Battelle

Pacific Northwest Laboratories
Battelle Boulevard
P.O. Box 999
Richland, Washington 99352
Telephone (509) 376-3286

FAX: (509) 373-0169
internet: sc_goheen@pnl.gov

May, 1995

Dear Recipient:

We are pleased to distribute the April 1995 addendum of *DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods)*. Starting next year, updates to *DOE Methods* will be distributed annually. Please note the questionnaire attached to this letter. To help ensure that *DOE Methods* will be a useful tool for sampling and analysis activities, we need your feedback to help us determine its current value and future growth. Returning the completed questionnaire in the enclosed envelope by May 31 will allow us to keep you on the distribution list.

Please do not discard your October 1994 issue of *DOE Methods*. The April 1995 addendum is to be interwoven into the earlier edition. A table with chronological step-by-step instructions for assembly is enclosed with this letter. Please follow instructions in sequence, and after completing the process, double check with the new Table of Contents to ensure that everything is in the proper order. It is important to watch exact page numbers carefully because sometimes only a few pages from a chapter are being replaced.

When an entire chapter has been extensively revised, that chapter is designated as "Draft." After responding to reviewer comments, the draft status will be removed for the next issue. When smaller portions of a chapter are revised, those portions are highlighted in gray. Also, the print for the text is slightly lighter. Methods that have not yet been verified (see Appendix A for an explanation of the verification process) are designated as "Draft."

DOE Methods is now available through the Internet. The World Wide Web URL address is <http://www.pnl.gov.2080/methods>. The Gopher address is <gopher://gopher.pnl.gov:2070/methods>. New methods may be added to the Internet version throughout the year. New methods will be added to the hardcopy document in June 1996.

We encourage you to send us comments relating to *DOE Methods*. Any help you could give that would help us verify draft methods or add useful information to any method would be greatly appreciated. Comments are welcome at any time, but if they are received by March 1, 1996, we will work with you to incorporate them into the June 1996 revision. Please send comments to me at

Pacific Northwest Laboratory
P.O. Box 999, MS P8-08
Richland, Washington 99352

Thank you.

Sincerely,

Steven C. Goheen, Ph.D.
Project Manager
Chemical Sciences Department

SCG:gkr

encl.

P.S. Please remember to fill out the survey and return it if you wish to continue receiving updates to *DOE Methods*. *DOE Methods* will also be available through the Office of Scientific and Technical Information (DOE staff and contractors) and the National Technical Information Service (all others).

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Questionnaire
DOE Methods for Evaluating Environmental and Waste
Management Samples

1) Do you wish to continue receiving updates to *DOE Methods*? Y N

2) Have you used your copy of *DOE Methods*? Y N If yes, then

What did you use it for? Method Source _____ Contracts _____ Project Planning _____

Other (describe) _____

Which method(s) did you use (as is, or modification of) from *DOE Methods*? _____

Did using methods from *DOE Methods* save methods-development costs? Y N

If yes, please estimate how much cost or time was saved. \$ _____ and/or _____ hr

3) What analytes/matrices would you like to see added to *DOE Methods*? _____

4) What chapter(s) of the document would you like to see added/expanded/deleted? _____

5) Is your organization responsible for field sampling? Y N

6) What type(s) of analyses do you perform at your company?

	Site Characterization/ Monitoring	Remediation	Tank Waste Characterization	Waste Streams	Other (specify)
Radiochemistry					
Inorganic					
Organic					

7) What are the drivers that determine which methods/procedures you select for analysis?

EPA (RCRA, CERCLA, etc.) _____

State (Health, Ecology, etc.) _____

Local DOE office _____

Other (Specify) _____

8) What type(s) of procedures/methods do you use?

	In-House Developed	EPA (e.g., SW-846)	ASTM	DOE Methods	Other (Specify)
Sampling					
Radiochemistry					
Inorganic					
Organic					

9) Additional comments for the editorial staff: _____

Return to

Georgia K. Ruebsamen
Pacific Northwest Laboratory
P.O. Box 999, MS P8-08
Richland, Washington 99352

Name _____

Internet Address _____

Remove from Oct. 1994 Issue	Insert from April 1995 Supplement
• Remove TOC-vii to xii	• Insert TOC-vii to TOC-xii
• Remove Intro-1 to Intro-5	• Insert Intro-1 to Intro-4
• Remove 1-1 to 1-15	• Insert 1-1 to 1-14
• Remove 4-1 to 4-24	• Insert 4-1 to 4-24
• Remove 6-1 to 6-11	• Insert 6-1 to 6-11
• Remove 7-1 to 7-16	• Insert 7-1 to 7-17
• Nothing to remove	• Insert SD010-1 to SD010-33 Place after ST011R-21
• Nothing to remove	• Insert ST011R-1 to ST011R-21 Place after ST010-17
• Nothing to remove	• Insert SO010R-1 to SO010R-14 Place after SD010-33
• Nothing to remove	• Insert SW010R-1 to SW010R-6 Place after SO010R-8
• Remove 8-1 to 8-10	• Insert 8-1 to 8-10
• Remove OS020-13 to OS020-14	• Insert OS020-13 to OS020-14
• Nothing to remove	• Insert OS060-1 to OS060-19 Place after OS050-14
• Nothing to remove	• Insert OP040R-1 to OP040R-20 Place after OP030R-7
• Nothing to remove	• Insert OM500R-1 to OM500R-9 Place after OH100R-16
• Nothing to remove	• Insert OM510R-1 to OM510R-16 Place after OM500R-9
• Remove 9-1 to 9-7	• Insert 9-1 to 9-7
• Remove MB100-11 to MB100-12	• Insert MB100-11 to MB100-12
• Remove MP110R-7	• Insert MP110R-7
• Remove MU012R-1 to MU012R-8	• Insert MU012R-1 to MU012R-10
• Remove 10-1 to 10-11	• Insert 10-1 to 10-11
• Remove RS100-3 to RS100-6	• Insert RS100-3 to RS100-6
• Nothing to remove	• Insert RP450-1 to RP450-11 Place after RP330-11
• Remove RP530-1 to RP530-14	• Insert RP530-1 to RP530-16
• Nothing to remove	• Insert RP570-1 to RP570-12 Place after RP550-9
• Remove RP580-1 to RP580-10	• Insert RP580-1 to RP580-11
• Remove RP710-3 to RP710-4	• Insert RP710-3 to RP710-4
• Remove RP735-7 to RP735-8	• Insert RP735-7 to RP735-8
• Remove A-1 to A-3	• Insert A-1 to A-3
• Remove B-1 to B-4	• Insert B-1 to B-4
• Remove Glossary-1 to Glossary-11	• Insert Glossary-1 to Glossary-12
• Remove Index-1 to Index-17	• Insert Index-1 to Index-22
• Remove Dist-1 to Dist-20	• Insert Dist-1 to Dist-23

Table of Contents

Abstract	iii
Acknowledgments	v
Contents	vii
Introduction	Intro-1
Background and Scope	Intro-1
Need for New Methods	Intro-2
Proposed Action to Fill Needs	Intro-2
Structure and Organization of This Document	Intro-3
Method Numbering System	Intro-4
Chapter One Guidance for Effective Project Planning	
Scope and Application	1-1
General Considerations	1-1
Definitions	1-3
Project Plan Development - Steps Before Initiation of DQOPP	1-4
Project Plan Development - DQOPP Steps	1-4
Project Plan Guidance	1-9
References	1-11
Further Reading	1-11
Chapter Supplements	1-12
Chapter Two Quality Assurance	
Scope and Application	2-1
General Considerations	2-1
Quality Assurance Program	2-2
Program Design	2-2
Quality Assurance Management Plan	2-2
Quality Assurance Project Plan	2-2
Reference	2-9
Further Reading	2-9
Chapter Three Quality Control	
Scope and Application	3-1
General Considerations	3-1
Definitions	3-2
Quality Control Criteria	3-5

	Data Reporting	3-7
	QC Samples Submitted by Outside Organizations	3-8
	Reference	3-8
	Further Reading	3-8
Chapter Four	Safety	
	Scope and Application	4-1
	General Considerations	4-1
	Definitions	4-2
	Guidelines for Selecting Laboratory Facilities	4-4
	Sample Handling	4-4
	Radiation Protection	4-6
	Safe Handling of Hazardous Chemicals	4-11
	References	4-24
	Further Reading	4-24
Chapter Five	Waste Handling	
	Scope and Application	5-1
	Waste Minimization	5-1
	Disposal Guidance	5-2
	Liquid Effluents	5-6
	References	5-9
Chapter Six	Choosing the Correct Method	
	Scope and Application	6-1
	Sampling Methods	6-1
	Analytical Methods	6-2
	General Considerations	6-2
	Radiological Screening	6-4
	References	6-4
Chapter Seven	Sampling Methods	
	Scope and Application	7-1
	Limitations	7-1
	Definitions	7-1
	Sampling Environment and Types of Sampling	7-1
	Monitoring Facility Operations	7-12
	Offsite Sample Shipping	7-13
	Safety	7-13

	Quality Control	7-14
	Summary of Methods	7-14
	Data Reporting	7-14
	References	7-14
Methods	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	
	SD010R: Collecting Samples from TRU Waste Drums Containing Solid Process Residues and Soils (Sludges)	
	ST010: General Method for Sampling Liquids and Solids in Low-Level Waste Storage Tanks	
	ST011R: General Methods for Sampling Liquids and Solids in High-Level Waste Storage Tanks	
	SO010R: Collection of Liquid Samples for Effluent Monitoring of Operations Facilities	
	SW010R: Core Samples in Cement Solidified Low-Level Liquid Waste	
Chapter Eight	Organic Methods	
	Scope and Application	8-1
	Limitations	8-1
	Definitions	8-4
	Quality Control	8-4
	Data Reporting	8-6
	Summary of Methods	8-6
	References	8-7
Methods	OS010: Total Organic Chlorine in Oil: Field Test Kit Method	
	OS020: Immunoassay for Polychlorinated Biphenyls in Soils, Rev. 1	
	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	
	OS060: Immunoassay for Petroleum Fuel Hydrocarbons in Soil	
	OC010R: Preparation and Cleanup of Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds	
	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
OP040R:	Reduced-Scale Zero Headspace Extraction for TCLP Volatiles in Shielded or Containment Conditions
OP100R	PCBs in Aqueous Radioactive Mixed Wastes using Solid Phase Extraction Disks and GC-ECD
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
OG015R:	Major Nonhalogenated Volatile Organics in Radioactive Aqueous Liquids Analyzed by Direct Aqueous Injection Gas Chromatography, Rev 1
OG100R:	Analysis of Polychlorinated Biphenyls as Aroclors in Solid Radioactive Mixed Wastes. Rev 1
OH100R:	Direct Analysis of TCLP Acidic Semivolatile Compounds in Radioactive Liquid Wastes or Leachates Using HPLC with Ultraviolet Absorbance Detection
OM500R:	Qualitative Analysis for Low-Molecular-Weight Organic Acids in Mixed Hazardous Waste Samples by Thermospray LC-MS
OM510R:	Determination of Chelators and Their Degradation Products in Mixed Hazardous Waste Samples by Derivatization GC/MS

Chapter Nine	Inorganic Methods	
	Scope and Application	9-1
	Limitations	9-1
	Definitions	9-2
	Quality Control	9-2
	Data Reporting	9-4
	Summary of Methods	9-5
	Reference	9-5

Methods	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
	MB100:	Immunoassay for Mercury in Soils, Rev. 1
	MP100R:	Solvent Extraction of Uranium and Thorium from Radioactive Liquid Wastes

MP110R:	Cleanup of Transuranic Liquid Wastes using Extraction Chromatography
MU012R:	Total Cyanide by Remote Microdistillation and Argentometric Titration
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

Chapter Ten	Radiochemistry Methods	
	Scope and Application	10-1
	Limitations	10-1
	Definitions	10-2
	Quality Control	10-4
	Data Reporting	10-5
	Summary of Methods	10-6
	References	10-6
	Further Reading	10-6

Methods	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 Membranes
	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
	RP330:	Separation of Niobium for Niobium-93m and Niobium-94 Determination
	RP450:	Determination of Radium-226 in Aqueous Samples
	RP500:	Purification of Strontium in Water Before Strontium-89/Strontium-90 Measurement
	RP501:	Determination of Total Radioactive Strontium in High-Level Samples using Extraction Chromatography, Rev. 1
	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
	RP570:	Radiochemical Determination of Thorium Isotopes in Aqueous Samples
	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 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
RI010:	Gamma-Ray Spectrometry
RI100:	Liquid Scintillation Instrumentation Method
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

Chapter Eleven Miscellaneous Methods

Scope and Application	11-1
General Considerations	11-1
Definitions	11-1
Quality Control	11-1
Data Reporting	11-1
Summary of Methods	11-1

Appendix A Criteria for Method Publication

Scope	A-1
Draft and Verified Methods	A-1

Appendix B Guidance for Selecting and Evaluating Methods to Ensure Generation of Qualified Analytical Data: A Performance-Based Approach

Introduction and Purpose	B-1
Method Selection	B-1
Method and Laboratory Qualification	B-3
Method and Laboratory Requalification	B-3
Data Qualification	B-3
References	B-4

Glossary Definition of Terms**Index****DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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 Revision 2 (Oct. 1994), this addendum (April 1995) includes highlighted text and (occasionally) a "Draft" designation at the top of the page. Text to be deleted has a line through it (e.g., ~~delete~~). Changes in tables are indicated by thick brackets (**|**). All draft designations will be removed from chapters (not methods) in the October 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 selecting and using methods. 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, Addendum 1) the order of the first five 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

S. C. Goheen, Ph.D.
Pacific Northwest Laboratory
P. O. Box 999, P8-08
Richland, Washington 99352
Fax: (509) 373-0169
e-Mail: sc_goheen@pnl.gov

Method Numbering System

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

1. The first two letters designate classes of methods, as indicated in Table 1.
2. Each method is given a distinct number (the next three digits).
3. 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
O	Organics	MIxxx	ICP Methods
OSxxx	Screening	MMxxx	ICP-MS Methods
OCxxx	Cleanup	MVxxx	Uncategorized Methods
OPxxx	Sample Prep	R	Radionuclides
OGxxx	GC Determinative/Various Detectors	RFxxx	Field Screening
OHxxx	HPLC Determinative/Various Detectors	RExxx	Sample Prep
OMxxx	GC-MS or LC-MS Determinative	RIxxx	Instrumentation
Olxxx	IR or GC-IR Determinative	RAxxx	Miscellaneous Radiochemistry
OVxxx	UV-VIS Determinative	X	Miscellaneous Methods
OXxxx	TOC, TOX		

Abbreviations 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

This chapter provides general guidance for designing an environmental and/or waste-management project plan, based on careful consideration of project goals and data quality needs. A U.S. Department of Energy (DOE) environmental restoration and waste management (EM) policy requires that a data quality objectives process (DQOP) be performed for all EM projects where a need may exist to collect significant environmental data.^(a) During this DQOP, project data quality objectives (DQOs) are defined and documented. This chapter provides an overview of the DQOP and addresses implementing the outputs of the DQOP in the project plan and assessing project data against requirements defined in the plan.

The guidance for completing the DQOP contained in this chapter is based upon the U.S. Environmental Protection Agency's (EPA's) DQOP (EPA 1994).

roadmap for achieving those DQOs. It also provides a plan for assessing the quality of the data against project data 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

General Considerations

Quality assurance project plans (QAPPs), frequently referred to as project plans, implement the outputs of the DQOP.

A complete project plan provides 1) a clearly defined project scope, 2) a set of project DQOs, and 3) a

(a) U.S. Department of Energy memorandum by Thomas P. Grumbly (control number 941068.SF) dated September 7, 1994.

- 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 DQOP 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 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 DQOP 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 DQOP 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 DQOP says that data quality can be established only after limits on (the probability of) decision errors are established.

Generally, the description of a DQOP 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. 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.

The first six of the DQOP 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 DQOP 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 DQOP. Without understanding the DQOP 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 DQOP 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 DQOP is appropriate. Projects with limited scopes may not require the rigorous application of each step within the DQOP whereas large, complex projects may require considerable time to work through the DQOP in more detail. Similarly, projects that involve safety issues where making a decision error could have serious consequences require a more rigorous DQOP. 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 DQOs. Included were "estimation-only" and "preliminary" DQO studies^(a).

The DQOP is an iterative process, and it is entirely appropriate that, if one step of the DQOP 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 DQOP 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 DQOP 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 PARCC terms. 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.

Data Quality Objectives Process (DQOP) - A total quality management (TQM) tool developed by the EPA to facilitate the planning of environmental data-collection activities. The DQOP 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 DQOP are the DQOs.

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

(a) Draft report entitled *TWRS Data Quality Objectives Implementation Guidance: Requirements, Content and Style Guide* by B. A. Pulsipher, D. Michael, D. Neptune, R. Ryt, 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-DQOP 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	

Project Plan Development—Steps Before Initiation of DQOP

Project Plan Development—DQOP 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 DQOP 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 partici-

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

pate in the DQOP. 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, appropriate individuals should be added to the DQOP 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 DQOP to go forward. If the project can be better defined in terms of multiple problems, the DQOP 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 DQOP 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 DQOP 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 DQOP should be described in detail and documented.

In addition to supporting the decision(s) to be made, the collected data may have secondary uses. 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 DQOP 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 DQOP 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 DQOP 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 DQOP 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 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 DQOP 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 DQOP 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 analyti-

cal methods or equipment, and/or with the planned number of samples, then the DQOP 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 DQOP team should look into initiating a pilot study to get better estimates of parameters that affect the decision to be made. The DQOP 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 needed to assess the quality of project data against DQOs
- the mechanism to draw together the DQOP team and renegotiate the DQOs, if it becomes necessary
- an operational decision rule.

The DQOP 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 DQOP 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 DQOP. 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 DQOP team members. This introduction should include a brief summary of the DQOP and the results of the process. It should contain a list of DQOP team members and participants, and it should provide dates when the DQOP was begun and completed.

