
²³⁰ Th #10943	9.77	252.8	95	2.662
²³⁹ Pu #1399/89	9.80	331.7	93	3.567
²⁴¹ Am #M1040	38.5	205.3	21.6	9.507
²⁴¹ Am #M2020	41.5	257.1	24	10.714
²⁴⁴ Cm #170-86-3	444	161.8	1.60	101.108
²⁴¹ Am #170-86-1	532	241.9	1.72	140.644
²³⁷ Np #180-21-1	632.6	271.7	1.45	187.36

Figure 5. ATD Detector Response versus Reference Source Activity.

- 11.4 Detector Response vs. Alpha-Particle Energy.** In the preceding section, it was implicitly assumed that the ATD response was independent of alpha-particle energy. No particular a priori reason exists to justify this assumption. To examine the inherent energy response of the detector, each detector response in Table 4 has been normalized to its respective source activity to arrive at the inherent alpha-to-track conversion efficiency *for each particular source*. These conversion efficiency data are tabulated in Table 5 and plotted in Figure 6. The solid line in the figure is a guide to the eye that connects individual data (when only a single radionuclide source was available) and the average data (when multiple sources of the same radionuclide were available).

Figure 6 demonstrates that the detector response has a small but significant alpha-particle energy dependence. The detector efficiency increases from 57% to 73% as the alpha energy increases from 4.2 MeV to 5.1 MeV, then decreases to ~40% as the energy is further increased to 5.8 MeV.

The alpha-to-track conversion efficiency depends on the details of processing the chips, including the type and concentration of etchant used, the etchant temperature, and the etch duration. These detectors were originally developed for long-term passive radon measurements (Espinosa and Gammage 1993; Tommasino 1989), and the processing steps were developed to optimize the detector's response to radon and its daughter products. It may be possible in the future to modify the processing to obtain an optimum flat energy-independent detector response for all radionuclides likely to be encountered in field applications.

The observed energy dependence has been accounted for in calculating the isotope calibration factors, as will be discussed in the next section.

Figure 6. ATD Detector Response Versus Alpha-Particle Energy.

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11.5 Isotope Calibration Factors. The calibration factors that relate the detector response to

the source activity are obtained simply by plotting the known source activity versus the measured detector response. The slope of the line, calculated using linear regression analysis, is the calibration factor CAL. These factors have been calculated, using the detector response measurements in Table 5 and are tabulated in Table 6. The first row in the table shows the result when *all* sources are included in the regression analysis; this would be the appropriate factor to use if the radioisotope(s) were unknown in a given field measurement. The second row shows the results of the linear regression analysis carried out on the measurements obtained with the four ^{241}Am reference sources. The ^{244}Cm calibration factor was obtained by dividing the source activity by the detector response, for each of the two sources used, and taking the average of the two results. The remaining calibration factors are single-source calculations obtained by dividing the source activity by the detector response for each particular source.

The uncertainties listed in Table 6 are standard deviations of the mean. For the two linear regression analyses, the listed uncertainties correspond to the calculated standard deviations of the mean for the estimated slope of the line. The uncertainty listed for the ^{244}Cm radioisotope is the estimated standard deviation of the average results obtained with the two available sources. The remaining uncertainties are all for single-source measurements. Each listed uncertainty is the standard deviation obtained for five duplicate measurements for each source.

Table 5. Detector Response vs. Alpha-Particle Energy

Source	Weighted Alpha Energy (MeV)	Activity (dpm/mm ²)	Detector Response (w/mm ² /mm)	Alpha-to-track Conversion Efficiency (Tracks/Alpha)
^{238}U #177-30-2	4.18	2.9	0.83	0.571
^{230}Th #10943	4.67	9.77	2.7	0.544
^{237}Np #180-21-1	4.74	632.6	187.4	0.592
^{239}Pu #1399/89	5.09	9.80	3.57	0.728
^{241}Am #DL124	5.47	4.49	1.16	0.517
^{241}Am #M1040	5.47	38.5	9.5	0.494
^{241}Am #M12020	5.47	41.5	10.7	0.516
^{241}Am #170-86-1	5.47	530.6	140.6	0.530
^{244}Cm #93-Cm-470	5.79	0.297	0.051	0.344
^{244}Cm #170-86-3	5.79	444	101.1	0.455