Plan Purpose

The project plan should contain a purpose statement that documents details relating to the DQOP, 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 in 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 provide data required to perform an assessment of data quality and 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 DQOP and documented in the project plan. Project sample hold times should be established based on applicable requirements contained in pertinent requirements documents such as 40 CFR 261.4, Appendix 2 of 261.

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. If SOPs are

Data Management

proved by regulators such as Regional EPA Offices or state authorities are required for the project, these approvals should be obtained and documented. 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.

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/mileston 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).

Reference

U.S. Environmental Protection Agency (EPA). 1994. *Guidance for the Data Quality Objectives Process*. EPA/QA/G-4.

Further Reading

Blacker, S. M., and J. P. Maney. 1993. "The System DQO Planning Process," *Env. Testing Anal.*, 2(4):46-55.

U.S. Environmental Protection Agency (EPA). 1991. *Data Quality Objectives Process for Planning Environmental Data Collection Activities*. Draft, April 1991. Quality Assurance Management Staff, Office of Research and Development.

U.S. Environmental Protection Agency (EPA). 1992. *Characterizing Heterogeneous Wastes: Methods and Recommendations*, EPA/600/R-92/033. Office of Research & Development, Washington, DC.

U.S. Environmental Protection Agency (EPA). 1992a. *Superfund Accelerated Cleanup Model*. Office of Solid Waste and Emergency Response. Publication Number 9203.1-01.

U.S. Environmental Protection Agency (EPA). 1992b. *Guidance for Data Usability in Risk Assessment*. Office of Emergency and Remedial Response. Part:9283.7-09A.

U.S. Environmental Protection Agency (EPA). 1993. *Data Quality Objectives Process for Superfund*. EPA/540/G-93/071.

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

<u>Sample Types</u>	<u>Definition</u>	<u>Purpose</u>
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.

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)
-------------------	---	---

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 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	Thulium-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 high-efficiency particulate air (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)

- 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 (1000)	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 discrete 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

The following additional controls should apply to work in a laboratory fume hood.

Work with dispersible or potentially dispersible radioactive material in quantities greater than the limits for benchtop work should have additional containment.

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

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.

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

Radionuclide	Form	Allowable Quantity, Bq (μCi)
Tritium	Water vapor	3.7×10^5 (1×10^4)
	Powders	3×10^2 (8×10^{-3})
	Volatile liquids	3×10^3 (8×10^{-2})
	Normal liquids	3×10^4 (8×10^{-1})
^{90}Sr	All	3.7×10^4 (1)
	All	3×10^3 (8×10^{-2})
	Powders	1.48×10^1 (4×10^{-3})
	Volatile liquids	1.48×10^2 (4×10^{-4})
^{131}I	All	3×10^3 (8×10^{-2})
	All	3×10^4 (8×10^{-1})
	Powders	1.48×10^1 (4×10^{-3})
	Volatile liquids	1.48×10^2 (4×10^{-4})
^{239}Pu	Normal liquids	1.48×10^2 (4×10^{-4})
	Powders	1.48×10^1 (4×10^{-3})
	Volatile liquids	1.48×10^2 (4×10^{-4})
	Normal liquids	1.48×10^2 (4×10^{-4})

Table 4.4. Allowable Quantities of Radioactive Materials for Bench-Top Work

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 MBq (< 1 mCi)
II	¹³⁷ Ce ⁶⁰ Co ¹³¹ I ⁹⁰ Sr	< 3.7 GBq (< 100 mCi)
III	¹⁴ C ¹³² I ³² P ⁶⁵ Zn	< 370 GBq (< 10 Ci)
IV	³ H ⁸⁵ Kr Natural Th. Natural U	< 37 TBq (< 1000 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).

Table 4.6. Classes of Flammable and Combustible Liquids

Flashpoint °C (°F)	Class	Boiling Point	Category
Below 22.8 (73)	IA, IB	Below 37.8°C (100°F)	Flammable
22.8 (73) to 37.8 (100)	IC	Below 37.8°C (100°F)	Flammable
37.8 (100) to 60 (140)	II	Below 37.8°C (100°F)	Flammable
60 (140) to 93 (200)	IIIA	Below 37.8°C (100°F)	Combustible
Above 93 (200)	IIIB	Below 37.8°C (100°F)	Combustible

- 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 1984).

- 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 1A and 1B 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

Table 4.8. Maximum Storage Quantities for Flammable or Combustible Liquids			
Material	Class	Quantity, liters (gal)	
Flammable Liquid	IA	2.3 x 10 ² 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.
 - For all storage areas, ample ventilation should be provided to dissipate toxic or other hazardous vapors.
 - Acids and bases should be stored below eye level and away from heat and light.
 - Oxidizers should be stored separately from reducers.
- New shipments should be rotated with existing stock so the oldest stock is used first.
 - Finely divided metals should be stored outside or in other appropriate storage areas away from personnel and facilities (turnings and powders may be combustible and even explosive).
 - 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.
 - Oxidizers should be stored separately from reducers.

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/m³ 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-

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.

References

- 10 CFR 835. 1993. "Occupational Radiation Protection." U.S. Code of Federal Regulations.
- 29 CFR 1910. 1992. "Occupational Safety and Health Standards." U.S. Code of Federal Regulations.
- American National Standards Institute (ANSI). 1981. *American National Standard for Emergency Eye-wash and Shower Equipment*. ANSI Z358.1, New York.
- CRC Handbook of Radiation Measurement and Protection*. 1982. Section A, Volume 2. Biological and Mathematical Information. Boca Raton, Florida.
- National Fire Protection Association (NFPA). 1984. *National Electric Code*. NFPA 70, Quincy, Massachusetts.
- National Fire Protection Association (NFPA). 1991. *Manual of Hazardous Chemical Reactions*. NFPA No. 491M. Quincy, Massachusetts.
- U.S. Department of Energy (DOE). 1985. *Contractor Industrial Hygiene Program*. DOE Order 5480. Washington, DC.
- ## Further Reading
- Beavis, L. C., V. J. Harwood, and M. J. Thomas. 1979. *Vacuum Hazards Manual*. 2nd Edition, American Vacuum Society Monograph Series, Published by the American Institute of Physics, New York.
- Budavari, S., ed. 1989. *The Merck Index*. 11th Edition, Merck and Company, Inc., Rahway, New Jersey.
- Steere, N. V., ed. 1971. *CRC Handbook of Laboratory Safety*. 2nd Edition, CRC Press, Inc., Boca Raton, Florida.
- U.S. Department of Transportation, U. S. Coast Guard. 1970. *Bulk Liquid Cargoes: Guide to Compatibility of Chemicals*. NVIC 5-70.

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), project-driven DQOs, project budgets, or alternative methods may be available in this publication. Sometimes these methods are not appropriate for sampling or sample analysis (e.g., because of sample matrix incompatibilities). Then project-driven data quality objectives (DQOs) and project budgets should be used to select alternative methods through 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. Quality control data included in methods contained in *DOE Methods* should be used as aids in selecting methods that are appropriate for the project. Methods should be selected during the project data quality objectives process (DQOP)

(Chapter 1) and should meet project needs. Procedures in the database can be used for some applications, but caution should be exercised since procedures not represented in *DOE Methods* may not yet have 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.

To qualify as verified methods (Appendix A), analytical methods described in *DOE Methods* may be followed as written, or comparable methods can be substituted. The guidelines provided in Appendix B should be considered when deciding what activities are necessary to qualify methods for use.

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 add to the value 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 multiphase. Gas-phase samples will usually be delivered to the analytical laboratory 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 requirements can be acceptable substitutes. However, methods chosen for use in a project should meet project-driven DQOs. All methods, either selected from consensus standards, *DOE Methods*, or other sources, or newly developed or modified, should be appropriately qualified before being used (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

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.

References

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

	Solids	Liquids	Air
Drums 【SW010R】*	【SD010R】*	SA011*	SA010*
Tanks	ST010* 【ST011R】*	ST010* 【ST011R】*	
Facilities			【SQ010R】*

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

【SD010R】 【Collecting Samples from TRU Waste Drums Containing Solid Process Residues and Soils (Sludges)】

【SQ010R】 【Collection of Liquid Samples for Effluent Monitoring of Operations Facilities】

ST010 General Method for Sampling Liquids and Solids in Low-Level Waste Storage Tanks

【ST011R】 【General Method for Sampling Liquids and Solids in High-Level Waste Storage Tanks】

【SW010R】 【Core Samples in Cement Solidified Low-Level Liquid Waste】

Table 6.2. Organic Methods

	Field	Sample Prep	Lab. Analysis
Volatile	OS030 OS040* {OS060*}	OC010R OP010R* OP020R OP030R {OP040R*}	OG015R OP010R*
Semi-volatile	OS010 OS020 OS050*	OP100R OP120R OG100R OP130R* OP150R	OG100R OH100R OP100R OP130R*
Non-volatile		OP150R	{OM500R*} {OM510R*}
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
{OM500R}	{Qualitative Analysis for Low Molecular Weight Organic Acids in Mixed Hazardous Waste Samples by Thermospray LC-MS}
{OM510R}	{Determination of Chelators and their Degradation Products in Mixed Hazardous Waste Samples by Derivatization GC-MS}
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

Table 6.2. (Contd)

OP040R	Reduced-Scale Zero Headspace Extraction for TCLP Volatiles in Shielded or Containment Conditions
OP100R	PCBs in Aqueous Radioactive Mixed Wastes Using Solid Phase Extraction Disks and GC-ECD
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
OS060	Immunoassay for Petroleum Fuel Hydrocarbons in Soil

Table 6.3. Inorganic Methods

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

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

Screens	Field	Sample Prep. and Analysis
Alpha/Beta		RP710; RP720*
Tritium		RP720*
Gamma (gross)		RP730*
Actinides		RP725*, (RP735*)
Gamma (spec)	RS100	(RI010*)
<u>Chemical Separations</u>		
¹²⁹ I, ¹³¹ I		RP230
²¹⁰ Pb		RP280*
⁵⁹ Ni, ⁶³ Ni		RP300
^{93m} Nb, ⁹⁴ Nb		RP330*
(²²⁶ Ra)		(RP450*)
⁸⁹ Sr, ⁹⁰ Sr		RP500; RP501, RP510, RP520*
⁷⁹ Se		RP530
⁹⁹ Tc	RS551*	RP550
(Th)		(RP570*)
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*

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
RP4501	Determination of Radium-226 in Aqueous Samples
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
RP5701	Radiochemical Determination of Thorium Isotopes in Aqueous Samples
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	In Situ 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, environmental contamination/disposal scenarios (waste-disposal sites, dispersed contamination, drums, waste forms, and disposal options), and monitoring of facility waste streams.

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, 5) waste forms, and 6) facility waste streams. 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

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 ^g	
Veihmeyer sampler		X ^h	
Grab	X ^h	X ⁱ	
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 tool drilling/slurry sampling method	X ^{l,n}	X ^{l,n}	
SEAMIST TM	X ^{l,n}	X ^{l,n}	X ^o

- a See EPA 1984, EPA 1987, and EPA 1991 for guidance and/or descriptions of standard soil/sediment sampling methods
- b Most suitable for dry, granular, powdery materials
- c Works best in sticky or solid samples at >3 in. in depth
- d Collects undisturbed sample
- e Most suitable for granular material
- 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.
- g Collects samples through open water
- h Works best on stony, rocky, or very wet soil/sediment
- i Sample obtained manually using a cutter and trowel
- j Areas from which the samples are taken may be gridded/surveyed. Used also for sampling soils/solid wastes in drums.
- k Active sampling from soil probes into canisters, glass bulbs, and gas sampling bags. Passive sampling on to buried adsorptive substrates.
- l Used to retrieve radioactive samples from holes.
- m Collects undisturbed samples. Works best in intermediate moist soils.
- n Runs concurrently and is a preferred method for collecting radioactive samples.
- o *In situ* collection of soil gas from membrane-lined borehole.

should be considered to minimize the negative impacts of sampling and sample transport on data quality. Where this is not possible, techniques should be 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 SAO10 and SAO11 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. Aqueous liquid samples suspected of containing VOC should be sampled using 20 or 40 mL vials with a Teflon®-faced-silicone cap liner and no headspace. All samples held for organic analysis should be placed in amber or opaque containers to prevent photodecomposition.

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

Environmental 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

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 ^l	
Diaphragm		X ^k	
Siphon		X ^k	
Weighted bottle		X ^l	
Manifold (SUMMA TM cartridges)			X ^m
Direct canister (SUMMA TM cartridges)			X ⁿ
Bin headspace sampling system			X ^o
[Thin walled tube]	[X ^p]		
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.		
[p]	[A remotely operated coring device is used to collect samples in radioactive sludge from drums (see SO010R).]		

Table 7.3. Water Sampling^a

Samplers		Groundwater	Surface Water
Pumps			
Submersible		X ^b	
Hydrostar		X ^b	
Bladder		X ^b	
Teflon bailer		X ^{b,e}	
Miniaturized bailer		X ^c	
Air lift		X ^{c,d}	
Continuous filtration			X ^f
Automated composite			X ^g
Grab			X ^h
SEAMIST TM		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., 24 hr or 11-wk intervals (see SO010R))
 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

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 interest (e.g., ¹³¹I) 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).

Table 7.4. Air Sampling^a

	Material Types	
	Particulates	Air
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.
 Silica gel is used for collecting ³H.
 Soda lime is used for collecting ¹⁴C as CO₂.
 Silver zeolite is used for collecting radioiodine for emergency sampling.
 Cartridges are incorporated into the filter-head assembly.
^d Emergency sampling of particulates for radioactivity.
^e For collection of ⁸⁵Kr.

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

Table 7.5. Tank Sampling^a

Samplers	Material Types		
	Solids	Liquid	Gas
High-Level Wastes			
Thief and Trier Type Bottle on a String	X ^b	X ^c	
Cryogenic SUMMA™ Canisters	X ^e		X ^d
Sorbent Trap (Hydraulic scoop)	(X ^g)		X ^f
(Cylinder with retractable nose cone)	(X ^h)		
(Auger)	(X ⁱ)		
(Bacon Bomb)	(X ^j)		
Low-Level Wastes			
Vacuum Pump		(X ^k)	
Soft Sludge	(X ^l)	(X ^m)	
Hard Sludge	(X ⁿ)		
Organic Layer		(X ^p)	
Pump Module ("Isolock")		(X ^q)	

- 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); Gray 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 (Stainless steel vials) (100 to 1000 mL) are lowered into the tank to obtain liquid sample (see ST011R).
- 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 3L hydraulically operated scoop lowered into tank via a cable for sludge collection (see ST011R).
- h 25L cylindrical collector containing a retractable nose cone is lowered into tank to collect sludge samples (see ST011R).
- i Auger sampler mounted at bottom of sections of stainless steel pipe is lowered into tank to collect samples of salt cake (see ST011R).
- j Sampler used for variable depth sampling in tank (see ST011R).
- k 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).
- l A bottom opening (spring loaded) device capable of collecting a 1.5-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).
- m 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).
- n 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).
- o 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).
- p 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).
- q Pumps and sampling compartments (Isolock System) installed on tanks where there is no access through risers. Only liquid samples are collected.

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).

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 SAO10 and SAO11). 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.

Monitoring Facility Operations

DOE Order 5400.1 entitled "General Environmental Protection Programs" (DOE 1990a) requires that DOE-owned facilities with significant inventories of hazardous materials characterize and monitor their waste streams. The EPA Clean Air Act (EPA 1989) and the DOE Environmental Regulatory Guide (DOE 1991c) require monitoring for radionuclide emissions from DOE facilities. Responsibility for monitoring of chemical air emissions is being relegated to the states under Title III of EPA's Clean Air Act Amendment (EPA 1990). Facility waste streams in general consist of two components - process and retention process sewer waste waters and stack air emissions.

In addition to the above guidelines, process waste-waters may be treated and discharged to a public water supply under a National Pollutant Discharge Elimination System (NPDES) permit issued by the EPA or the state. The content of the permit is negotiated by interested parties and addresses radiological, chemical, and biological discharge limits relevant to the specific operation. Waste waters that exceed radiological limits are disposed of by alternate means (e.g., discharged to a controlled radioactive waste site).

Sampling of liquid waste streams consists of the collection of grab samples and/or composite (e.g., collected over a 24-h time period) samples. Samples are transported to the laboratory under chain-of-custody protocols and analyzed using standard methods taking into account radiological screening requirements. Continuous monitoring of pH, conductivity and flow of the waste streams are also conducted. Programs for monitoring of hazardous chemical air emissions from facilities are under develop-

ment at DOE sites based on EPA implementing a source category schedule under section 112 Title II of the Clean Air Act Amendment (Federal Register 1992). In general, sampling methods used for the conduct of air sampling follow those approaches described in Table 7.4 as a starting point.

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 re-

quire 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 1990b).

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.

References

40 CFR 136. 1991. U.S. Environmental Protection Agency (EPA). "Appendix A." U.S. Code of Federal Regulations.

49 CFR 173. 1992. U.S. Department of Transportation. "Shippers—General Requirement for Shipments and Packagings." U.S. Code of Federal Regulations.

Annual Book of ASTM Standards. 1993. Volumes 04.08, 11.01, 11.02, 11.03, 11.04 and 12.01. American Society for Testing and Materials, Philadelphia, Pennsylvania.

Gray, P. L., V. L. Skidmore, T. K. Bragg, and T. Kerrigan. 1994. Sampling of Content of High-level Waste Tanks. In: Waste Management '94 Proceedings, Volume 1.

Greensburg, A. E., L. S. Clesceri, and A. D. Eaton, eds. 1992. *Standard Methods for the Examination of Water and Wastewater*. American Public Health Association, 18th Ed, Washington, DC.

Hill, J. G., W. I. Winters, B. C. Simpson, J. W. Buck, P. J. Chamberlain, and V. L. Hunter. 1991. *Waste Characterization Plan for the Hanford Site Single-Shell Tanks, Appendix I-Test Plan for Sampling and Analysis of Ten Single-Shell Tanks*. WHC-EP-0210, Rev. 3. Westinghouse Hanford Company, Richland, Washington.