Table 6. Isotope Calibration Factors

Source	CAL (disintegrations/track)	r^2	F	degrees of freedom	SS _{regression}	SS _{residual}
All	3.69 ± 8.6% (a)	.9857	621.7	9	43760	633.
²⁴¹ Am	3.78 ± 0.8% (a)	.9998	22761	3	13413	1.77
²⁴⁴ Cm	5.10 ± 19.7% (b)			1		
²³⁸ U	3.50 ± 2.5% (c)					
²³⁰ Th	3.68 ± 8.3% (c)					
²³⁷ Np	3.37 ± 13.5% (c)					
²³⁹ Pu	2.75 ± 6.9% (c)					

r^2 = correlation coefficient
F = F-statistic
SS_{regression} = regression sum-of-squares
SS_{residual} = residual sum-of-squares

(a) Specified error is the standard deviation of the mean of the slope, derived from the linear regression analysis.
(b) Error estimated on basis of measurements using two different reference sources.
(c) Single-source measurement; error specified is the standard deviation of the mean of five duplicated measurements.

12.0 References

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Chapter 11

Miscellaneous Methods

Scope and Application

This chapter focuses on methods that are currently used at DOE sites for analyzing radioactive and mixed contaminant waste and environmental samples. The methods will be those that do not fit within the radiochemistry, inorganic, or organic chapters. Examples of the types of analyses to be included in this chapter are analyses for ignitability, corrosiveness, and reactivity.

General Considerations

The samples to be analyzed by the methods in this chapter may be highly radioactive.

Definitions

Terms used in this chapter will be defined here and in Appendix B.

Quality Control

Quality control considerations are addressed in Chapter 2 unless otherwise noted.

Data Reporting

Data reporting will be addressed within the individual methods.

Summary of Methods

To be completed as methods become available.

Appendix A

Criteria for Method Publication

Scope

This appendix describes method publication criteria for *DOE Methods*. It delineates the difference between the draft and verified methods status. Criteria for incorporating the method in a *draft* or *verified* status are described.

Draft and Verified Methods

Methods published in *DOE Methods* are designated as either “*draft*” or “*verified*” methods. The two designations differentiate whether a method has undergone a peer review and/or whether performance information is provided in a method. The applicability of a method for a particular matrix is not guaranteed based on a *verified* method status. Therefore, the applicability of an analytical method should always be demonstrated based on performance-indicating parameters such as bias, precision, and detection limits by using quality control (QC) samples for the matrix of interest. The applicability of a sampling method should be determined by criteria established during the data quality objectives (DQO) planning process and documented in the quality assurance project plan (QAPP). Details delineating requirements to obtain the *draft* method status and *verified* method status are given below.

For both *draft* and *verified* methods, user comments are always welcome (see Introduction). If either type of method is used, the QC data and other information (e.g., nature of interferences) generated

are respectfully requested. These data will enhance the QC basis of the method and help potential users of the method better determine specific applicability to their needs.

Draft Methods

Draft methods are provided in *DOE Methods* in an effort to make promising methods immediately available. The use of *draft* methods should be evaluated during the sampling and analysis planning stage. The applicability of a *draft* method should be confirmed before it is used according to criteria for new or revised methods identified in Appendix B.

The main criterion for incorporating a method as *draft* is that it must fit into the scope of *DOE Methods*. That is, the method must

- meet U.S. Department of Energy environmental and waste management (DOE/EM) needs
- be a sampling or analysis method
- be different from standard methods (e.g., EPA and ASTM methods).

Draft methods are published in a prescribed method format. Some *draft* methods are consolidated from selected procedures in the *DOE Procedures Database*. Other methods have been developed to meet unique DOE needs. Availability of method performance information in a *draft* method is not required, but is highly desirable, as it helps method users evaluate the method.

Inclusion of a *draft* method in *DOE Methods* does not constitute final approval of the method or permanent inclusion in the document. It is the intention of the editorial staff to eventually remove the *draft* status from the *draft* method by meeting the criteria for verification (see next section). If the method cannot be verified, it will be deleted from *DOE Methods*. The author is expected to play a lead role in upgrading the method from the *draft* status to the *verified* status. After external reviewer comments are returned to the author, the author must appropriately address all the reviewer comments. If any reviewer/user comments depicting *technical* inadequacy of the *draft* method cannot be resolved, the method will be removed. If the theory of the *draft* method is questioned by more than one independent user, then the question will be forwarded first to the author for comment and/or modification of the method. Failure by the author to satisfactorily address the question will result in forwarding the method and the question to DOE (or DOE's designee) for comment. Inability to satisfactorily resolve the question by the author or DOE will result in removal of the method from *DOE Methods*. The intention of this review process is to ensure that methods in *DOE Methods* are based on sound scientific principles and have sufficient acceptance among the end users to warrant inclusion in the document.