Ligotke, M. W., T. R. Clauss, J. S. Fruchter, R. B. Lucke, G. W. Dennis, G. M. Mong, R. E. Hohimer, M. McCulloch, M. T. Dana, and S. C. Goheen. 1993. *Aerosol and Vapor Characterization of Tank 241-C-103: Data Report for In-Tank OVS Samples Obtained 12/2/93*. PNL-9368. Pacific Northwest Laboratory, Richland, Washington.

Ligotke, M. W., T. R. Clauss, J. L. Huckaby, G. W. Dennis, R. B. Lucke, and S. C. Goheen. 1993. *Aerosol and Vapor Characterization of Tank 241-C-103: Flammability Assessment Sampling System, and Method Validation*. PNL-8875. Pacific Northwest Laboratory, Richland, Washington.

Lewis, T. E., A. B. Crockett, R. L. Siegrist, and K. Zarrabi. 1991. *Soil Sampling and Analysis for Volatile Organic Compounds*. EPA/540/4-91/001. U. S. Environmental Protection Agency, EMSL-LV, Las Vegas, Nevada.

Pope, R. B., L. G. Blalock, and M. J. Conroy. 1993. *The Challenge of Packaging and Transporting Mixed Waste Samples and Residues Arising from the Department of Energy's Analytical Services Program*. CONF-930873-26, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Sears, M. B., J. L. Botts, R. N. Ceo, J. J. Ferrada, W. H. Griest, J. M. Keller, and R. L. Schenley. 1990. *Sampling and Analysis of Radioactive Liquid Wastes and Sludges in the Melton Valley and Evaporation Facility Storage Tanks at ORNL*. ORNL/TM-11652. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

U.S. Department of Energy (DOE). 1990a. *General Environmental Protection Program Requirements*. Order 5400.1 (6-29-90).

U.S. Department of Energy (DOE). 1990b. *Radiation Protection of the Public and the Environment*. Order 5400.5 (2-8-90). (is this referenced)

U.S. Department of Energy (DOE). 1991a. *Waste Characterization Program Sampling and Analysis Guidance Manual*. DOE/WIPP 91-016, Rev. 1, Idaho Falls, Idaho

U.S. Department of Energy (DOE). 1991b. *Vapor Space Sampling of Ferrocyanide Tanks*. DOE/EA-0533. Office of Environmental Restoration and Waste Management, Washington, DC.

U.S. Department of Energy (DOE). 1991c. *Environmental Regulatory Guide for Radiological Effluent Monitoring and Environmental Surveillance*. DOE/EH-0173T. Office of Environmental Restoration and Waste Management, Washington, DC.

U.S. Environmental Protection Agency (EPA). 1984. *Characterization of Hazardous Waste Sites-A Methods Manual: Volume 2*. Available Sampling Methods, 2nd Edition. EPA-600/4-84-076. U.S. EPA Environmental Monitoring System Laboratory, Las Vegas, Nevada.

U.S. Environmental Protection Agency (EPA). 1986. *Test Methods for Evaluating Solid Waste: Volume 2, 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.

U.S. Environmental Protection Agency (EPA). 1987. *Compendium of Superfund Field Operations Methods*, Washington, DC.

U.S. Environmental Protection Agency (EPA). 1989. *National Emission Standards for Hazardous Air Pollutants; Radionuclides; Final Rule and Notice of Reconsideration*. 40 CFR Part 61, Federal Register 54 (240): 51654-51715.

U.S. Environmental Protection Agency (EPA). 1990. Clean Air Act Amendments, CQ 3934. Washington, DC.

U.S. Environmental Protection Agency (EPA). 1991. *Description and Sampling of Contaminated Soils. A Field Pocket Guide*. EPA/625/12-91-002. U. S. EPA Center for Environmental Research Information, Cincinnati, Ohio.

Winters, W. I., L. Jensen, L. M. Sasaki, R. L. Weiss, J. F. Keller, A. J. Schmidt, and M. G. Woodruff. 1990. *Waste Characterization Plan for the Hanford Site Single-Shell Tanks*. WHC-EP-0210, Rev. 1. Westinghouse Hanford Company, Richland, Washington.

57 Federal Register 31, 576 (1992)

Table 7.6. Methods for Sampling Waste and Environmental Media

Method Number	Title	Summary
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. [Method performance data is included.]
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. [Method performance data is included.]
【SD010R】	【Collecting Samples from TRU Waste Drums Containing Solid Process Residues and Soils (Sludges)】	【Guidance is provided for collecting sludge samples contained in a containment area (e.g., glovebox) using drilling equipment, coring tools, and sample collection equipment. Method performance data is included.】
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.
【ST011R】	【General Method for Sampling Liquids and Solids in High-Level Waste Storage Tanks】	【Guidance is provided for several different sampling devices for collecting liquids (i.e., dip or bacon-bomb samplers), sludges (i.e., hydraulically operated scoop or cylinder with retractable nose cone) and saltcake (i.e., auger).】
【SO010R】	【Collection of Liquid Samples for Effluent Monitoring of Operations Facilities】	【Guidance is provided for collection of process and retention process sewer waste waters for chemical and radiological analysis. Method performance data is included.】

Table 7.6. Contd

<u>Method Number</u>	<u>Title</u>	<u>Summary</u>
【SW010R】	【Core Samples in Cement Solidified Low- Level Liquid Waste】	【Core samples are obtained from square drums containing cemented liquid radioactive wastes. Samples are used for physical tests, chemical analyses, and determination of long-term stability of the waste.】

SD010R^(a)

Collecting Samples from TRU Waste Drums Containing Solid Process Residues and Soils (Sludge)

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 Much of the transuranic (TRU) waste in storage at U.S. Department of Energy (DOE) generator/storage sites is stored in 208-L (55-gal) drums and classified as "solid process residues and soils" (DOE 1994). The physical properties of these wastes are described in Table 1. The DOE plans to dispose of these wastes in the Waste Isolation Pilot Plant near Carlsbad, New Mexico. However, before disposal, the wastes must be characterized to satisfy the Resource Conservation and Recovery Act's land disposal restrictions (40 CFR 268), and general waste analysis requirements (40 CFR 270).
- 1.2 This method may be used to collect samples from 208-L (55-gal) drums of TRU waste classified as "solid process residues and soils" (DOE 1994). Although the primary focus of this method is on 208-L (55-gal) drums, it may also be used to collect samples of TRU waste from smaller containers (e.g., 3.8-L polyethylene bottles) stored in 208-L (55-gal) drums.
- 1.3 For the purposes of this method, "solid process residues and soils" are referred to as "sludge."
- 1.4 This method is applicable to characterizing a sludge on a "waste-stream" basis rather than an "individual-drum" basis. This is because the samples are collected from one randomly selected location within the sludge that may, or may not, be homogenous with the sludge in other areas of the drum.

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

DRAFT

1.5.1 If the sludge is not known to be homogeneous in the horizontal plane, the horizontal variability should be estimated by collecting a core from each of three randomly selected locations.

Note: Guidance for coring and sampling on an individual-drum basis is provided in section 8.8.

1.5 Individuals wishing to characterize the sludge on an individual-drum basis should modify this method in accordance with the following considerations:

Table 1. Description of Waste Physical Properties ^(a)	
Solid Process Residues and Soils	Description
Inorganic Waste-Water Treatment Sludge	Soft ferric-hydroxide sludge packed with cement on top and bottom, packed as alternating layer of sludge and cement, or as a hard mixture of sludge and cement
Organic Liquid and Sludge	Soft sludge formed by mixing oil and grease with calcium silicate packed with adsorbent on top and bottom or as alternating layers of adsorbent and sludge
Solidified Liquid	Hard, brittle sludge formed by mixing alkaline aqueous waste water with Portland and magnesia cement
Cation and Anion Exchange Resins	A slurry of ion-exchange resins mixed with cement to form a hard-cement matrix that immobilizes the resins
Pyrochemical Salts	Solid crystalline waste salts from a molten salt extraction process
Soils	Contaminated soil generated from cleanup of spills, decontamination and decommissioning activities
(a)	Summarized from the Waste Isolation Pilot Plant Transuranic Waste Baseline Inventory Report, CAO-94-1005, U. S. Department of Energy, Carlsbad Area Office, Carlsbad, New Mexico, 1994

1.5.2 If the sludge is not known to be homogenous in the vertical plane, the sample from each core should be collected using splitting or homogenizing techniques such that it is representative of the core.

1.6 A waste stream is a waste material generated from a single process or activity; the entire stream is similar in material, physical form, isotopic make-up, and hazardous constituents^(a). To adequately characterize a waste stream, several drums in that waste stream must be sampled. The requirements for drum selection and sludge characterization are described in DOE's TRU Waste Characterization Quality Assurance Program Plan (QAPP)^(a).

2.0 Summary of the Method

- 2.1 The procedures in this method are based on sampling methods similar to those approved by U.S. Environmental Protection Agency (EPA) for solid waste and soil sampling contained in SW-846 (EPA 1992a), "Standard Practice for Thin-Walled Tube Sampling of Soils" (ASTM 1983) and "Standard Practice for sampling Waste and Soils for Volatile Organic Compounds" (ASTM 1991).
- 2.2 This method requires drilling equipment, coring tools, and sample-collection equipment. This equipment is designed to provide laboratories the minimum amount of required sample. This minimizes the quantity of sample requiring transport to a laboratory and minimizes the quantity of investigation-derived waste. The quantities of sludge required for analysis and the sample handling requirements are listed in Table 2.
- 2.3 The drum lid and inner-liner lid (if present) are removed, and the surface of the sludge is exposed. The sludge is tested for hardness to determine the type of coring tool required. A non-rotational coring tool is used to core soft sludges, and a rotational coring tool is used when the sludge is too hard for penetration with the non-rotational coring tool. Before use, each coring tool must be lined inside with eight removable transparent liners to contain the sludge.
- 2.4 As presented in Figure 1, the coring tool is mounted vertically above the drum and pressed or drilled to the bottom of the sludge at a coring location randomly selected on the sludge's surface.
- 2.5 The coring tool is removed from the sludge, and the transparent liners containing the core are extruded from the coring tool. The sludge is visually examined for evidence of non-homogeneity (e.g., stratification) and disturbance due to coring; then its length is.

(a) Draft DOE document entitled *TRU Waste Characterization Quality Assurance Program Plan*, Rev. B. National TRU Program Office, Carlsbad Area Office, Carlsbad, New Mexico (1994).

DRAFT

Table 2. Sample Handling Requirements				
Analysis	Minimum Quantity Required	Preservative	Container	Holding Time (a)
Volatle Organic Compounds	15 g	Cool to 4°C	40 mL vial (b)	14 days Prep/ 40 days analyze (c)
Semi-Volatile Organic Compounds	50 g	Cool to 4°C	250 mL jar (d)	14 days Prep/ 40 days analyze
Polychlorinated Biphenyls	50 g	Cool to 4°C	250 mL jar (d)	14 days Prep/ 40 days analyze
Metals	10 g	Cool to 4°C	250 mL jar (d)	180 days
(a) Holding time begins when the sample has been placed in the sample container. (b) 40-mL glass vial with a septum cap or adapter cap that allows vial to be directly connected to the analytical instrument without removing the cap. (c) 40-day holding time allowable only for methanol extract. (d) 250-mL (8 oz) wide-mouth glass jar with Teflon® lined cap.				

measured. The core's length is then compared to the depth of the borehole to determine % recovery, which must be 50% or greater.

2.6

A location from which to collect samples is randomly selected along the length of the core, and the liner at this location is separated from the other liners to expose the sludge.

2.7

If the exposed sludge is soft, the specified weight of sludge (see Table 2) is immediately collected, using a modified (with its tip removed) plastic syringe, and sealed in a vial for volatile organic compound (VOC) analysis. Specified weights of sludge for semi-VOC and metals analyses (see Table 2) are also collected from this location with the syringe or a scoop, and the sludge is placed in sample jars.

2.8

If the sludge is hard, the core is removed from the liner and broken into pieces, and the pieces are placed in sample containers to meet the specified weights and handling requirements (see Table 2).

Figure 1. Core and Sample-Collection Scheme

3.0 Limitations and Interferences

3.1 Limitations

This method is performed in accordance with the following limitations:

- 3.1.1 Coring and sample-collection activities must be conducted in a containment area (e.g., glovebox).
- 3.1.2 Liquids are not allowed in the containment area.

3.2 Interferences

- 3.2.1 The parts of the coring tool that come in contact with the sludge (e.g., cutting edge of the auger) have the potential to contaminate the surface of the core with metals such as nickel, chromium, and lead (metals commonly found in coring tool components), especially through abrasion of the coring tool when coring hard sludges. To minimize or eliminate this potential interference, individuals should

- use a plastic basket retainer instead of a spring-steel basket retainer

Note: It is recommended that the basket retainer not be used when it is relatively certain that the core will not fall out as it is removed from the drum.

- design the coring tool such that the liners are placed as close as possible to the tool's leading edge
 - collect the sludge sample (for metals analysis) from an area of the core that did not contact the coring tool (i.e., the longitudinal center of the core)
- 3.2.2 The polycarbonate liners specified in this method have the potential to contaminate the core with organic compounds, such as methylene chloride and chlorobenzene, when the sludge contains solvents. To minimize or eliminate this potential interference, individuals should
 - assess the potential for the liners to leach compounds that are on the list of analytes, especially in the presence of solvents
 - use liners made from relatively inert material, such as Teflon® or glass.

Note: Translucent Teflon[®] piping with a 5-cm (2-in.) outer diameter and 1.6-mm (0.063-in.) wall thickness may require a special order.

3.2.3 Additional information regarding these potential interferences can be found in the *Idaho National Engineering Laboratory Simulated Transuranic Waste Sampling Program* (Connolly 1994).

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 Chapter 3.0 and 4.0 for a complete discussion of these issues.

5.0 Apparatus and Materials

The apparatus and materials necessary for coring and sampling TRU waste drums containing sludge consists of drilling equipment, coring tools, sampling tools, and sample containers. These are described below.

5.1 Drilling Equipment

- 5.1.1 It is not the intent of this method to provide detailed specifications for the drilling equipment necessary for core collection. The facilities are expected to differ between sites designated to conduct coring and sampling activities, and these differences will dictate the types and configuration of required equipment.
- 5.1.2 It is expected that eight major components of drilling equipment will be necessary to collect representative cores of the sludge. These components include a feed frame, rotation unit, slide frame, coring-tool guide, power pack, control unit, drilling platform, and drum platform. The purpose of each component is described in Table 3.
- 5.1.3 Figure 2 provides a conceptual configuration for a hydraulically powered drilling system arranged for core collection inside a containment area. As shown, the slide frame, feed frame, rotation unit, and coring tool guide are operated inside the containment area. The power pack, control panel, and drum platform are outside of the containment area. A manipulator arm in the containment area facilitates coring operations and allows areas not accessible by glove ports to be reached.

DRAFT

5.2 Non-Rotational Coring Tool

5.2.1

The non-rotational coring tool, found in Standard Practice for Thin-Walled Sampling of Soils (ASTM 1983), is used to collect a representative core of soft sludge. As presented in Figure 3, it consists of a stainless steel ball check valve and a stainless steel core barrel. The liners and basket retainer described in section 5.4 fit inside the non-rotational coring tool.

Table 3. Major Components of Drilling Equipment		Component Name	Purpose
	Feed Frame	Applies downward (push) and upward (pull) forces to the coring tool. It has a minimum feed length of 122 cm (48 in.) and should be equipped with an adjustable mechanism to limit travel distance up and down. It is capable of applying a minimum force of 4448 N (1000 lb).	
	Rotation Unit	Applies clockwise and counterclockwise rotation to the rotational coring tool. It can be operated at variable speeds up to 1,000 rpm. It is capable of supplying a minimum of 54.24 Nm (40 ft lb) torque.	
	Slide Frame	Permits the feed frame/coring tool to be moved and locked in position over the horizontal centerline of the drum, or pushed back out of the way.	
	Coring Tool Guide	Provides lateral support to the coring tool to prevent the coring tool from "walking" during rotational coring activities.	
	Power Pack	Provides the power necessary to drive the rotational unit and feed frame.	
	Control Unit	Provides the drill operator with the ability to control and monitor the forces required to position, push, pull, and rotate the coring tool. It allows the operator to control the speed and direction of the rotation unit, control the forces of the feed frame, and energize and shutdown the power pack. The control panel does not provide rotational speeds. The rotational speeds are measured with a hand-held tachometer. The control panel does not operate the feed-frame tilt mechanism. This is done manually.	
	Drilling Platform	Supports the feed frame and rotation unit above the drum.	
	Drum Platform	Supports and braces the drum to prevent movement during coring activities.

Figure 2. Conceptual Configuration of Drilling Equipment

DRAFT

OD - Outer Diameter

ID - Inner Diameter

All numerical values are approximate.

Figure 3. Non-Rotational Coring Tool

- 5.2.2 The non-rotational coring tool is designed such that the tool's kerf width is minimized. Kerf width is defined as one-half of the difference between the outer diameter of the tool and the inner diameter of the tool's inlet. This minimizes resistance as the tool is pressed into the sludge and enhances core recovery.
- 5.2.3 The ball check valve allows air to escape from inside the liners as the tool is pressed into the sludge. The ball check valve also provides a relatively air tight seal above the sludge to help prevent the sludge from slipping out of the liners when the tool is withdrawn from the drum.
- 5.2.4 The core barrel is sharpened and tapered at its leading edge to an inner diameter slightly smaller than the inner diameter of the liners that line its interior. This tapering prevents the liners from falling out, and the sharpening enhances the core barrel's ability to penetrate the sludge. The core barrel is constructed to allow placement of the liner's leading edge as close as possible to the core barrel's leading edge. This minimizes the core's contact with stainless steel and minimizes the surface area that must be cleaned (wiped) before reuse.