Verified Methods

Verified methods may be used with more confidence than *draft* methods because they have undergone a peer review and have been demonstrated to perform according to the indicated method performance criteria in at least one laboratory. The use of *verified* methods should be identified during the DQO planning process and specified in the QAPP. In keeping with the concept of performance based methods, however, the *verified* method should be run with sufficient QC samples to determine if DQOs are being met.

The criteria for establishing verification are three-fold:

1. The method has undergone a peer review, and the reviewer comments have been appropriately addressed by the author.
2. The method has established performance parameters and generated QC data for at least one applicable matrix; however, in the case of sampling methods, performance parameters may be non-quantitative or qualitative.
3. The method has been successfully tested on actual samples for which the method applies.

The review process entails sending a method already in *draft* status to several method reviewers. The reviewers evaluate the method based on its technical adequacy in their field of expertise. The reviewer comments are forwarded to the author who will respond to each comment by adjusting the method text/equations as appropriate or by writing an appropriate rebuttal to the comment.

Specific method-performance parameters may vary depending on what is appropriate for the method. Bias and precision should be evaluated with at least three samples, and the results should be included with the method. These samples may be matrix spikes or standard reference materials. The detection limit should be reported with the associated parameters used to arrive at the stated quantity (such as sample volume, count time, and background count rate in the case of radiochemistry). Other means of establishing or defining method performance may be included where deemed appropriate. For example, analyte recovery from soil-leaching techniques may be compared to total dissolution by fusion. A definition of the analytical working range may also be appropriate. The means used by the author to estab-

lish the method performance ultimately hinges on what is most appropriate for the method and its application. At a minimum, the bias, precision, and detection limit are necessary to evaluate whether a method has the potential for meeting the required DQOs.

Demonstrated method applicability needs to be included as part of the method performance. This entails publishing the results of actual samples to which the method applies. Matrix spike and matrix-spike duplicates or sample duplicates results indicating bias and precision should be included.

As more analysts use a given method, additional information regarding its applicability and ruggedness will be obtained. Users of a method are encouraged to submit information regarding interferences as well as all other QC information. The editors will add this new information to the method as appropriate. The addition of information to each method will continue to help demonstrate ruggedness and enhance method applicability.

Appendix B

Guidance for Selecting and for Qualifying Methods to Meet Project Analytical Data Quality Needs: A Performance-Based Approach

Introduction and Purpose

This appendix describes considerations in selecting methods to support U.S. Department of Energy environmental and waste management (DOE/EM) activities. It also describes method qualification guidance to help assure that methods selected will provide data that meet quality requirements determined during the data quality objective planning process (DQOPP) and documented in the Quality Assurance Project Plan (QAPP). Methods should be selected from national or international consensus standards if those methods meet analytical needs defined during the DQOPP and are appropriate for the matrices and analytes of interest. If consensus standard methods are not appropriate for the scope of analytical testing defined in the DQOPP, methods may be selected from other sources or developed specifically to meet the DQOPP needs. Method selection and method evaluation that follow the guidance provided in this appendix should result in method qualification, regardless of the source of the methods. Qualified methods should provide legally defensible data and should meet most EM project requirements. Although method qualification can increase costs of a project early in the project life cycle, these up-front costs provide assurance that expensive resampling and reanalysis costs will be avoided.

Method qualification is defined as

a formal process to provide a desired level of confidence that measurement methods used will produce data suitable for their intended use. The methods must meet established criteria prior to use and must be used under conditions established for qualifications.

(ASTM 1986)

Before implementing any analytical test method, the analytical laboratory should evaluate method performance to assure data are suitable for their intended use and also to assure data produced by that laboratory will be comparable to data produced by the same method in other laboratories. The following activities should be considered when planning studies to qualify a method:

- Method detection limit (MDL) study
- Method/matrix blank analysis
- Round robin participation
- Method comparability tests
- Ruggedness testing
- Periodic requalification

Method Sources

During the QAPP, methods from two general source types can be evaluated and selected for use:

1. Methods that have been published as national or international consensus standards
2. New methods or methods taken from consensus standard that have been modified.