5.3 Rotational Coring Tool

- 5.3.1 The rotational coring tool, presented in Figure 4, is used primarily to collect samples from hard sludge. It may also be used for coring softer sludges. The rotational coring tool is designed to minimize disturbance to the core by containing the core inside an inner core barrel that remains stationary as the auger is rotated and pressed into the sludge.
- 5.3.2 Its design permits placement of the liners and basket retainer, described in section 5.4, as close as possible to the coring tool's leading edge. This minimizes the core's contact with the metal parts of the tool.
- 5.3.3 Thin flights, made from a 3 mm (0.125 in.) square rod, are spiraled up and around the outside of an 84-cm (33-in.)-long auger. They lift the sludge cuttings from the borehole as the auger is pressed and rotated into the sludge.
- 5.3.4 The leading edge of the auger is sharpened and tapered to a diameter slightly smaller than the inner diameter of the liners. The flights protrude slightly below this edge where they are hardened and sharpened for cutting the sludge.
- 5.3.5 The inner core barrel, which is equivalent to a non-rotational coring tool without a tapered leading edge, holds the liners inside with a core-barrel tip (tapped into place). This facilitates placement and removal of the liners and basket retainer.

DRAFT

Item	Component Name	Length (cm)	OD (cm)	ID (cm)	No. of Flights	Flight Width (cm)	Weight (kg)	Kerf Width (cm)
1	Drill Rod	—	4.44	—	—	—	—	—
2	Thrust Bearing Ball Check Valve	23	6.032	—	—	—	3	—
3	Liners	81	5.080	4.762	—	—	—	0.160
4	Core Barrel	86	5.398	5.080	—	—	1.4	0.160
5	Basket Retainer (optional)	0.318	5.1	4.508	—	—	—	0.287
6	Core Barrel Tip	2.54	5.398	4.508	—	—	—	0.494
7	Auger and Pin	94	6.032	5.715	8	.318	3	0.160
Total		104	6.032	4.508	8	.318	7	0.762

OD - Outer Diameter

ID - Inner Diameter

All numerical values are approximate.

Figure 4. Rotational Coring Tool

- 5.3.6 The assembled coring tool is secured to the drill rod with a pin. A key and screws hold the auger to the thrust bearing/ball check valve.
- 5.3.7 The thrust-bearing ball check valve prevents the core barrel from rotating with the auger and provides a vent to release the air inside the liners as sludge is pushed up inside. The ball check valve also provides a relatively air tight seal above the sludge to help prevent it from slipping out of the liners when the tool is withdrawn from the drum.

5.4 Common Components

Three components are common to the coring tools. These include liners to contain the sludge, a basket retainer to prevent the sludge from dropping out of the coring tool when it is withdrawn from the drum, and an extruder to remove the liners from the coring tool, when necessary. These components are described below.

5.4.1 Liners

- 5.4.1.1 The liners are constructed of rigid clear (transparent) polycarbonate. The liner's transparency allows visual examination of the core after sampling.

Note: Teflon® or glass may be used in place of polycarbonate; however, the effectiveness of visually examining the sludge through Teflon®, which is generally not as transparent as polycarbonate, may be reduced. Metal liners (e.g., stainless steel, brass) may be used if the sludge is not going to be analyzed for metals content.

- 5.4.1.2 The liner's outer diameter is 5 cm (2 in.). The liner's wall thickness is 1.6 mm (0.0625 in.).
- 5.4.1.3 Before cleaning, as described in section 9.3, and use, each liner is cut to a length of 10 cm (4 in.). Several liners are also cut with the width of the basket retainer subtracted from the length.
- 5.4.1.4 Plastic or Teflon® end caps should be placed over the ends of the liners if a substantial delay is necessary (>60 min) between core recovery and sample collection. If the liners are to remain inside the core barrel during the delay, then end caps should be placed over the exposed ends of the core barrel. End caps should fit tight.

5.4.2 Basket Retainer

- 5.4.2.1 A basket retainer is used with each coring tool when the physical properties of the waste are such that the waste may fall out of the liners and back into the drum when the coring tool is removed from sludge.
- 5.4.2.2 Basket retainers are made from either metal or plastic. Each has very thin flexible flaps made from spring steel or plastic. The flaps are attached to a ring with an outer diameter of 5 cm (2 in.) and an inner diameter of 4.8 cm (1.875 in.). The ring is made of stainless steel or plastic.
- 5.4.2.3 The basket retainer is placed inside at the leading tip of the coring tool in front of the liners. As the coring tool is pressed into the sludge, the sludge pushes the spring steel, or plastic, flaps up against the inside wall of the first liner. When the coring tool is withdrawn from the drum, the force created by pulling pulls the flaps closed, which cuts the sludge and seals the inlet to prevent the sludge from falling back into the drum.

5.4.3 Extruder

- 5.4.3.1 An extruder may be necessary to force the liners from the inside of the tool if they do not slide freely. Whether this device is needed depends on how tightly the liners fit inside the coring tool and how much sludge may have wedged between the liners and the coring tool.
- 5.4.3.2 The extruder for use with the rotational coring tool is made of stainless steel. It is approximately 76 cm (30 in.) long with a 5-cm (2-in.)-diameter piston-shaped head.
- 5.4.3.3 The extruder for use with the non-rotational coring tool is made of stainless steel approximately 84 cm (33 in.) long with a 4.5-cm (1.77-in.)-diameter piston-shaped head. A flexible ring fits in a slot that is machined near the leading edge of the head. The ring is compressed for insertion through the leading edge of the non-rotational coring tool. Once through, the ring expands to approximately 5 cm (2 in.) diameter to push against the basket retainer and liners.

5.5 Sampling Tools

Small disposable tools are used to sample cores for waste characterization on a waste-stream basis. The intent is to minimize equipment costs and the quantity of investigation-derived waste. Additional sampling tools (e.g., mixer, bowls) are necessary for waste characterization on an individual-drum basis. Sample-collection tools and their respective uses for waste characterization on an individual-drum or waste-stream basis are described in Table 4.

5.6 Sample Containers

Sample containers are described in Table 3.

6.0 Preplanning

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

7.0 Reagents, Preservation Measures and Handling

Handling requirements for sludge samples must conform to the specified sample quantities, containers, preservation measures, and holding times listed in Table 2. The sample quantities provided are the approximate amounts to be collected for each parameter. If other parameters are to be measured, the method should be reviewed, and the laboratory conducting the analysis should be consulted to determine the proper sample size.

8.0 Method

8.1 Pre-Coring Preparations

8.1.1 The identification of the waste drum selected for sampling is recorded, and the height of the drum (X_1) is measured and recorded on the Field Log Sheet presented in Figure 5. The drum is positioned underneath the containment area and sealed (bagged in) to an opening in the containment area floor. Once the drum is braced inside the containment area and secured to the drum platform, the drum's lid is removed.

Note: Headspace gas-sample collection in accordance with requirements specified in the QAPP (see footnote a, p. SD010R-3) may be necessary before removing the drum lid.

Table 4. Sample Collection Tools

Sampling Tool Description	Use Soft Sludges	Use Hard Sludges
Syringe ^(a) , 10 cc capacity, high-density polyethylene with tip removed.	Collect samples for VOC, semi-VOC, and metals analyses.	Not used.
Lab scoop, stainless steel, 16.5 cm (6.5 in.) long.	Collect samples for semi-VOC and metals analyses.	Scrape longitudinally down length of core to collect samples for semi-VOC and metals analyses.
Lab scoop, high density polyethylene, 16.5 cm (6.5 in.) long.	Collect samples for semi-VOC and metals analyses.	Not used.
Preparation knife ^(b) , hardened steel, overall length 25 cm (10 in.), blade length 15 cm (6 in.).	Split (slice) core longitudinally before homogenization and/or sample collection.	Scrape longitudinally down length of core to collect samples for semi-VOC and metals analyses.
Mixer ^(b) , typical cake mixer, 600 watt, 3.8-L glass or high-density polyethylene bowl, beater blades.	Homogenize entire core or split of core before sample collection.	Not used.
Mortar and Pestle ^(b) , 1 L (32 oz) clear, heavy, flint glass.	Not used.	Pulverize and mix core, or pieces of core, before sample collection.
Hammer, carpenter's steel.	Not used.	Shatter core into pieces before sample collection.
Chisel, hardened steel, 2.5-cm (1-in.) blade.	Not used.	Shatter core into pieces before sample collection.
Forceps, plastic or stainless steel.	Not used.	Transfer pieces of core to sample container.
Bags, tubular polyester film, 24 cm (9.5 in.) wide, 4.5 mil thick.	Not used.	Contain pieces of core during shattering process.
Film, disposable plastic or Teflon™.	Drop cloth to contain and remove sludge debris.	Drop cloth to contain and remove sludge debris.
Balance, top loading, readability 0.1 g, weighing capacity 6000g.	Measure the quantity of sample required by the lab.	Measure the quantity of sample required by the lab.

(a) Clear high-density plastic syringe with a 10-cc volume available through laboratory suppliers. Luer-Lok™ tip and plunger with rubber stopper. OD approximately 1.6 cm. Graduations are marked every 0.2 cc of volume. The syringe is modified by removing the Luer-Lok™ tip with a razor blade and sharpening the syringe's leading edge with a file. In addition, the plunger's rubber tip and holding post are removed, allowing free movement of the plunger inside the barrel.

(b) This tool is necessary only when sampling on an individual-drum basis.

DRAFT

Sampling

FIELD LOG SHEET

Location: _____ Begin Time: _____
Date: _____ End Time: _____
Drum ID: _____ Sampling Personnel: _____

$$X_4 = X_1 - X_2 - X_3$$

X₁: _____
X₂: _____ X₄ = _____
X₃: _____ Feed frame stroke setting: _____
where X₁ = height of drum
X₂ = distance from top of drum (rim) to surface of sludge
X₃ = 5 cm (2 in.) estimated distance from bottom of sludge to bottom of drum
X₄ = estimated depth of sludge and the stroke length that which the feed frame is set

Coring Information

Core distance from perimeter of sludge: _____

Sludge hardness: soft 1 2 3 4 5 6 7 8 9 10 hard

Item Description/QC Batch Number(s)	Item Description/QC Batch Number(s)
Coring tool	
Liners	

Borehold depth: _____

Visual observations of core: _____

Comments: _____

Sample Collection Information

Length of core: _____

Recovery: _____ %

Sampling location (distance from leading edge of first sleeve): _____

Item Description/QC Batch Number(s)	Item Description/QC Batch Number(s)
Coring tool	
Liners	

Comments: _____

Analysis	Container/QC Batch Number	Weight (g)	Identification
VOCs			
Semi-VOCs			
PCBs			
Metals			

Comments: _____

Figure 5. Example Field Log Sheet

8.1.2 The lid of the drum's inner liner, if present, is also removed along with packaging materials (e.g., vermiculite) to expose the surface of the sludge. The distance from the top of the drum (rim) to the surface of the sludge (X_2) is measured and recorded on the Field Log Sheet. The depth of the sludge (X_4) is then estimated as indicated on the Field Log Sheet.

8.1.3 A coring location is selected along the centerline of the drum. This location is selected by measuring the diameter of the sludge in centimeters and randomly selecting a number between 5 cm and the diameter of the sludge minus 5 cm. This location is recorded, and the feed frame is moved horizontally along the slide frame until the drill rod is directly above this location. The feed frame is then secured to the slide frame.

8.1.4 The sludge is tested for hardness by placing the sharp edge of a chisel or metal punch on the surface of the exposed sludge and striking it with a hammer. Alternately, a sharp object is attached to the drill rod, and the feed frame is advanced to press the sharp object into the sludge.

Note: Process knowledge indicates a hardened layer of cement may be present on the surface of the sludge in many of the TRU waste drums. With pressure from a sharp object, this layer should fracture, if present.

8.1.5 Segments of fractured cement that may obstruct core collection are removed from underneath the coring tool before continuing. The hardness determination is recorded on the Field Log Sheet.

8.1.6 Based on the hardness of the sludge, the appropriate coring tool is selected. The tool and its protective covering are visually inspected for cleanliness. If confirmed clean and in good condition, the tool is removed from its protective covering and mounted to the drill rod held secure by the rotation unit. The coring tool's quality control (QC) batch number is recorded on the Field Log Sheet. The protective covering is discarded.

8.2 Collecting a Core of Soft Sludge

8.2.1 If the sludge is determined to be soft, the non-rotational coring tool is selected and connected to the drilling rod. The leading edge of the coring tool is lowered until it touches the surface of the sludge. The feed frame is then adjusted to deliver a stroke no greater than the depth of the sludge (X_4).

Note: This is a safety mechanism to ensure that the coring tool is not punched through the bottom of the drum or drum liner, if present.

8.2.2 The non-rotational coring tool is pressed into the sludge using a steady, continuous stroke. The feed-frame pressure is monitored during the stroke, which should require no more than 10 sec to complete. The stroke is complete when one of the following conditions has been met:

- The pre-set stroke length has been achieved.
- The feed frame is near the pre-set stroke length, and the coring tool has encountered a hard layer halting its advancement.

Note: Process knowledge indicates that a hardened layer of cement may be present at the bottom of the sludge in many of the TRU waste drums.

8.2.3 The length of the feed-frame stroke is measured and recorded on the Field Log Sheet as the "borehole depth."

8.2.4 Slow, clockwise rotation (approximately 30 rpm) is applied to the coring tool, the feed frame is reversed, and the coring tool is slowly removed from the sludge.

Note: It is recommended that clean rags be used to remove sludge from the tool's outer surface as it emerges from the sludge. This will assist in maintaining a clean work area and reducing the potential for cross contamination if this coring tool is reused.

8.2.5 The core barrel containing the core is detached from the ball check valve. At this point, the entire core may be sent to the sample-collection area for sampling in accordance with section 8.6 if an end cap is sealed to each end. Individuals wishing to reduce the quantity of sludge requiring transfer to the sample-collection area may implement, in the drilling area, the procedures described in section 8.5.

8.3 Collecting a Core of Hard Sludge

8.3.1 If the sludge is determined to be hard, the rotational coring tool is selected and connected to the drilling rod. The leading edge of the coring tool is lowered until it touches the surface of the sludge. The feed frame is then adjusted to deliver a stroke no greater than the depth of the sludge (X_4).

Note: This is a safety mechanism to ensure that the coring tool is not drilled through the bottom of the drum or drum liner, if present.

- 8.3.2 A constant clockwise rotation of 300 to 600 rpm is applied to the coring tool, and sufficient pressure is applied with the feed frame to complete the stroke as quickly as possible without compromising the structural integrity of the drum, drilling equipment, and containment area.

Note: The results of the Idaho National Engineering Laboratory Simulated Solidified Transuranic Waste Sampling Program (Connolly 1994) indicate that rapid coring of hard sludge minimizes heat generation and subsequent transfer of heat to the core. Heating the core is not desirable in that it cause target analytes to evaporate and escape during coring.

- 8.3.3 Rotational speed is reduced, if necessary, to control the generation of visible dust.

- 8.3.4 The stroke should require no more than 60 sec to complete. The feed-frame pressure, rotational speed, and torque are monitored during the stroke, and the stroke is complete when the hardness of the sludge prevents the coring tool from advancing or when the pre-set stroke length has been achieved.

- 8.3.5 The length of the feed-frame stroke is measured and recorded on the Field Log Sheet as the "borehole depth."

- 8.3.6 The pin connecting the auger to the thrust bearing-ball check valve is removed and, using the feed frame, the core barrel is lifted from the auger.

Note: As the core barrel is lifted from the auger, it is recommended that clean rags be used to remove any sludge visible on the core barrel's outer surface. This will assist in maintaining a clean work area and reduce the potential for cross contamination if this coring tool is reused.

- 8.3.7 The core barrel containing the core is detached from the thrust-bearing ball check valve. At this point, the entire core may be sent to the sample-collection area for sampling in accordance with section 8.7 if an end cap is sealed to each end. Individuals wishing to reduce the quantity of sludge requiring transfer to the sample-collection area may implement, in the drilling area, the procedures described in section 8.5.

10.0 Method Performance

Information not available.

11.0 Reference

Gray, P. L., V. L. Skidmore, T. K. Bragg, and T. Kerrigan. 1994. "Sampling the Contents of High-Level Waste Tanks." In *Waste Management '94 Proceedings*, Volume 1, 581-583, Tucson, Arizona.

8.4 Preparing the Sampling Area

8.4.1 Before receiving core barrels or individual liners containing sludge, the sample-collection area and balance are covered with clean plastic film. All sample-collection tools should be available and contained in their protective coverings.

8.4.2 All sample containers (e.g., vials, jars) into which sludge samples will be placed should be available with their caps in place.

Note: It is recommended that sludge-sample information (e.g., site location, date, waste container number, type of analysis) be recorded on the sample container's label before placement in the sample collection area.

8.4.3 The balance should be available and operating within manufacturer specifications.

8.4.4 The cap of the vial designated and pre-labeled to contain the sample for VOC analysis is removed, and the vial is placed on the balance. The balance is tared, and the vial's QC batch number is recorded on the Field Log Sheet.

8.5 Selecting the Sampling Location

8.5.1 The liners are extruded from the core barrel, and the core is visually examined and measured. The visual observations and core length are recorded on the Field Log Sheet.

8.5.2 A random number generator is used to randomly select a number between zero and the length of the core. This number represents the distance from the leading edge of the first liner (bottom of sludge) from which the sample is to be collected.

8.5.3 The location is measured and marked on the outside surface of its respective liner. If the location falls at a break between two liners, the sample is collected toward the first liner. If the location falls near the top of the core, and the quantity of sludge is insufficient for sample collection, then the bottom edge of this liner and top edge of the adjacent liner that contains sludge are selected.

8.5.4 The liner containing the sampling location is selected and separated from the other liners. For soft sludge, a clean separation may require slicing between the liners with a thin sharp object (e.g., knife). If the sludge is hard, separation may require a hack saw.

Note: Once the sludge at the ends of a liner is exposed to ambient air, sample collection for VOC analysis should be conducted as quickly as possible to minimize the loss of target VOCs present in the sludge. Additional guidance for this type of sampling is provided in *Soil Sampling and Analysis for Volatile Organic Compounds* (EPA 1991a) and *Review of Current and Potential Future Sampling Practices for Volatile Organic Compounds in Soil* (Hewitt 1992).

- 8.5.5 If a delay in sampling sludge for VOC analysis is anticipated (i.e., greater than 60 sec), the ends of the liner are sealed with end caps. Any sludge protruding from the ends of the liner is chipped or cut flush before sealing.