The QAPP should document requirements for method selection (e.g., requirements to use consensus standard methods and/or method performance criteria) and method qualification. Generally, consensus methods have been thoroughly evaluated, and the performance of the methods has been well documented in the form of quality control (QC) data that relate to specific matrices. These QC data can be very useful in method selection. Frequently, new or modified methods have limited or no QC data associated with them. Factors determining which of these types of methods are selected depend on the intended use of the data. For example, in demonstrating compliance to some regulatory requirements, use of consensus methods may be mandatory. In other cases, "as low as reasonably achievable" (ALARA) considerations may drive method selection, and/or no consensus standards may be available for the analyses required. In these cases, new or modified methods may be the only methods available for use.

Method Qualification

The nature and extent of method qualification will depend on the source from which the method was selected. Qualification criteria for methods should be defined in the QAPP. These qualification criteria may or may not be similar to QC data that are included as part of the method. The qualification process is described below and is shown in Figure 1.

Consensus Methods

In the case of consensus methods, a laboratory needs to establish confidence that the analysts in that labo-

ratory who will be performing those analyses with the specific matrices of interest can produce data that meet QC criteria documented in the QAPP. To use consensus methods, it simply may be necessary for the laboratory to document that bias, precision, and the analytical range meet defined QC criteria.

The laboratory should consider performing a minimum detection level (MDL) test for organic and inorganic analytes. In this study, at least seven spike samples are analyzed (spiking level between one and ten times the anticipated MDL). Three times the standard deviation determined from these seven analytical results is then defined as the MDL in 40 CFR, Ch. 1, Appendix B, to Part 136.

Analysis of spike and replicate samples of the matrix of interest will provide assurance that the precision and bias of the method will be acceptable for those matrices. When it is not possible to perform these studies on a portion of the actual sample matrix, the tests should be performed using a matrix that exhibits as many of the physical and chemical characteristics of the actual sample matrix as possible.

In addition, a minimum of three method blanks should be analyzed to ensure that reagents and equipment will not be sources of contamination. The results of those three analyses should be documented.

If possible, data from analysis of matrix blanks, matrix spikes, and duplicates should be generated and documented to better understand interferences and limitations as they apply to the matrix of interest.

When applicable, the laboratory should consider participating in "round-robin" interlaboratory comparison studies to compare their data with that produced by other laboratories.

Figure 1. Method Selection and Qualification Process.

New or Modified Methods

In the case of new or modified methods, the laboratory should perform the tests described in the previous paragraph that apply to the use of consensus methods.

Method comparability tests should be performed and documented in cases where a new or modified method has been selected for use, but the analytes of interest could be measured by consensus methods. This comparability test can, in some cases, be accomplished by performing the consensus method in parallel with the new or modified method on the matrix of interest. In cases where ALARA or other constraints prohibit the use of consensus methods, no comparability test is possible. The ruggedness of the method should be investigated as in Youden and Steiner (1975).

Method Requalification

The S&AP should contain some requirement for laboratory requalification of methods.

Requalification should be performed if a specified period of time has elapsed during which the method was not used, and no control standards were analyzed. Requalification should be considered by the laboratory when different analysts assume responsibility for the performance of methods. Documentation of method requalification by a different analyst also serves to demonstrate that analyst's proficiency. Methods that are modified following initial qualification should also be requalified.

References

American Society for Testing and Materials (ASTM). 1986. "Standard Guide for Qualification of Measurement Methods by Laboratory Within the Nuclear Industry." C1068-1086. *Annual Book of ASTM Standards*, Vol. 1201.

Youden, W. J., and E. H. Steiner. 1975. *Statistical Manual of the Association of Official Analytical Chemists*. Washington, DC.

Glossary

Definition of Terms

AA - atomic absorption

AAS - atomic absorption spectrometer

ACS - American Chemical Society

ADC - analog to digital converter

AEA - alpha energy analysis

AES - atomic emission spectroscopy

AES - automatic external standardization

air lift sampler - Air pressure is applied to a well borehole by a high pressure pump forcing a water sample out of a discharge tube at the top of the well into a collection vessel.

ALARA - as low as reasonably achievable

ALI - allowable limit of intake

AMD - Associated Manufacturing and Design, Alexandria, Virginia

ANL - Argonne National Laboratory

ANS - American Nuclear Society

ANSI - American National Standards Institute

AR - analytical reagent

ASQC - American Society for Quality Control

ASTM - American Society for Testing and Materials

ATD - alpha-track detector

automated composite sampler - A system that automatically collects non-discrete samples composed of more than one specific aliquot collected at various locations or at different points in time. Analyzing this type of sample produces an average value for the locations or time period covered by sampling.

AWWA - American Water Works Association

bar - 10^5 newtons per square meter

B & K - Bruel & Kjaer

B & K M-gM - Bruel & Kjaer multi-gas monitor

BFB - bromofluorobenzene

bladder pump sampler - A system which consists of a collapsible membrane inside a long, rigid housing; a compressed gas supply; tubing and check valves. Water enters the collapsible membrane through the bottom check valve. After the membrane has filled, gas pressure is applied to the annular space between the rigid housing and the membrane forcing the water upward through a sampling tube to a collection vessel. When the membrane is empty, the top check valve closes, the bottom check valve opens, and the process recycles.

Bq - becquerel

BT - breakthrough

BV - bed volume

Bz - benzene

C - celsius

C - coulomb

CAL - calibration display

calibration check - Verification of the ratio of the instrument response to analyte amount.

CAM - continuous air monitor

CAS - Chemical Abstract Services

cable tool/slurry sampling - Samples are collected from a slurry generated from water added and combined with formation during cable tool drilling.

CCB - continuing calibration blank

CCBS - conventional core barrel sampling

CCV - continuing calibration verification

CERCLA - Comprehensive Environmental Response, Compensation and Liability Act of 1980, as amended; often referred to as Superfund

CFR - Code of Federal Regulations

CFWTL - chronic freshwater toxicity level

CHD - chlordane

CH-TRU - contact handled TRU waste

Ci - curie

CIBz - chlorobenzene

CLP - Contract Laboratory Program

cm - centimeter

CMPO - carbomoyl-methylphosphine oxide

CN - cyanide

COLI/WASA - composite liquid waste sampler. A glass, plastic, or Teflon tube designed to collect a liquid sample from the full depth of a drum and maintain it in the tube until delivery to the sample bottle. A neoprene stopper at one end attached by a rod running the length of the tube to a locking mechanism at the other end. Manipulation of the locking mechanism opens and closes the sampler by raising and lowering the neoprene stopper.

consensus methods - methods that have been published as national or international consensus method (e.g., EPA, SW-846)

cpm - counts per minute

CPS - counts per second

CRC - Chemical Rubber Company

CRI - low-concentration check standard

CRL - certified reporting limit

c/s - counts per second

CV - coefficient of variation

CWA - Clean Water Act

DAC - derived air concentration

DAI-GC - direct aqueous injection - gas chromatographic

DCB-1,4 - dichlorobenzene

DCBP - decachlorobiphenyl

DCE - dichloroethane

DCG - derived concentration guides — the analyte limits by which DOE regulates radioactive releases

dead time - percentage of time the detector cannot record another decay event.

dip sampler - An adjustable clamp attached to the end of a wooden, plastic, or metal pole of the desired length. Samples are collected in a jar or beaker that is secured in the clamp.

DIW - deionized water

DLC - decision level concentration

DLR - decision level count rate

DMG - dimethylglyoxime

DMG-ETOH - A process where .5 g of dimethylglyoxime is placed into a beaker, followed by 50 mL of ethanol. The mixture is then stirred and heated as needed to aid dissolution.

DMG-MIC - A process within the DMG-ETOH process, where 10 milliliters of basic buffer solution are added to a slurry and vigorously stirred.

DNT-2,4 - dinitrotoluene

DOE - U. S. Department of Energy

DOE Methods - DOE Methods for Evaluating Environmental and Waste Management Samples

DOE-HQ - Headquarters Office of the DOE

DOT - U. S. Department of Transportation

DQA - data quality assessment

DQOs - data quality objectives

DQOPP - data quality objectives planning process

dpm - disintegrations per minute

drive tube - A one-piece sampling barrel that may or may not contain removable tube or ring liners. The sampler is used to collect vadose zone samples.

DSITMS - direct sampling ion trap mass spectrometry

DST - double-shell tank

dual-wall core barrel - A sampler that consists of inner and outer tubes, with a special hardened steel drive shoe attached to the cutting edge of the outer tube. Used for obtaining samples of radioactive soil/sediments to prevent releasing contamination to the general environment.