8.6 Collecting Samples from Soft Sludge

- 8.6.1 A modified syringe is selected, and its QC batch number is recorded on the Field Log Sheet. The syringe's barrel is pressed into the sludge at the end of the liner closest to the sampling location. It is offset from the liner's longitudinal center and pressed until the sludge reaches the 10-cc graduation. The syringe's plunger is allowed to rise freely.
- 8.6.2 The syringe is removed from the sludge, and the outside surface of its barrel is quickly wiped with a clean tissue.
- 8.6.3 The leading edge of the syringe is inserted through the mouth of the vial, and the sludge is extruded by pressing down on the plunger.
- 8.6.4 The weight registered by the balance is observed, and additional sludge is collected as necessary to obtain approximately 15 g. As presented in Table 5, it is expected that 1.5 to 2 syringe volumes will be required to obtain the weight specified in Table 2.
- 8.6.5 The mouth of the vial is quickly wiped with a clean tissue (to remove any particulates that could prevent a proper seal), and the vial's cap is tightened into place.
- 8.6.6 Samples for semi-VOC, metals, and PCB analyses are collected from the same end of the liner using the same syringe or other sample-collection tools (e.g., scoop). The prelabeled sample jars are tared, and the sludge is transferred from the liner to the jar until the balance indicates the weight specified in Table 2. As presented in Table 5, as much as 94% of the sludge in a liner may be needed for laboratory analyses. Each sample-collection tool and sample jar's QC batch number are recorded on the Field Log Sheet.

Table 5. Estimated Sludge-Sample Availability

Waste form ^(a)	Quantity required for analysis ^(b) (g)	Estimated density ^(c) (g/cc)	Number of full syringes to obtain 15g ^(d)	Estimated quantity of sludge in liner ^(e) (g)	Percentage In Liner required for analysis
Inorganic Waste-Water Treatment Sludge	125	0.96	1.5	173	72%
Organic Liquid and Sludge	125	0.74	2	133	94%
Solidified Liquid	125	1.01	NA	182	69%

(a) Waste forms were simulated for the *Idaho National Engineering Laboratory Simulated Solidified Transuranic Waste Sampling Program* (Connolly 1994). These simulated waste forms were based on information in the *Waste Isolation Pilot Plant Transuranic Waste Baseline Inventory Report* (DOE 1994).

(b) The sum of sludge quantities required for VOC, semi-VOC, polychlorinated biphenyl (PCB), and metals analyses (see Table 2).

(c) Density averaged from tests conducted on simulated waste in the *Idaho National Engineering Laboratory Simulated Solidified Transuranic Waste Sampling Program* (Connolly 1994).

(d) A syringe with its tip removed will hold approximately 10 cc of sludge. Analysis for VOCs requires 15 g of sludge.

(e) The internal volume of a liner is 180 cc.

8.6.7 The sampling tools, plastic film, core barrel tip, and basket retainer, if used, are discarded. All remaining sludge is returned to the waste drum, and the empty liners are discarded.

8.6.8 If the core barrel is to be reused, it is cleaned in accordance with the procedure described in section 9.3, or the appropriate procedure in section 9.4. Otherwise, the core barrel is discarded.

8.6.9 The vials and jars containing sludge are handled in accordance with the requirements specified in Table 2.

8.7 Collecting Samples from Hard Sludge

8.7.1 If the sludge inside the sleeve is solid (monolithic), it is extruded or pushed into a clean, clear plastic bag. A hammer and chisel, if necessary, are used to strike the monolith to break it into pieces small enough to fit through the mouth of the vial for VOC analysis.

Note: The purpose of the clear plastic bag is to contain the sludge as it is broken apart. Other containers may be used provided they are disposable and not likely to affect the composition of the sludge.

- 8.7.2 After the monolith has been sufficiently fractured, the clear plastic bag is opened, and forceps are used to select the largest pieces that will fit inside the vial. The QC batch number of the forceps is recorded on the Field Log Sheet. The weight registered by the balance is observed, and additional pieces are added as necessary to obtain approximately 15 g. The mouth of the vial is wiped with a clean tissue (to remove any particulate that could prevent a proper seal), and the vial's cap is tightened into place.

Note: If the sludge inside the liner exhibits extensive fracturing and pulverization, use of the clear plastic bag may not be necessary. The largest pieces that will fit inside the vial may be transferred directly from the liner to the vial.

- 8.7.3 Samples for semi-VOC and metals analyses are collected with a lab scoop. The prelabeled sample jars are tared, and the sludge is transferred from the bag or liner to the jar until the balance indicates the weights specified in Table 2. As presented in Table 5, as much as 69% of the sludge in a liner may be needed for laboratory analyses. The sample-collection tool and sample jar's QC batch numbers are recorded on the Field Log Sheet.
- 8.7.4 The sampling tools, plastic film, core barrel tip, and basket retainer, if used, are discarded. All remaining sludge is returned to the waste drum, and the empty liners are discarded.
- 8.7.5 If the core barrel is to be reused, it is cleaned in accordance with the procedure described in section 9.3, or the appropriate procedure in section 9.4. Otherwise, the core barrel is discarded.
- 8.7.6 The vials and jars containing sludge are handled in accordance with the requirements specified in Table 2.

8.8 Guidance for Coring and Sampling on an Individual-Drum Basis

- 8.8.1 Three cores are collected from TRU-waste-drum sludges requiring characterization on an individual-drum basis. The coring locations are randomly selected in the horizontal plane of the sludge using a similar approach to the procedure described in section 8.1.3.
- 8.8.2 The liners are extruded from the core barrel, and the core is measured and visually examined. Visual observations and the core length are recorded on the Field Log Sheet. The core barrel tip is discarded. The core barrel tips and basket retainers, if used, are also discarded.

- 8.8.3 The length of each core is divided by three, and the liners are marked at 33 and 67% of the core's length. A sampling location, randomly selected in a manner similar to the procedure described in section 8.5, is selected for each third. The sampling locations are marked on the outside of the liner.
- 8.8.4 If the sludge is soft, samples for VOC analyses are collected from these locations in accordance with the procedure described in section 8.6. The remaining sludge is extruded into a bowl and homogenized with a mixer, or manually with a spatula, to a uniform consistency. The QC batch numbers of the sampling tools are recorded on the Field Log Sheet. Scoops of the mixture are placed in prelabeled sample jars for semi-VOC and metals analyses. The jars are tared, and sludge is transferred until the balance indicates the weight specified in Table 2. Each sample-collection tool and sample jar's QC batch number are recorded on the Field Log Sheet.
- Note:** In lieu of homogenizing the core (after sample collection for VOC analysis), the sludge is extruded from the liners, placed end to end, and split longitudinally with a knife until a split reaches the weight specified in Table 2. This split is placed in its respective sample jar.
- 8.8.5 If the sludge is hard, samples for VOC analyses are collected from these locations in accordance with the procedure described in section 8.7. The contents of the liners are then combined, pulverized with a mortar and pestle, and mixed with a spatula to a uniform consistency. The QC batch numbers of the sampling tools are recorded on the Field Log Sheet. Scoops of the mixture are placed in prelabeled sample jars for semi-VOCs and metals analyses. The jars are tared, and sludge is transferred until the balance indicates the weight specified in Table 2. Each sample-collection tool and sample jar's QC batch number are recorded on the Field Log Sheet.
- Note:** In lieu of pulverizing the core (after sample collection for VOC analysis), an equal amount of sludge is scraped from the core's outside surface and placed in sample jars until the sample reaches the weight specified in Table 2.
- 8.8.6 The remaining sludge is returned to the drum, and the empty liners are discarded. The sampling tools are discarded.
- 8.8.7 The sampling tools and plastic film are discarded. The core barrel is discarded or cleaned in accordance with section 9.3 if it is to be reused.

Note: The cleaning procedure described in section 9.4 is not applicable when characterizing TRU waste on an individual-drum basis.

- 8.8.8 The vials and jars containing sludge are handled in accordance with the requirements specified in Table 2.

9.0 Quality Control

Several features inherent to coring and sampling techniques enhance the quality of collected samples. The design of the coring tools maximizes core recovery and minimizes disturbance to the core. The liners that contain the core are placed close to the coring tool's leading edge to minimize contact with the tool's metal surfaces. Hard sludges are cored as quickly as possible to minimize heat generation and potential loss of target analytes. The techniques used to collect samples for VOC analysis (e.g., time constraints, use of modified syringe) are designed to minimize the potential loss of target analytes.

Quality control for sludge sampling also includes collecting co-located cores to determine method precision and equipment blanks to verify cleanliness of the coring and sampling tools. Reagent blanks are analyzed to ensure that the deionized water, or high-pressure liquid chromatography (HPLC) water, used as a rinsate, is of sufficient quality and that the calibration of the balance used to weigh the samples is maintained. The procedures used to determine and control the quality of the method are described below.

9.1 Co-Located Cores

- 9.1.1 Co-located cores are collected to determine the combined precision of the coring and sampling procedures. Co-located cores are collected side-by-side (as close as possible to one another), handled in the same manner, visually inspected through the transparent liners, and sampled in the same manner at the same randomly selected sample location.
- 9.1.2 If physical differences are observed at the sampling locations, co-located cores may again be collected at another randomly selected sampling location in the drum. Samples from co-located cores should be submitted blind to the analytical laboratory.
- 9.1.3 Co-located cores are collected at a frequency of 1 for every 20 cores collected, or 1 per waste stream, whichever is most frequent.

9.2 Equipment Blanks

- 9.2.1 Equipment blanks are collected from fully assembled coring tools (including liners) before first use at a frequency of 1 per 20 coring tools or 1 per batch, whichever is more frequent. A batch of coring tools is the quantity of tools cleaned together under the same conditions. The equipment blank is collected by pouring clean water (e.g., deionized or reagent) down the inside of the liners inside the assembled coring tool. The water is collected in a clean, certified sample container placed at the leading edge of the coring tool. The container is labeled with the batch's unique QC batch number and analyzed for the analytes of concern. If the results of the equipment blank analysis indicate the presence of an analyte greater than the MDL specified in the quality assurance project plan (QAPP) (see footnote a, p. SD010R-3), the batch is discarded or inspected and cleaned again before use.
- 9.2.2 Equipment blanks are collected from liners cleaned independently of coring tools at a frequency of 1 for every 20 liners cleaned or 5 per batch, whichever is more frequent. A batch is 100 liners. The equipment blank is collected by randomly selecting 5 liners from the batch, pouring clean water (e.g., deionized or reagent) across their surfaces, and collecting the water in a clean, certified container. The container is labeled with the batch's unique QC batch number and analyzed for the analytes of concern. If the results of the equipment blank indicate the presence of an analyte at a concentration greater than the MDL specified in the QAPP (see footnote a, p. SD010R-3), the batch is discarded or inspected and cleaned again before use.
- 9.2.3 Sampling tools (e.g., modified syringes, scoops, chisels) are cleaned in batches. Equipment blanks are collected for the sampling tools at a frequency of 1 for every 20 tools cleaned or 1 per batch, whichever is more frequent. A batch is 20 or less of the same type of sampling tool cleaned together under the same conditions. After the batch of sampling tools has been cleaned, 1 item from the batch is randomly selected, and water is passed over its surface and collected in a clean, certified container. The container is labeled with the batch's unique QC batch number and analyzed for the analytes of concern. If the results of the equipment blank indicate the presence of an analyte at a concentration greater than the MDL specified in the QAPP (see footnote a, p. SD010R-3), the associated batch is inspected and cleaned again before use.

Note: It is recommended that the equipment blank results for the coring tools, liners, and sampling tools be reviewed before use. A sufficient quantity of these items should be maintained in storage to prevent disrupting sampling operations.

9.3 Initial Coring and Sampling-Tool Cleaning Procedures

Coring and sampling tools and components that will come into contact with the sludge should be thoroughly cleaned before first use. This cleaning is conducted at a location outside of the containment area. At the minimum, the following procedure, adapted from an EPA-approved field-sampling-equipment cleaning procedure (EPA 1991b), should be followed.

- 9.3.1 Identical tools (e.g., non-rotational coring tools, modified syringes) and components (e.g., basket retainers) are assembled into batches of 20 identical components. Liners, pre-cut to 10-cm (4 in.) lengths, are assembled in batches of 100. A unique QC batch number should be assigned to each batch.
- 9.3.2 The tools and components are washed with a non-phosphate detergent solution (e.g., Alconox™).
- 9.3.3 The tools and components are rinsed with tap water.
- 9.3.4 The tools and components are rinsed with 10% nitric acid.
- 9.3.5 The tools and components are rinsed with distilled/deionized water.
- 9.3.6 The metal parts are rinsed with reagent-grade hexane followed by reagent-grade methanol.
- 9.3.7 The tools and components are rinsed with ASTM Type II or HPLC grade water.
- 9.3.8 The non-metallic tools and components are dried in an oven at 50°C for 12 to 24 h. The metallic tools and components are dried in an oven at 100°C for 12 to 24 h.
- 9.3.9 A minimum of 1 component from each batch of 20 components is randomly selected. Five liners from each batch of liners are randomly selected. An equipment blank is collected as described in section 9.2.
- 9.3.10 The batch is placed in a clean protective covering (e.g., clear plastic bag), and the bag is labeled with the proper QC batch number.

Note: Before using any of the components in the batch, it should be verified that no significant levels of target analytes were detected in the equipment blank.

9.4 Routine Coring-Tool Cleaning Procedures

This procedure applies to non-rotational and rotational coring tools and components that will be used more than once before being discarded or cleaned in accordance with section 9.3. This cleaning procedure applies only when coring and sampling is conducted on a waste-stream basis and only on drums containing similar wastes (e.g., wastes from the same operation). This cleaning is conducted inside the containment area. The procedure described in section 9.3 is used if coring and sampling is conducted on an individual-drum basis.

9.4.1 Non-Rotational Coring Tool

- 9.4.1.1 The core barrel is inspected for damage (e.g., dents, deformations). If damage is observed, the core barrel is discarded or repaired before further use.
- 9.4.1.2 Clean rags are used to remove as much residual sludge as possible from the outside surfaces of the coring tool.
- 9.4.1.3 A clean rag is used to remove all residual sludge within 2.5 cm (1 in.) of the outside and inside of the leading edge of the core barrel such that no residual sludge is visible.
- 9.4.1.4 A clean basket retainer is installed in the core barrel, if necessary, and the retainer's QC batch number is recorded on the Field Log Sheet.
- 9.4.1.5 Eight clean liners, each pre-cut to 10 cm (4 in.) in length, are placed inside the core barrel and the liners' QC batch numbers are recorded on the Field Log Sheet.
- 9.4.1.6 The core barrel is connected to the ball check valve, and the coring tool is attached to the drill rod.

Note: This coring tool should be used only on a TRU waste drum containing sludge similar in characteristics to the TRU waste drum previously cored.

9.4.2 Rotational Coring Tool

- 9.4.2.1 Scrapers, brushes, and clean rags are used to remove as much residual sludge as possible from the outside and inside of the auger.

- 9.4.2.2 The auger and core barrel are inspected for damage (e.g., dents, deformations). If damage to the core barrel, or cutting edge of the auger, is observed, the tool is discarded or repaired before use.
- 9.4.2.3 Clean rags are used to remove as much residual sludge as possible from the outside surfaces of the core barrel.
- 9.4.2.4 A clean rag is used to remove all residual sludge within 2.5 cm (1 in.) of the outside and inside of the leading edge of the core barrel such that no residual sludge is visible.
- 9.4.2.5 A clean core-barrel tip is tapped in place at the leading edge of the core barrel, and the tip's QC batch number is recorded on the Field Log Sheet.
- 9.4.2.6 A clean basket retainer is installed in the core barrel, if necessary, and the retainer's QC batch number is recorded on the Field Log Sheet.
- 9.4.2.7 Eight clean liners, each pre-cut to 10 cm (4 in.) in length, are placed inside the core barrel, and the liners' QC batch number is recorded on the Field Log Sheet.
- 9.4.2.8 The auger and core barrel are connected to the thrust bearing ball check valve, and the rotational coring tool is attached to the drill rod.

Note: This coring tool should be used only on a TRU waste drum containing sludge similar in characteristics to the TRU waste drum previously cored.

9.5 Sample-Container Cleaning Procedures

The sample containers specified in Table 2 are cleaned in accordance with the procedures described in EPA's Specifications and Guidance for Contaminant-Free Sample Containers (EPA 1992b). The 40-mL vials are cleaned in accordance with container type B and the 250-mL (8-oz) jars are cleaned in accordance with container type A.

9.6 Maintenance and Calibration

9.6.1 Good-Housekeeping Procedures

Potential cross-contamination problems are minimized by maintaining the containment and sample-collection areas clean of residual sludge and debris (e.g.,

discarded plastic bags and common components). Drilling equipment is maintained as specified by the manufacturer. Hydraulic lines and fittings are maintained leak free and inspected on a routine basis. Inspection, maintenance, and repair records are maintained at the site.

Note: The routine use of a vacuum cleaner with a high efficiency particulate air (HEPA) filter is recommended in the containment and sample-collection areas. Vacuum bags and HEPA filters are discarded as necessary with the coring and sampling tools.

9.6.2 Balance

The balance is maintained in accordance with manufacturer's specifications and calibrated on a routine basis with weights traceable to the National Institute of Standards and Technology. Calibration and maintenance records are maintained at the site.

10.0 Method Performance

10.1 This method was developed from the results of a sampling demonstration program (Connolly 1994) conducted by EG&G Idaho Inc. to identify which coring and sampling techniques and tools were most effective for collecting representative samples of sludge from drums of TRU waste. A key program objective was to develop and demonstrate coring tools that could collect undisturbed cores of soft and hard sludge with greater than 50% recovery. A core that appeared relatively undisturbed and met this recovery specification was deemed to be representative of the sludge in the drum. Percent recovery was determined as follows:

$$\%R = L_c/L_s * 100$$

where L_c is the length of the core and
 L_s is the length of feed frame stroke.