DW - deionized water

DWPF - defense waste processing facility

EC - electron capture

ECD - electron capture detection

ECD - electron capture detector

E/D - Environmental Devices, Inc.; Sacramento, California

EDTA - ethylenediaminetetraacetic acid

EIC - electret ionization chamber

EM - Environmental Restoration and Waste Management

EML - Environmental Measuring Laboratory

EMSL - Environmental Monitoring System Laboratory

EMV - electron multiplier voltage

END - endrin

EPA - U. S. Environmental Protection Agency

EQL - estimated quantitation limit

ER - environmental restoration

ER - external ratio

ERR - error display

ES&H - environment, safety, and health

eV - electron volt

F - Fahrenheit

FCV - free-column volumes

FI - flow injection

FIAS - flow-injection analysis system

FID - flame ionization detection

FM - Factory Mutual

ft - foot

FTIR - Fourier transform infrared

FWHM - full width half maximum

g - gram

gain shift - new channel position of a peak (PHA systems) of specific energy relative to a previous channel location

gal - gallon

GBq - giga becquerel

GC - gas chromatography

GC-ECD - gas chromatography - electron capture detector

GFAA - graphite furnace atomic absorption

glass open tube sampler - Hollow glass tube (~4 ft in length) that contains a constricted orifice to facilitate plugging the opening to maintain a vacuum in the tube.

GM - Geiger Müller

grain thief - A device that consists of two slotted telescoping tubes, usually made of brass or stainless steel. The outer tube has a conical, pointed tip on one end that permits the sampler to penetrate the material being sampled. The sampler is opened and closed by rotating the inner tube.

gravity corer - A metal (brass or steel) tube with a replacement tapered nosepiece on the bottom and a check valve on the top. The check valve allows water to pass through the corer or descend but prevents a washout during recovery of sludge or sediment sample. Many accept plastic liners.

grap sampling - Collection of discrete aliquots representing a specific location at a given point in time. The sample is collected all at once and at only one particular point in the sample medium.

Gy - gray

h - hour

hand auger sampling - A device that is attached to the bottom a length of pipe that has a crossarm at the top. The device moves down in the ground by turning the crossarm at the same time the operator applies downward pressure. As the device advances and becomes filled with soil, it is taken from the hole and soil is removed and placed in a sample container.

hand corer - A thin-walled tube with attached T handle which facilitates driving the corer. A check valve present at the top of the tube prevents loss of sample during tube withdrawal. Used for collecting sludge and surface soils.

hand corer sampling - A stainless steel tube with beveled nosepiece and handle used for collecting solid samples. Corer may come with extension handle for sampling under water and brass or polycarbonate liners.