10.2 The results of the sampling demonstration program found that

10.2.1 Soft sludge core recoveries averaged 99% using the non-rotational coring tool specified in this method.

10.2.2 Hard sludge core recoveries were 97% using the rotational coring tool specified in this method.

- 10.2.3 Cores of soft sludge collected with the non-rotational coring tool specified in this method appeared relatively undisturbed, with the exception of cores from drums that had alternating layers of soft sludge and hard cement.
- 10.2.4 Cores of hard sludge collected with the rotational coring tool specified in this method exhibited some disturbance (e.g., fracturing, pulverization); however, the degree of disturbance was notably less than with the other hard-sludge coring tools tested.
- 10.3 Data are not available for determining method precision as described in section 9.1. The simulated sludge was not spiked nor analyzed for any analytes of concern.
- 10.4 Data are not available for determining method accuracy. To determine method accuracy, coring and sampling of a drum of homogenous sludge with known analytes at known concentrations will be required. No such drum was available for the sampling demonstration program.

11.0 References

40 CFR 268. August 1993. "Land Disposal Restrictions." *Code of Federal Regulations*. Office of the Federal Register National Archives and Records Administration, Washington, D.C.

40 CFR 270. August 1993. "EPA Administered Permit Programs: The Hazardous Waste Permit Program." *Code of Federal Regulations*,. Office of the Federal Register National Archives and Records Administration, Washington, D.C.

American Society for Testing and Materials (ASTM). 1983. "Standard Practice for Thin-Walled Tube Sampling of Soils." ASTM D1587-83. *Annual Book of ASTM Standards*, Philadelphia, Pennsylvania.

American Society for Testing and Materials (ASTM). 1991. "Standard Practice for Sampling Waste and Soils for Volatile Organic Compounds." ASTM D4547-91. *Annual Book of ASTM Standards*, Philadelphia, Pennsylvania.

Connolly, M. J. 1994. *Idaho National Engineering Laboratory Simulated Solidified Transuranic Waste Sampling Program*. EGG-WM-11222. EG&G Idaho, Inc., Idaho National Engineering Laboratory, Idaho Falls, Idaho.

Hewitt, A. D. 1992. *Review of Current and Potential Future Sampling Practices for Volatile Organic Compounds in Soils*. Proceedings of the 16th Army Annual Environmental R&D Symposium. June 23-23, 1992. Williamsburg, Virginia.

U. S. Department of Energy (DOE). 1994. *Waste Isolation Pilot Plant Transuranic Waste Baseline Inventory Report*. CAO-94-1005. Carlsbad Area Office, Carlsbad, New Mexico.

U. S. Environmental Protection Agency (EPA). 1991a. *Soil Sampling and Analysis for Volatile Organic Compounds*. EPA/540/4-91/001. T. E. Lewis, A. B. Crocket, R. L. Siegrist, K. Zarrabi, Office of Research and Development.

U. S. Environmental Protection Agency (EPA). 1991b. *Compendium of ERT Soil Sampling and Surface Geophysics Procedures*. EPA/540/P-91/006. OSWER Directive 9360.4-02. Interim Final. Environmental Response Team, Emergency Response Division, Office of Emergency and Remedial Response.

U. S. Environmental Protection Agency (EPA). 1992a. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846. Third Edition, Final Update I and Proposed Update II. Office of Solid Waste and Emergency Response, Washington, D.C.

U. S. Environmental Protection Agency (EPA). 1992b. *Specification and Guidance for Obtaining Contaminant-Free Sample Containers*. Directive No. 9240.0-05A. Office of Solid Waste and Emergency Response.

12.0 Further Reading

U. S. Department of Energy (DOE). 1989. *TRUPACT-II Content Codes (TRUCON)*. DOE/WIPP 89-004, Rev. 3. Waste Isolation Pilot Plant, Carlsbad, New Mexico.

ST011R(a)

General Method for Sampling Liquids and Solids in High-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. 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 used to sample radioactive liquids (aqueous), sludge materials, and saltcake from high-level waste storage tanks with limited access.
- 1.2 Figure 1 summarizes the scope of this method and lists the method's sampling tasks.
- 1.3 The method has been applied to obtain samples from F and H Area waste tanks located at the Savannah River Site. These tanks contain high-level wastes derived from the chemical separation of nuclear-reactor products. Collected samples were used to characterize and monitor tank contents and in waste-treatment process development.

2.0 Summary of Method

- 2.1 This method employs several different sampling devices for collecting liquids, sludges, and saltcake from high-level waste storage tanks.
- 2.2 For liquids that may be sampled from the top of the liquid layer, a dip sample is obtained by lowering a sample vial a few inches below the liquid surface, allowing the vial to fill with liquid, and subsequently retrieving the vial.
- 2.3 When liquids require variable-depth sampling or trace organic analyses, a bacon-bomb sampling device is deployed to collect samples. The bacon-bomb sampler is a cylindrical apparatus with valves at the top and bottom that are opened by pulling on a sash cord. A length of aircraft cable is used to lower the sampler into a tank. When the sampler is

(a) This method was submitted by J. Pike (Westinghouse Savannah River Company, Aiken, South Carolina).

Figure 1. Scope of Method

suspended at the desired depth, the sash cord is pulled, allowing liquid to flow into the sampler through the bottom. The sample is recovered by lifting the sampler from the tank and dispensing the liquid into a mixing container. Samples are normally collected from two different tank depths and mixed before bottling the sample fluid.

- 2.4** Depending on the required sample volume, sludge specimens are obtained with either a 3-L or a 25-L collection device. Both samplers are briefly described below.

2.4.1 The 3-L collector is a hydraulically operated scoop that is opened and lowered to the sludge level of a tank by a cable. After allowing the sampler to sink down into the sludge, the scoop is closed, trapping sludge inside. The sample is recovered by lifting the scoop into a shielded cask.

2.4.2 The 25-L collector is a cylinder with a retractable nose cone at the bottom. Sections of pipe are connected to the collector, and the assembly is lowered into a tank with a crane. The collector is pushed through the sludge by the combined weight of the sampler and the pipe sections. By retracting the cone into the collector body, sludge is allowed to enter through an annulus formed between the cone and collector body. A vent at the top of the cylinder enables air or supernate to pass through the collector without being retained. Accumulated sludge is retrieved by raising the closed collector into a shielded cask. Radiation exposure is reduced by flushing the outside of the collector as the collector is removed from the tank.

- 2.5** Saltcake samples are obtained using an auger sampler that is mounted at the bottom of several sections of steel pipe. A handle is mounted at the top of the apparatus to enable an operator to bore into the salt. Sample material is collected and held by friction in a hollow cavity at the bottom of the sampler.

- 2.6** In general, containerized samples are sealed in plastic bags and placed in a shielded container (lead cask or depleted-uranium doorstop). The shielded container is then double bagged with plastic for transport.

- 2.7** Equipment should be surveyed and decontaminated after sampling to reduce radiation exposure to personnel.

3.0 Limitations and Interferences

- 3.1** This method was not designed for sampling organic fluids. Decontamination measures may need to be modified if organic samples are to be taken or if samples are to be acquired from tanks containing organic layers.

- 3.2 Highly radioactive liquids should not be sampled using the bacon-bomb apparatus due to the sampler's lack of shielding and relatively large (1 L) capacity.
- 3.3 Solid samples are compacted by the auger sampling device.

4.0 Safety

- 4.1 In general, a plastic windbreak (i.e., hut) should be constructed around the tank riser before sampling commences. However, dip samples may be taken without a windbreak if the wind speed is low (i.e., less than 12 mph).
- 4.2 Sampling personnel should be trained in handling high-level waste and in the proper use of sampling equipment.
- 4.3 Protective clothing should be worn by all operators handling radioactive wastes. Depending on the radiation and contamination levels of the tank, required protection may include coveralls, cloth and rubber overshoes, rubber and/or lead-lined gloves, lead aprons, and a full-face respirator.
- 4.4 In addition to thermoluminescent dosimeter (TLD) finger rings and wrist badges, self-reading dosimeters should be worn by all sampling personnel.
- 4.5 Continuous monitoring of sampling activities by radiation-protection staff is recommended.
- 4.6 Plastic bags and liners should be used where possible to limit the spread of contamination from sample equipment. Wipes and other waste materials should be placed in a plastic-lined waste container.
- 4.7 Where possible, extended tools should be used to handle sample containers and reduce radiation exposure.
- 4.8 The contents of all containers should be identified by appropriate labeling.

5.0 Apparatus and Materials

Note: All equipment used for sampling should not have sharp edges that could tear protective clothing. Moreover, the equipment should be free of cracks, which could hold raw wastes and spread contamination.

5.1 Liquid Sampling (Top of the Liquid Layer)

5.1.1 Stainless steel sample vials (100 to 1000 mL). A steel loop should be welded onto each vial to enable attachment of a lowering device, as shown in Figure 2.

5.1.2 A nylon sash cord or a rod of sufficient length for obtaining dip samples.

5.2 Liquid Sampling (Variable Depth or for Trace Organic Analysis)

5.2.1 A bacon-bomb sampler (1-L capacity) with a nylon sash cord and aircraft cable.

5.2.2 A metal, beaker-shaped mixing container for use with the bacon-bomb sampler. The mixing container should be large enough to hold at least 1 gal of fluid.

5.2.3 Plastic sample vials (200 mL).

5.3 Sludge Sampling (3-L Sample)

5.3.1 A 3-L sludge collector, which consists of the following components (Figure 3):

- A lead-shielded cask and retrieval reel. The combined weight of these components is 1575 lb.
- A spray ring assembly, which fits inside the tank-riser opening.
- A cylindrical, hydraulic scoop with an extendible cone at the bottom.
- Chokers and shackle bolts for lifting the cask.
- A hand-operated pump with a water reservoir and hose.

5.3.2 Mop heads for drying the 3-L sludge collector's spray ring.

5.3.3 A motor crane for lifting and positioning the shielded cask.

5.4 Sludge Sampling (25-L Sample)

5.4.1 A 25-L sludge collector and its auxiliary components (Figure 4):

- The collector consists of a 3.5-in.-diameter, 21-in.-long pipe stem and a 10-in.-diameter, 37.5-in.-long cylinder with a retractable cone at the bottom. An internal hydraulic cylinder opens and closes the collector by retracting

Figure 2. Dip Sampling

Figure 3. Three-Liter Sludge Collector

DRAFT

Figure 4. Twenty-Five-Liter Sludge Collector

or extending the cone. When the cone has been withdrawn (i.e., the collector has been opened), sludge may enter through an annulus formed between the cone and the collector body. A vent at the top of the collector shaft allows air and supernate to pass through the collector without being retained.

- Three-inch diameter, stainless steel drive-pipe sections (four 9-ft, 6-in. sections and one 5-ft section). A single lock bolt is used at each pipe joint to connect the pipe sections. The joints are sealed by "O-rings" to prevent seepage of sludge and supernate into the joint.
- A pipe clamp for supporting the collector and drive-pipe sections during assembly. The pipe clamp is a steel ring that may be opened and fastened concentrically around a pipe. When installed, the clamp fits inside grooves machined in the collector pipe stem or drive-pipe end fittings.
- Upper and lower cover shielding with a built-in spray ring. The lower cover shield fits directly over the tank riser and is 4 ft square, with 3 in. of lead shielding. A 13-in.-diameter hole is located in the center of the lower shield to accommodate the sludge collector. The upper cover shield (17 in. square with 3 in. of lead shielding) slides on top of the lower shield and is used to partially cover the hole in the lower cover shield. A sleeve is welded into the center of the upper cover shield to accommodate the collector pipe stem and drive pipes.
- A hand-operated hydraulic pump with tubing and a disconnect wire.
- An 8-ton transport cask with a built-in, battery-powered winch mounted at the top. The winch is enclosed in a Plexiglas housing to seal against contamination.
- A secondary container, which is used during transport to catch any sludge that leaks out of the collector. The secondary container is a can with six spring-loaded clips at the top. The clips fasten onto the top of the sludge collector to hold the secondary container in place.

5.4.2 A motor crane for lifting and positioning the transport cask.

5.5 Saltcake Sampling

5.5.1 A saltcake sampling apparatus, which consists of the following components (Figure 5):

- An auger attachment, which is comprised of an auger bit mounted inside a 2-in.-diameter, 3-in.-long section of steel pipe. The cavity between the auger bit and the walls of the pipe is capable of holding approximately 100 cm³ of sample.
- Stainless steel pipe sections (3/4 in. diameter) with a loop welded onto the side of each. The first pipe section (i.e., the pipe section fastened to the auger attachment) is 8 ft long, and the middle and upper pipe sections are 9.5 ft long. Where convenient, an additional 5-ft pipe section may be used as the topmost pipe. All of the pipe sections have male threads at the bottom end and an enlarged, female-threaded coupling at the top.
- A 1/4-in. steel cable with a small loop at each end.
- A handle that fits on the topmost section of pipe. The handle is similar in shape to a "D-ring" and is used to suspend the apparatus during assembly and to apply torque to the sampler.
- A holder plate, which is used to support the apparatus during assembly. The plate has a hole and an offset slot near its center. When used for support, a pipe section is slid into the slot, and the pipe's enlarged coupling rests on top.
- A tripod and a winch for holding, lowering, and lifting the sampling apparatus.
- Collapsible plastic tubing for storing the pipe sections.

5.6 Miscellaneous Items (Generally Required for All Sampling Activities)

- 5.6.1 Shielded containers (lead casks or depleted-uranium doorstops) for liquid and saltcake sample holding and transport (Figure 6). Depending on the weight of the containers, a portable hydraulic hoist or other lifting device may be required for lifting the containers.
- 5.6.2 A high-pressure water hose.

Figure 6. High-Level-Waste Uranium Doorstop with Sample Vial Inside

- 5.6.3 Plastic buckets and water for rinsing equipment.
- 5.6.4 Disposable wipes for wiping off sampling equipment.
- 5.6.5 Plastic sheeting, reinforced paper liners, and absorbent pads for covering the work area.
- 5.6.6 Plastic bags for containing samples and waste disposal.
- 5.6.7 Sample labels and tape.

6.0 Preplanning

- 6.1 The depths of liquid, sludge, and solid layers in the tank to be sampled should be measured (e.g., with a steel tape) or determined from site records.
- 6.2 The current and planned operations of the tank to be sampled should be determined. Sampling activities should be scheduled during periods when slurry pumps will not be operating and when water additions and tank transfers will not occur.

- 6.3** Final plans should be made for collecting samples. This should include a review of the radiation-protection measures needed and arrangements for any special equipment (e.g., forklift, portable hoist, motor crane) required for lifting shielded containers.
- 6.4** Preparation of Sampling Equipment. Based on the depths determined in section 6.1, equipment should be marked with tape, as appropriate, to ensure that sampling is performed at the proper tank depth. For example, the lifting cable for use with the bacon-bomb sampler should be marked at distances coincident with the desired liquid depths. Similarly, the tubing used with the 3-L collector, the 25-L collector's drive pipe, and the auger sampler's upper pipe section should be marked at positions that correspond to the appropriate tank depths. Sample bottles should be labeled with tape or engraved.
- 6.5** Preparation of Work Area. The work area should be radiologically barricaded by radiation-protection personnel. When dip sampling is to be performed, the tank riser around the plug should be covered with one layer of plastic sheeting, followed by one layer of reinforced paper. For other sampling procedures, a plastic windbreak, approximately 8 ft high, 10 ft wide, and 12 ft long, should be constructed around the tank riser. The floor of the hut should consist of one layer of plastic covered with one layer of reinforced paper.
- Note:** For saltcake sampling, the tripod should be erected over the tank riser before the windbreak is constructed.
- 6.6** A flush-water supply with a hose fitting should be provided at the site.

7.0 Reagents, Preservation Measures, and Handling

Preservation measures and holding times should be reviewed based on sampling constraints, safety considerations, and project-specific data quality objectives.

8.0 Procedure

- 8.1** Radiation and hydrogen levels should be monitored as the tank access is opened and sampling is performed. Flammable vapors should also be monitored when sampling tanks containing volatile organic compounds.
- 8.2 Liquid Sampling (Top of the Liquid Layer)**
- 8.2.1** Stainless steel sample vials (Figure 2) are used to obtain dip samples. Before sampling, the sash cord or rod should be attached to the steel loop welded onto the vial.

- 8.2.2 The tank access plug is removed, sealed in a plastic bag, and placed on the reinforced paper lining the sampling area. The sample vial is carefully lowered into the tank until the vial is a few inches below the liquid surface. (**Note:** Sampling personnel should have visual contact with the vial at all times.) After allowing the vial to fill with solution, the vial is raised near the top of the tank riser, and a hand dose rate is obtained from the sample vial. (**Note:** If a sash cord is being used, it should be placed into a plastic-lined waste box as the vial is raised.) In the event the radiation level is greater than 5 R/hour, special handling measures, as determined by health protection personnel, are required. If the radiation level is less than 5 R/hour, the vial is capped and lowered a few feet below the open riser. The vial is flushed with water and allowed to drain before raising the vial out of the riser. To reduce exposure, tongs or another holding device may be used to handle the vial.
- 8.2.3 The lowering device is disconnected from the sample vial, and the sample vial is wiped dry and prepared for transport according to the instructions in section 8.7.1. If a rod was used to dip the vial, the rod should be decontaminated by rinsing with water and drying with disposable wipes.

8.3 Liquid Sampling (Variable Depth or for Trace Organic Analysis)

- 8.3.1 The bacon-bomb sampler is used to obtain liquid samples at variable tank depths. Usually, samples are collected at depths corresponding to 2 ft below the top of the liquid layer and 2 ft above the bottom of the liquid layer. The two samples are then mixed in a mixing container. However, samples may be collected from other liquid depths, as needed.
- 8.3.2 Before sampling, the aircraft cable should be attached to the lifting eye of the sampler, and the sash cord should be threaded through the sampler's guide hole and attached to the valve actuator. Sample bottles, 1-gal buckets (one per sample) filled with water, a plastic-lined waste container, and a metal mixing container should be placed in the windbreak with the sampler.
- 8.3.3 After removing the tank riser plug, the sampler is lowered into the tank until the depth marker (section 6.4) is level with the top of the riser. (**Note:** To avoid sampling at the wrong depth, care should be taken so that the sash cord is not pulled while the sampler is lowered.) Once the marker is level with the riser, the sash cord is pulled and held for 20 sec, allowing the sampler to fill with solution. The sash cord is released.
- 8.3.4 The sampler is lifted up toward the riser. As the sampler is raised, the sash cord and lifting cable are fed into a waste container. When the sampler is about 4 ft

from the top of the riser, the sampler is rinsed with 1 gal of water from a bucket. After allowing most of the water to drip off the sampler, the sampler is raised above the riser and immediately positioned directly over the mixing container. The sash cord is pulled upward to drain the sample fluid into the mixing container. After the sampler has drained, the sash cord is released.

- 8.3.5 Normally, the sampling process in steps 8.3.3 and 8.3.4 is repeated at a second tank depth, and the two samples are mixed. Additional samples may be acquired by repeating the sampling process at the appropriate tank depths.
- 8.3.6 Sample fluid is poured into vials, which are capped and labeled. Any non-bottled sample liquid is poured back into the tank. Samples are prepared for transport according to the instructions in section 8.7.1.
- 8.3.7 The bacon-bomb sampler and mixing container are decontaminated with a water rinse and are wiped dry. The sampler and cords are placed in a plastic bag and stored in a radiological storage area.

8.4 Sludge Sampling (3-L Sample)

- 8.4.1 The 3-L collector (Figure 3) is used to obtain relatively small-volume sludge samples. To prepare for sampling, the shielded cask is lifted by a crane and is placed adjacent to the riser (outside the windbreak) on disposable sheets of plastic. After unbolting the base of the cask, the cask is covered with a plastic bag, and a hole is cut for the hand-operated winch. A small plastic bag is used to cover the winch handle.
- 8.4.2 The tank riser plug is removed and placed in a plastic bag, and the spray-ring assembly is installed inside the tank opening. A hose is connected to the spray ring and a flush-water supply, and the water-supply valve is opened briefly to check the spray ring for proper operation. Tubing is connected to the hydraulic pump, and the water reservoir and pump assembly are placed outside the windbreak. The top portion of the shielded cask is lifted inside the hut and placed on two plastic-covered, 4- x 6-in. blocks positioned near the riser.
- 8.4.3 The retrieval-reel cable is released and attached to the collector scoop, which should be in the open position. (**Note:** The scoop may be opened by depressing the check valve, pushing in the latches at the top of the scoop, and pulling the scoop open by hand.) After filling the water reservoir two-thirds full, the hose and its disconnect cable are attached to the scoop.

- 8.4.4 The scoop is carefully lowered (by hand) into the tank until the cable becomes slack, indicating that the scoop has reached the tank's sludge level. (**Note:** When lowering the scoop, the disconnect cable and tubing should be kept taut and apart from the reel cable to prevent the scoop from twisting.) After the scoop has reached the sludge level, a slight amount of slack should be left in the cable and tubing to assist in detecting when the scoop has closed (see section 8.4.5). The scoop is allowed to settle for 15 min (Figure 3).
- 8.4.5 The discharge valve on the hydraulic pump is opened, and water is pumped from the reservoir to the scoop. When the pressure rises to approximately 50 psi, the water level in the reservoir should begin to decrease, indicating that the scoop is closing. Pumping is continued until the scoop is fully closed and latched; this should occur at a pressure of approximately 200 psi.
- 8.4.6 Flush water is supplied to the spray ring by opening the water-supply valve. The disconnect cable is pulled to release the tubing from the scoop, and the tubing and disconnect cable are removed from the tank. (**Note:** As the tubing and disconnect cable are withdrawn, they should be placed into a plastic-lined waste container for disposal.) A crane is used to position the top portion of the shielded cask approximately 4 in. above the spray ring. Using the hand-operated winch, the scoop is slowly raised until it reaches the spray-ring zone.
- 8.4.7 The cask is gently lifted from the riser until the scoop's two top latches can be inspected. (**Note:** The cask should not be shipped unless one or both of the latches are fastened.) If neither latch is secure, sampling is discontinued until an appropriate course of action has been approved by management and health-protection personnel. If at least one of the latches is secure, the scoop is raised into the cask as far as possible. The retrieval reel is locked and wrenched in place. The scoop is allowed to drip dry for 5 min, and the cask is positioned over and bolted onto the cask's base plate.
- 8.4.8 The plastic covering is removed from the cask, and the cask is surveyed. If necessary, the cask is decontaminated by rinsing with water. The cask is prepared for transport according to the instructions in section 8.7.2.1.
- 8.4.9 The hose is disconnected from the spray ring, and, if all sampling activities are completed, the windbreak is removed. The spray ring is removed, wiped with absorbent pads, and placed on a clean piece of plastic. Several mop heads are pushed through the spray ring to absorb moisture, and the spray ring is placed in a plastic bag for storage. If necessary, the hydraulic pump is decontaminated by flushing and rinsing with water.

8.5 Sludge Sampling (25-L Sample)

- 8.5.1 Large-volume sludge samples are obtained using a 25-L sludge collector (Figure 4). Before sampling, the tank depths at which the collector will be opened and closed should be determined. In general, these depths should correspond to the top and bottom of the sludge layer of interest.
- 8.5.2 The tank riser plug is removed, and the upper and lower cover shields are placed over the open riser. A water hose is connected to the spray ring inlet and a flush-water supply. The upper shield is slid into the open position. After unfastening the bolts holding the cask bottom, a motor crane is used to position the upper portion of the cask and the collector over the shield. The cask should be situated directly over the hole in the lower cover shield.
- 8.5.3 The collector is lowered into the riser with the battery-operated winch until the collector's pipe stem is approximately 6 in. below the lower cover shield. The upper shield is slid into the closed position, and the collector is raised so that its pipe stem extends through the sleeve in the upper shield. The pipe clamp is installed on the collector stem, and the collector is lowered with the winch until the pipe clamp is resting on the shield (thus supporting the weight of the collector). After winding out the excess winch cable, the cask is positioned to the side of the cover shield, and the winch is disconnected from the collector. The crane is disconnected from the collector and is used to temporarily set the upper portion of the cask back on its bottom.
- 8.5.4 A coupling capable of holding the collector's pipe stem is attached to the motor crane and the collector pipe stem. The crane is then used to raise the collector slightly, and the pipe clamp is removed. The collector is lowered until the pipe stem is approximately 6 in. below the lower cover shield. After sliding the upper cover shield to the open position, the collector is raised until its top is level with the lower cover shield. The hydraulic pump is installed outside the windbreak, and the tubing and disconnect wire are attached to the collector.
- 8.5.5 The collector is lowered again until the top of the pipe stem is approximately 6 in. below the lower cover shield. The upper shield is closed and fastened to the lower shield. (Note: Care should be taken to prevent the hydraulic tubing from being crimped.) The tubing should be positioned in the slot in the upper cover shield.
- 8.5.6 The collector is raised until the groove in the pipe stem is positioned slightly above the upper shielding. The pipe clamp is fastened onto this groove, and the collector is lowered until the pipe clamp is supporting the weight of the collector.

DRAFT

- 8.5.7 After disconnecting the crane from the collector, the crane is used to position a drive-pipe section over the collector pipe stem. The drive pipe is coupled to the pipe stem, and the assembly is raised to enable removal of the pipe clamp. The clamp is removed, and the assembly is lowered into the tank with the crane.
- 8.5.8 Additional pipe sections are subsequently added to the assembly, and the apparatus is lowered until the collector is at the desired depth in the tank. (Note: The support clamp is used to brace the assembly while each pipe section is installed.)
- 8.5.9 The valve on the hydraulic pump is opened, and the pump is operated until the pressure gauge reads 150 psi, indicating that the collector has opened. The collector is slowly lowered to the depth specified for closing. After leaving the collector open for at least 1 h, the collector is closed by positioning the pump valve in the "close" position and operating the pump until the pressure rises to 500 psi. (Note: Depending on the density and adhesiveness of the sludge, the collector may need to be raised and lowered three or four times to ensure that the collector has been filled with sludge.)
- 8.5.10 Water is supplied to the spray ring for rinsing the drive pipes and collector as they are removed from the tank. The disconnect wire is pulled to disconnect the pump tubing from the collector, and the tubing and wire are removed from the tank. (Note: As they are removed, the pump tubing and cable should be wiped down and placed in a plastic storage box.) Using the crane and the support clamp, the drive-pipe sections are individually removed from the tank and disconnected from the apparatus. (Note: The assembly should be rotated slowly as it is raised to assist rinsing.) The drive pipes are placed in a regulated equipment storage box.
- 8.5.11 The crane is used to position the upper portion of the cask to the side of the cover shielding. The winch cable is attached to the collector, and the cask is centered over the collector. Using the winch, the collector is raised slightly, and the pipe clamp is removed from the collector pipe stem. The upper cover shield is slid open, and the collector is raised enough to be surveyed. If a high radiation level is observed, the collector should be lowered back through the spray ring and rinsed again. Once the outside of the collector has been decontaminated, the collector is raised into the cask.
- 8.5.12 After raising the cask and collector approximately 4 ft above the upper cover shield, the secondary container is positioned underneath the collector using remote tools. The cask is lowered until it is approximately 1 or 2 in. above the upper cover shield, and the collector is slowly lowered into the secondary

container until it latches. The collector is raised into the cask, and the cask is placed and bolted onto its bottom. The cask is surveyed, decontaminated, and prepared for transport according to the instructions in section 8.7.2.2.

- 8.5.13 The upper and lower cover shields should be surveyed and decontaminated, as necessary, by rinsing with water. After wrapping in plastic, the shields are placed into a storage container.

8.6 Saltcake Sampling

- 8.6.1 Salt samples are obtained with the auger sampler shown in Figure 5. (Note: An open-cup sampler has recently been deployed for obtaining saltcake from high-level waste tanks (Gray 1994); this new sampler may be included in future revisions of this method.)
- 8.6.2 Before sampling, a hose is connected to a flush-water outlet and placed inside the windbreak. The tank riser plug is removed, placed in a plastic bag, and set aside. The auger attachment is screwed onto the 8-ft pipe section, and the cable is attached to the loop on the pipe. The handle is coupled to the top of the pipe, and the winch cable hook is attached to the handle. Using the winch, the assembly is lowered into the tank until the sampler is slightly below the top of the riser.
- 8.6.3 The holder plate is placed over the riser hole and positioned so that the pipe is in the plate slot and the pipe coupling is resting on top of the plate. After the pipe is secure, the lifting eye and winch cable hook are transferred to a second 8-ft pipe section, and the assembly is lowered and coupled to the first pipe. The cable is threaded through the second pipe's loop, and the assembly is lowered until the pipe coupling is secured in the holder-plate slot. Additional pipe sections are added in the same manner until the sampler has reached the tank's salt depth.
- 8.6.4 Using the handle, the apparatus is rotated clockwise to bore into the salt. Augering is continued until the sampler has penetrated to the desired depth.
- 8.6.5 The assembly is slowly lifted using the winch until the coupling of the uppermost pipe section inside the tank can be placed in the holder-plate slot. (Note: Before removal, the pipe should be wiped thoroughly with a damp, disposable wipe.) Collapsible plastic tubing is placed over the pipe as it is withdrawn from the tank. The pipe section is disconnected, the tubing is sealed with tape, and the lifting eye is transferred to the next section of pipe. This process is repeated until all of the pipe sections have been removed and packaged in tubing.

- 8.6.6 The sample unit is placed in a plastic bag and prepared for transport according to the instructions in section 8.7.3.

8.7 Sample Packaging

- 8.7.1 **Liquid Samples:** Bottles containing highly radioactive samples should be sealed in plastic bags and placed into a shielded container (lead cask or depleted-uranium doorstop). The radiation level of the shielded container should be measured, and a sample label and radiation tag should be attached to the container. The shielded container should be placed in a doubled plastic bag, and the bag should be sealed with tape. A second sample label should be attached to the outside of the bag. Less radioactive samples (e.g., samples obtained with the bacon-bomb sampler) are sealed in plastic bags and placed in a cardboard box or metal bucket.

8.7.2 Sludge Samples

- 8.7.2.1 **Three-Liter Sample:** The shielded cask is re-bagged in plastic, and a sample label and radiation tag are attached to the bag.
- 8.7.2.2 **Twenty-Five-Liter Sample:** A sample label and radiation tag are attached to the cask.

- 8.7.3 **Saltcake Samples:** The sample unit is packaged in a plastic bag and placed in a plastic-lined shipping cask. A sample label and radiation tag should be attached to the cask.

8.8 Sample Transport

Protocols for sample transport should be guided by site regulations in addition to the sample's radioactivity, volume, and destination. In general, shielded containers should be secured during transit, and recipients should be notified when the sample has been shipped.

9.0 Quality Control

When sampling liquids, duplicate samples may be collected to verify results. A visual inspection of dip samples should be made to ensure that an adequate sample volume was obtained.

SO010R^(a)

Collection of Liquid Samples for Effluent Monitoring of Operations Facilities

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 provides guidance for the setup, collection, and transport of liquid effluent samples (i.e., facility process and retention-process sewers) that are generated in support of facility operations. The samples are analyzed for general indicator parameters, hazardous chemicals, and radiological constituents. These may include, but are not limited, to

- total radiological activity (screen)
- rads (alpha, beta, tritium)
- total carbon
- total organic carbon
- volatile organics
- semivolatile organics
- pesticides/polychlorinated biphenyls
- alkalinity
- ammonium
- chemical oxygen demand
- total dissolved solids
- anions
- metals {e.g., by inductively coupled plasma (ICP) or by graphite furnace atomic absorption (GFAA)}

(a) This method was submitted by D. A. Mueller, P. S. Henry, and J. Julya (Pacific Northwest Laboratory, Richland, Washington)

- 1.2 This method has been applied to sample effluent from facility process and retention process sewers. Data have been used to determine whether the effluent is suitable for release to a public water supply (e.g., a river) according to National Pollutant Discharge Elimination System (NPDES) permitting.

2.0 Summary of the Method

An automated, refrigerated liquid sampler (ISCO 3700FR/3720 or equivalent), consisting of a pump, refrigerator, sample bottle, and controller, is interfaced via tubing to an effluent line for sampling (Figure 1). The sampler should be programmable and capable of sequential (discrete) sampling and composite sampling.

The sampling of liquid effluent in this method consists of four activities. First, the composite sampling bottle is prepared and the automatic sampler is programmed to collect samples at the desired frequency during the chosen sampling period. Second, subsamples are collected from the filled composite bottle for specific laboratory analyses. Third, the samples are stored on ice, screened for radiological activity, and delivered for "in-house" analyses or offsite to an analytical services contractor (provided that radiological activity is below an appropriate level). Fourth, the sampling system is cleaned and reset to collect the next composite sample, and the sampling site is cleaned up.

3.0 Limitations and Interferences

- 3.1 Sampling should not take place in the presence of upwind sources of volatile organic chemicals, e.g., car or generator exhausts, open fuel tanks, open bottles of chemicals, coal-dust piles, or wet paint. Accordingly, the truck used to transport the sampling team should be parked downwind of the sampling area. Emissions from these types of sources could contaminate samples. If any such source of emissions is unavoidable, a note of their presence should be made on the field record form (FRF) (Figure 2).
- 3.2 Smoking, drinking, and eating should not occur in the control/work zone both because of safety considerations and because of potential contamination of samples with volatile organic chemicals.
- 3.3 Caps should be left on the sample containers until just before filling to minimize possible contamination. The Teflon[®] bottle-cap liners should not be touched. Liners that fall out of the cap and onto the ground or floor should not be used.
- 3.4 Plastic tubing can introduce organic contaminants (e.g., phthalates) to the sample. Therefore, Teflon[®] or Silastic medical-grade silicon rubber should be used in the sampler and to connect the sampler to the effluent line.

Figure 1. Sampling with the Refrigerated Composite Sampler

Figure 2. Field Record Form^(a)

- April 1995**

- 3.5 The ISCO sampler was not designed for acquiring grab samples, which are often specified for volatile organic analysis (VOA). However, representative VOA samples have been obtained using this method (see section 10.1).

4.0 Safety

- 4.1 The applicable radiation work procedure (RWP), safe operating procedure (SOP), safety plan, and building emergency procedures should be followed, and copies of these documents should be available at all times.
- 4.2 Appropriate spill containment and clean-up materials should be maintained and readily available within the work area. A large plastic containment tray should be placed on the ground in front of the open refrigerator to catch any effluent spilled during subsampling.
- 4.3 Appropriate protective clothing/equipment should be used as required while working in the control/work zone. Disposable or surgeon-type gloves should be worn when taking samples and when handling sample containers. If gloves become soiled, they should be replaced or washed. Safety glasses should be worn while working near the sample-collection apparatus and while filling sample bottles. Sampling personnel should hold bottles away from their faces when filling to minimize breathing fumes that may be generated from preservatives.
- 4.4 The site is checked for radioactivity before sampling to insure that levels are safe for sampling personnel. Samples are surveyed before release from the site to insure that DOT shipping requirements are met. When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.

5.0 Apparatus and Materials

- 5.1 Programmable, refrigerated sampler (ISCO 3700FR/3720 or equivalent, with composite conversion kit) including instruction manual, designed for composite sampling. A 120-V AC power source is needed. The sampler consists of three basic parts: a pump, refrigerator, and controller. The composition and size of the composite bottle should be consistent with the types, uses, and amounts of samples being collected. A 19-L glass bottle (or other size as appropriate) with Teflon[®] or Silastic tubing connected to an outlet near the bottom has been used in the application of this method. Silastic pump tubing was used and the pump rate was 3500 mL/min with a 3/8 in. ID suction line at 3 ft of head.