HC - heptachlor

HCB - hexachlorobutadiene

HCBz - hexachlorobenzene

HCE - heptachlor epoxide

HCl - hydrogen chloride

HCN - hydrogen cyanide

HDEHP - diethylhexylphosphoric acid

HEDTA - N-(2-hydroxyethyl) ethylenediaminetriacetic acid

HEPA - high efficiency particulate air

HLW - high-level radioactive waste

HP - Hewlett Packard

HP - high purity

HPG - high-pressure gas

HPGe - High-Purity Intrinsic Germanium

HPLC - high performance liquid chromatography

HPLC-UV - high performance liquid chromatography/ultraviolet detection

IA - immunoassay

IAEA - International Atomic Energy Agency

IAG - interagency agreement

IC - ion chromatography

ICB - interference calibration blank

ICP - inductively coupled plasma

ICP-AES - inductively coupled plasma-atomic emission spectroscopy

ICP-MS - inductively coupled plasma-mass spectrometry

ICP-OES - inductively coupled plasma-optical emission spectrometry

ICRP - International Committee for Radiation Protection

ICS - interference check sample

ICSA - Interference Check Standard part A

ICSAB - Interference Check Standard part AB	L - liter
ICV - initial calibration verification	LANL - Los Alamos National Laboratory
ID - identification	lb - pound
ID - inner diameter	LCD - liquid crystal display
ID - inside diameter	LCL - lower control limit
ID - isotope dilution	LCS - laboratory control sample
IDL - instrument detection limit	LDPE - low-density polyethylene
IDLH - immediately dangerous to life and health	LED - light-emitting diode
in. - inch	LEP - low energy photon
INEL - Idaho National Engineering Laboratory	LEPS - low energy photon spectroscopy
internal standard - a known quantity of one or more known compound(s) added to a sample for quantitation purposes.	LIN - lindane
IPL - Isotope Products Laboratory	LMD - Laboratory Management Division
IR - infrared spectroscopy	LLW - low-level radioactive waste
IR - isotope ratio	LSC - liquid scintillation counting
Kemmerer bottle - A messenger-activated water sampling device of brass or plastic construction. In the open position, water flows easily through the device. Once lowered to the desired depth, a messenger is dropped down the simple line tripping the release mechanism and closing the bottle. In the closed position, the bottle is sealed, both on top and bottom, from any additional contact with the water column and can be retrieved.	LSGAECF - Liquid Scintillation Gross Alpha Efficiency Calibration Form
Kg - kilogram	LSTECF - Liquid Scintillation Tritium Efficiency Calibration Form
	LWDF - Liquid Waste Disposal Facility
	M - molar
	MAX - maximum
	mbar - millibar

MBC - mass bias correction

MBq - megabecquerel

MC - methoxychlor

MCA - multichannel analyzer

μCi - microcurie

MCL - maximum contaminant levels

MDA - minimum detectable activity

MDC - minimum detectable concentration

MDL - method detection limit

MDL - minimum detection limit

MDR - minimum detectable count rate

MDTA/D - micro-distillation tube assembler/
disassembler

MEK - methyl ethyl ketone

MEM - memory display

method - a document describing an operation in
sufficient detail that a knowledgeable analyst or
sampler can perform that operation successfully.

MeV - million electron volts

μg/g - microgram per gram (parts per million)

μGy - microgray

M-gM - multi-gas monitor

mg - milligram

MIBK - methyl isobutyl ketone

mil - .0254 millimeter (10^{-3} inch)

min - minute

mis - membrane inlet system

μL - microliter

mL - milliliter

μm - micrometer

mm - millimeter

mR - milliroentgen

mRad - millirad

mrem - millirem

MS - mass spectrometry

MS-DOS - Microsoft disk operating system

MSDS - material safety data sheet

μSv - microsievert

mSV - milli sievert

MUST - Melton Valley Storage and the Evaporatory
Concentrate Storage Tank, located at Oak Ridge
National Laboratory

mV - millivolt

MV - molar volume

NAA - neutron activation analysis

NaK - sodium-potassium alloy	ORD - optical rotatory dispersion
NAREL - National Air and Radiation Environmental Laboratory	OSHA - Occupational Safety and Health Administration
NBL - New Brunswick Laboratory	OVA - organic vapor analyzer
NBz - nitrobenzene	OVS - OSHA versatile sampler
NCRP - National Council on Radiation Protection and Measurements	PAH - polycyclic aromatic hydrocarbons
NFPA - National Fire Protection Association	PAH - polynuclear aromatic hydrocarbons
ng - nanogram	PAM - portable alpha monitor
NIOSH - National Institute Occupational Safety and Health	PARCC - precision, accuracy, representativeness, completeness, comparability
NIST - National Institute of Standards and Technology	PC - personal computer
nm - nanometer	PCB - polychlorinated biphenyls
NNEDDC - N-[naphthyl(1)]-ethylenediamine	PCE - perchloroethene
NPDES - National Pollutant Discharge Elimination System	pCi - picocurie
NPH - normal paraffin hydrocarbons	PCP - pentachlorophenol
NPT - national pipe thread	PE - performance evaluation
NRC - U. S. Nuclear Regulatory Commission	PEEK - poly ether ether ketone
OD - optical density	peristaltic pump sampling - Sample is drawn through heavy-wall tubing (e.g., Teflon or medical-grade silicon) into a sample container. Alternatively, a sample volume can be collected in a vacuum trap avoiding the sample entering the pump.
OD - outside diameter	PHA - pulse height analyzer
OES - optical emission spectroscopy	plateau curves - A function of count rate vs. voltage setting
ORNL - Oak Ridge National Laboratory	

PNL - Pacific Northwest Laboratory

Ponar grab - A clamshell type scoop activated by a counter lever system. The shell is opened and latched in place and slowly lowered to the bottom. When tension is released on the lowering cable, the latch releases and the lifting action of the cable on the lever system closes the clamshell. The sampler is used to sample sludges and sediments.

PP - polypropylene

ppb - parts per billion

ppm - parts per million

ppmv - parts per million per unit volume

PQL - practical quantitation limit

procedure - a document describing an operation in great detail, usually site-specific, so that a trained analyst or sampler can perform that operation successfully.

PRP-1 -

psi - pounds per square inch

psig - pounds per square inch gauge

PTFE - polytetrafluoroethylene

PVC - polyvinyl chloride

QA - quality assurance

QA - quantitative

QAMP - quality assurance management plan

QAPP - quality assurance project plan

QC - quality control

QL - quantitation limit

RAM - radiation area monitor

RCRA - Resource Conservation and Recovery Act of 1976, as amended, including the Solid Waste Disposal Act of 1983, the Hazardous Waste Control and Enforcement Act of 1983. RCRA is a section of SDWA.

Rem - roentgen equivalent man

RGD - radiation-generating device

RH-TRU - remote-handled TRU waste

RLWS - radioactive liquid waste system

RMW - radioactive mixed waste. This waste contains both radioactive and hazardous components.

RPA - relative percent accuracy

RPD - relative percent difference

rpm - revolutions per minute

RSD - relative standard deviation

RWP - radiological work permit

RWP - radiation work permit

S - substrate

S&AP - Sampling and Analysis Plan

SA - standard addition

SAFER - Streamlined Approach for Environmental Restoration

sampling thief - A device that consists of two slotted, concentric stainless tubes with a pointed tip; the inner tube may be rotated to close off the sampler interior.

sampling trier - A long-stainless tube with a slot that extends almost its entire length. The tip and edges of the tube slot are sharpened to allow device to cut a core of the material to be sampled when rotated after insertion into the material.

SAS - Statistical Analysis System

sec - second

SF - spontaneous fission

SFE - supercritical fluid extraction

SGW - simulated groundwater

Shelby Tube - A sampler constructed out of cold drawn steel tubing and bent at the lower end to form a tapered cutting edge. The upper end is fastened to a check valve to help hold the sample in the tube when the tube is withdrawn from the ground. Used for collecting cohesive materials such as sludges or clays.

SI - System International d'Unitès

soil gas sampling - Insertion of sampling probes and collection of subsurface gas samples at depths of 4 to 6 feet.

SOP - standard operating procedures

SOW - statement of work

SPE - solid phase extraction

split spoon - A thick-walled steel tube that is split lengthwise and lined with ring or tube liners. A cutting shoe is attached to the lower end and the upper end contains a check valve and a means to attach to a drill rod or cable tool. Used to sample materials below the surface through the vadose zone.

SQA - semi-quantitative

SRM - standard reference materials

SRS - Savannah River Site

SS - sample stabilizer

SS - stainless steel

SST - single-shell tank

standard curve - A plot of concentrations of known analyte standards versus the instrument response to the analyte.

STD - standard deviation

SUMMA[®] - passivated gas sampling canister

summersible pump - Electric or compressed gas powered device used for the collection of groundwater. Generally construction of "more or less" non-contaminating materials.

Sv - sievert

TB - thymol blue

TBP - tributyl phosphate

TBq - teraBequerel

TCE - trichloroethene

TCL - target compound list

TCLP - Toxicity Characteristics Leach Procedure

TCMX - tetrachlorometaxylene

Teflon bailer - A tall narrow teflon-lined bucket equipped with a check valve on the bottom for collection of groundwater. The valve allows water to enter from the bottom as the device is lowered, then prevents its release as the device is raised.

TFT - trifluorotoluene

TOC - total organic carbon

Tol - toluene

TOPO - tri-n-octylphosphine oxide

TOX - total organic halides

TOX - toxaphene

TQM - total quality management

TRU - transuranic

TSIE - transformed spectral index of the external standard

UCL - upper control limit

UL - Underwriter's Laboratory

USATHAMA - U.S. Army Toxic and Hazardous Material Agency, now known as the Army Environmental Center

USN - ultrasonic nebulizer

UV - ultraviolet

V - volt

VC - vinyl chloride

Veihmeyer sampler - A chromium-molybdenum steel tube with specifically shaped points for penetrating specific soil types without pushing the soil/sediment ahead of it, thus preventing the core from compacting in the tube.

VOA - volatile organic analysis

VOA - volatile organic analyte

VOC - volatile organic chemicals

VOC - volatile organic compounds

WINCO - Westinghouse Idaho Nuclear Company

WIPP - Waste Isolation Pilot Plant

WM - waste management

WORM - write-once-read-many format

XRF - X-ray fluorescence

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