- 5.2 Teflon[®] tubing, 3/8 in. ID, with a polyethylene cover is used to connect the sampler to the effluent pipe.
- 5.3 Flow meter (ISCO 3200 or equivalent): The sampler allows samples to be collected at either user-definable time intervals (time-proportional) or at equal flow volume intervals (flow-proportional). The latter, which was used in the application of this method, requires an external flow meter to trigger a sampling event after a specific volume of effluent has flowed by.
- 5.4 Field printer (ISCO or equivalent): This is used to print the sampler's operating status, program settings, and sampling results stored in the sampler's memory (e.g., time, date, and flow rate for each sample event and any errors found).
- 5.4 Conductivity and pH probes and meters: Portable meters should be precalibrated before sampling.
- 5.5 Temperature vial mounted inside the sampler: This is a small glass vial filled with water. A thermometer is inserted through a hole in the top of the vial and is used for checking the temperature of the sampler.
- 5.6 Portable field thermometer: This is used to measure the temperature of the samples. It should be precalibrated before sampling.
- 5.7 Large plastic tray for use as a catch basin
- 5.8 Squirt bottle for rinsing composite bottle
- 5.9 Plastic bag to place sample bottles on
- 5.10 Trip or transfer blanks (as needed)
- 5.11 Site-specific sample kits: These kits include the prelabeled subsample bottles with appropriate preservatives and the paperwork necessary for the specific sampling activity.
- 5.12 Security tape for taping sample containers
- 5.13 Ice chest with ice: This is used to store and transport collected samples.
- 5.14 Thin squares of Teflon[®] to cover the mouth of the composite bottle
- 5.15 Razor knife

- 5.16 Waterproof markers and pens
- 5.17 Paper towels.
- 5.18 Plastic bag for garbage (i.e., gloves, paper towels, etc.)
- 5.19 Radiation detection instruments {portable alpha monitor (PAM), Geiger-Meuller (GM)}: These are used to survey the samples for radioactivity before release from the site.
- 5.20 Personnel safety equipment: rubber or leather gloves, disposable surgical gloves, radiation work protection clothes (when required), blue coveralls (as required), safety glasses, hearing protection (as required), safety shoes, hard hats (as required), water for washing hands, emergency eye wash, first aid kit

Dedicated equipment (e.g., the plastic tray, bags, etc.) may be stored at each sampling site.

6.0 Preplanning

- 6.1 The sampler is installed. It is connected to a 120-V AC power source, and the refrigerator is turned on to the desired sample temperature and allowed to equilibrate for 20 to 30 min. The suction line is attached to the sampler and placed in the liquid source; the tubing can extend up to 30 m from the sampler, but the maximum head (the vertical distance between the level of the liquid source and the pump) is 8 m (26 ft). The suction line should slope continuously downhill from the sampler to the pipe source. The intake should be placed in the main flow stream, not at the bottom or top of the pipe. If flow-proportional sampling is to be performed, the sampler is connected to a flow meter.
- 6.2 Portable field thermometers and pH and conductivity meters should be precalibrated before being taken into the field for sampling activities.
- 6.3 Composite sampler bottles should have been rinsed with deionized water after the previous sampling was completed.
- 6.4 When the sampling team arrives at outdoor sampling stations, the truck should be parked near but downwind of the point of sampling. This action ensures quality sample collections and convenient, safe, and efficient operation of sampling equipment.
- 6.5 A clearly marked control/work zone should be established around the sampling area, which allows the field team enough room to perform the required sampling activities and alerts outsiders to the boundary of the working area.

7.0 Reagents, Preservation Measures, and Handling

- 7.1 Deionized (DI) water
- 7.2 Reagent water: Reagent water is defined as water in which contaminants are not observed at the method detection limits for the compounds of interest. Volatile-chemical-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, which should be capped at all times when not in use.
- 7.3 After transport, samples should be stored in a refrigerator ($4^{\circ}\text{C} \pm 2^{\circ}\text{C}$) and must not be allowed to freeze.
- 7.4 Preservation measures depend on the type of analysis required. In some cases, refrigeration is all that is needed; in other cases, the pH needs to be adjusted (e.g., < 2 or > 12).
- 7.5 See Table 1 for examples of the amount of material needed, type of bottle, and preservative.

8.0 Method

8.1 Collection of Composite Sample

- 8.1.1 The sampler is programmed to suit the sampling needs. For example, in the application of this method, the sampler was programmed to collect 100 samples in a composite bottle at equal flow volumes (200-mL aliquots) during a 24-h period. In between each aliquot, the system was programmed to be backflushed with air by reversing the peristaltic pump; the purpose was to remove standing water from the sampling pipe so that fresh sample is obtained for each aliquot. Backflushing also serves as a safety precaution; if the liquid in the composite bottle reaches the inlet tube, the sample is backflushed back into the effluent pipe.
- 8.1.2 The composite sample is collected using the refrigerated sampler. Water should be purged out of the delivery hose, and the composite bottle should be properly positioned before sampler startup. After the sampling process has been completed, the composite sample bottle is ready to be subsampled.
- 8.1.3 A printer should be connected to the sampler to produce a hardcopy report of the sampler's status information, program settings, and results.

Table 1. Sample Bottle Preservation (Primary Lab)

Constituent	Minimum Volume (mL)	Preservative
ICP metals	500 ^(a)	HNO ₃ to pH<2
Arsenic	500 ^(a)	HNO ₃ to pH<2
Lead	500 ^(a)	HNO ₃ to pH<2
Selenium	500 ^(a)	HNO ₃ to pH<2
Thallium	500 ^(a)	HNO ₃ to pH<2
Mercury	500 ^(a)	HNO ₃ to pH<2
Nitrate (preserved)	125 ^(a)	H ₂ SO ₄ to pH<2
Ammonium	125 ^(a)	H ₂ SO ₄ to pH<2
Cyanide	1000 ^(a)	NaOH to pH>12
Sulfide	2 X 500 ^(a)	NaOH/ZnAc to pH>10
Volatile organics, GC ^(d)	3 X 40 ^(c)	HCl to pH<2
Volatile organics, GC/MS ^(d)	3 X 40 ^(c)	HCl to pH<2
Total organic carbon ^(d)	250 ^(c)	H ₂ SO ₄ to pH<2
Total organic halides ^(d)	1000 ^(c)	H ₂ SO ₄ to pH<2
Alkalinity	125 ^(a)	(e)
Conductivity	125 ^(a)	(e)
pH	125 ^(a)	(e)
Turbidity	125 ^(a)	(e)
Total dissolved solids	250 ^(a)	(e)
Pesticides and/or PCB	3 X 1000 ^(b)	(e)
Chlorinated herbicides	3 X 1000 ^(b)	(e)
Phosphorous pesticides	3 X 1000 ^(b)	(e)
Phenol	3 X 1000 ^(b)	(e)
Hydrazine	125 ^(a)	0.25mL HCl
Semivolatile	3 X 1000 ^(b)	(e)
Dioxin organics	3 X 1000 ^(b)	(e)
Total carbon ^(d)	60 ^(c)	(e)
Anions	125 ^(a)	(e)
Perchlorate	125 ^(a)	(e)
Coliform (memb. filter)	2 X 120 ^(a)	Sterile
Coliform (mult.tube.ferm)	2 X 120 ^(a)	Sterile
COD	125 ^(b)	(e)
Alpha	1000 ^(a)	HNO ₃ to pH<2
Beta	1000 ^(a)	HNO ₃ to pH<2
Radium	1000 ^(a)	HNO ₃ to pH<2
Uranium	125 ^(a)	HNO ₃ to pH<2
Gamma	1000 ^(a)	HNO ₃ to pH<2
Tritium	125 ^(a)	(e)
Technetium	1000 ^(a)	HNO ₃ to pH<2
Iodine 129	4000 ^(a)	(e)
Plutonium	1000 ^(a)	HNO ₃ to pH<2
Americium	1000 ^(a)	HNO ₃ to pH<2
Promethium	1000 ^(a)	HNO ₃ to pH<2
Strontium	1000 ^(a)	HNO ₃ to pH<2

(a) = poly
 (b) = glass Amber
 (c) = glass amber with septum cap
 (d) = no headspace
 (e) = no preservative

8.2 Collection of Subsamples from the Composite Bottle

- 8.2.1 The composite bottle should be checked to make sure an adequate volume of sampled water was obtained for the samples needed. Subsampling should take place based on a site-specific priority list. The priority list should indicate which analyses (and, therefore, which subsamples) are most important at that particular site. Low-priority subsamples should be eliminated first if the composite bottle does not contain sufficient sample volume. A note should be made on the FRF if the bottle contains less than the required volume.
- 8.2.2 A large plastic bag should be spread out on the ground next to the sampler. Sample bottles should be removed from the bottle kit, placed on the plastic, and counted to verify the bottle list shown on the FRF. Labels should be filled out as appropriate (see Figure 3).
- 8.2.3 The large plastic containment tray should be placed on the ground in front of the open sampler to catch any water spilled during subsampling activity.
- 8.2.4 The large composite bottle should be surveyed with beta/gamma radiation detection instruments (GM). The count rate should be recorded on the FRF, and an RWP should be used if appropriate.
- 8.2.5 Temperature, pH, and conductivity readings are taken from the composite sample using the portable field thermometer, pH meter, and conductivity meter. This information is recorded on the FRF.
- 8.2.6 The temperature on the thermometer inside the sampler should be recorded on the FRF.
- 8.2.7 Any sediment or discoloration in the composite sample water should be noted on the FRF. If sediment is present, the bottle should be swirled before each subsampling to minimize sample inhomogeneity.
- 8.2.8 If the composite sample volume is insufficient to adequately fill all subsample bottles, the sample bottles should be filled in the order specified on the site-specific sample constituent priority list found in each sampling kit. Otherwise, samples for volatile organic analysis are taken first, and the rest of the sampling may be done randomly. See section 1.0 or Table 1 for a list of typical constituents. The flow from the discharge line attached to the outlet near the bottom of the composite bottle is controlled by gravity (i.e., raising or lowering the end of the line to adjust the flow). The cap should be removed from the

DRAFT

Sampling-

N62961 BOCV69 1 of 3
ABN

Preservative: NA2S203
Lab: DATACH
Bottle Size: 1000 mL - gas
Schedule Date: 07/94
Date/Time:
Collector:

N62961 BOCV69 2 of 3
ABN

Preservative: NA2S203
Lab: DATACH
Bottle Size: 1000 mL - gas
Schedule Date: 07/94
Date/Time:
Collector:

N62961 BOCV69 3 of 3
ABN

Preservative: NA2S203
Lab: DATACH
Bottle Size: 1000 mL - gas
Schedule Date: 07/94
Date/Time:
Collector:

Figure 3. Sample Label

sample bottle, being careful not to touch the lip of the bottle or the Teflon[®] liner or the mouth of the discharge line. The mouth of the discharge line should not be allowed to touch the ground.

For those samples requiring zero headspace (i.e., samples in bottles having a septum top), the bottle should be filled completely so that a meniscus forms over the mouth. The bottle should be capped carefully to avoid the creation of a bubble underneath the bottle cap. If a bubble is present after capping, the cap should be removed and more sample added to the bottle, being careful not to let the sample bottle overflow (the latter would result in a loss of preservative). This process should be repeated until a bubble-free sample is obtained.

For those samples not requiring zero headspace, the sample bottles should be filled to the neck.

Each sample bottle should be filled slowly, placing the discharge line near the inner wall of the sample bottle to prevent trapping any air bubbles. Splashing or agitating the water should be avoided while the bottle is being filled.

Sample bottles containing preservatives should be filled in one attempt (i.e., the sample cannot be over filled or discarded and the bottle refilled).

- 8.2.9 Security tape should be attached to each filled sample container in such a way that the tape would be broken if the sample container were opened. For septum-top bottles, the security tape should be placed around the cap and bottle or offset so that the middle part of the septum is visible and not covered.

8.3 Site Cleanup, Sample Packaging, and Delivery

- 8.3.1 Each bottle should be surveyed with alpha/beta/gamma instruments before release. If the sample exceeds the site-release limits, the radiation-protection-technician's supervisor should be notified.
- 8.3.2 The sample bottles should be placed in the ice chest(s) in such a way that all bottles are surrounded and are in physical contact with ice. The ice chest(s) should be placed in a secure location in the vehicle for transport back to the preparation laboratory. The samples are stored there in a secured, controlled-atmosphere cargo container until radiological screen results are received and reviewed for shipping requirements.
- 8.3.3 All nondedicated sampling equipment that came into contact with sample water should be placed in a plastic garbage bag for appropriate disposal (i.e., depending

on whether the equipment is radiologically contaminated). Any water in the catch basin should be poured back into the composite bottle, and then the catch basin is wiped with a clean paper towel. The composite bottle and sample tubing are purged using the refrigerated sampler by connecting the discharge tube on the composite bottle to the tubing on the pump and then reversing the pumping direction. The sides and bottom of the empty composite bottle should be rinsed by swirling with a minimum of 1000 mL of deionized water. The waste water is pumped back into the waste stream.

- 8.3.4 Clean Teflon[®] covers are stretched over the mouth of the composite sample bottle and over the end of the discharge tubing, and both are then sealed securely with plastic tape. Precautions (e.g., wearing new, clean rubber gloves) should be taken to prevent contamination of the cleaned bottle. After the composite bottle is covered, a razor knife is used to make an "X" incision in the Teflon cover on the mouth of the bottle through which the sample line is put. The tubing clamp is placed on the discharge line, and the tubing and clamp are secured on the butterfly nut on the inside top of the refrigerator in the non-sample delivery position. The composite container and delivery line are now ready for the next composite sample collection.
- 8.3.5 The subsamples are transported to the appropriate laboratory for receipt by authorized personnel. A chain-of-custody (COC) procedure may be followed (see Chapter 1 of this document for an example of a COC form). Samples should be stored in a refrigerator ($4^{\circ}\text{C} \pm 2^{\circ}\text{C}$) and must not be allowed to freeze.

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 The analyst should demonstrate by analyzing trip blanks, bottle blanks, and equipment blanks that all glassware and equipment are free of contaminants. Reagent water may be used as a blank. Blank samples should be processed at all new locations and periodically at routinely monitored locations. Blanks should be carried through all stages of the sampling, transport, and analysis procedures, including matching the handling and storage times and location.

10.0 Method Performance

10.1 Grab sampling (with zero headspace) is the standard method for sampling VOAs. To determine the validity of using this composite sampling method for VOAs, a study was done comparing the concentration of one VOA in composite samples obtained using this method with that in grab samples collected on the same sampling dates. Both sample types were analyzed for chloroform. This is feasible because the chloroform concentration in the effluent analyzed is relatively constant, allowing a grab sample to be compared to a 24-h composite sample. Samples were taken from process and retention sewers located in the 300 Area of the U.S. Department of Energy's Hanford site, located in southeastern Washington State. The results for chloroform for 30 different samples taken during 3 1/2 months (Table 2) indicate that the composite and grab-sampling methods yield similar results. Chloroform concentrations in the composite samples were all within $\pm 110\%$ of those in the grab samples, and most values were within $\pm 50\%$.

Table 2. Comparison of Grab and Composite VOA Samples: Chloroform Results^(a)

Location	% Difference		
	Average ^(b)	Standard Deviation	Number of Samples ^(c)
Treated water	27.2	15.0	5
Building 320	14.6	12.3	18
Building 331	40.0	32.1	17
Building 3720	34.4	24.7	17
End of pipe	18.0	12.9	17

(a) Data taken during a 3 1/2 month period.

(b) The absolute values of the % difference values were used in calculating the average and standard deviation.

(c) A limited number of samples were eliminated based on a Q-test result.

SW010R^(a)

Core Samples in Cement Solidified Low-Level Liquid Waste

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 used to obtain core samples from 71-gal square drums containing cemented liquid radioactive wastes. The method is applicable to wastes that can be contact handled; it has been used for whole drum levels of 25 to 100 mrem/h.
- 1.2 Sampling is conducted on cemented waste that has cured for a minimum period of 6 months.
- 1.3 Samples are used to evaluate the chemical and physical stability of the waste form. Toxicity Characteristic Leach Procedure (TCLP) tests are performed to verify that the cement produced is, in fact, a nonhazardous waste.

2.0 Summary of Method

- 2.1 Slotted or split 3-in. diameter drill bits are used to obtain 10- to 12-in. length cement cores from 71-gal rectangular drums containing cemented low-level liquid waste. The coring drills are attached to the flat surfaces of the drum to obtain samples at top, middle, and bottom locations. The drum is also placed on its top to obtain samples from the bottom of the drum. Samples are distributed for physical tests (i.e., compressive strength) and chemical analyses (TCLP, radiochemistry analyses for specific isotopes) to determine long-term stability of the waste form and verify its nonhazardous condition. Samples are also archived for future evaluation (core cracking and spalling).
- 2.2 The method is currently being used to evaluate the long-term stability of cemented low-level liquid-waste supernatant from West Valley's high-level waste tank 8D-2. The 5-year evaluation involves sampling representative drums every 6 months.

^(a) This method was submitted by Garrett A. Smith (West Valley Nuclear Services Co., Inc., West Valley, New York).

3.0 Limitations and Interferences

- 3.1** Sampling is conducted on cemented waste that has cured for a minimum period of 6 months.
- 3.2** Samples taken for compressive strength testing should be prepared per American Society for Testing and Materials (ASTM) C-617 (1987) before crushing.
- 3.3** The drums are filled with two equal batches of cement from the cement-solidification system. Samples for compressive strength testing should not be taken from the batch-to-batch interface point.

4.0 Safety

- 4.1** At all times, the work area should be within a containment tent and ventilated through high efficiency particulate air (HEPA) filter systems used to remove radioactive material. The HEPA filters should have been tested before installation to 99.97% efficiency.
- 4.2** Operators should perform frequent checks on systems that are turned on or shut down to ensure that the system does what is expected (i.e., water flows and pressure rises, etc.)

5.0 Apparatus and Materials

- core drill motor and stand (see Figure 1)
- miter box and hand saw
- a HEPA-filtered vacuum cleaner
- four-wheel dolly
- load-tested nylon slings for lifting and handling 2000 pounds
- containment area with HEPA-ventilation setup
- glove bag for inside the tent
- port-a-band saw
- small poly bottle containing ~ 8 oz of water
- 1 gal wide-mouth containers with lids.

DRAFT

Tank Sampling

Figure 1. Core Drilling Machine

6.0 Preplanning

- 6.1 All personnel doing the work must be briefed on the methods and equipment to be used.
- 6.2 Appropriate work procedures (e.g., radiation work procedures) should be obtained before initiating sampling.
- 6.3 A containment area (e.g., tent) with adequate ventilation should be identified and set up. A glove bag for preparing the sample should be available in the designated area before starting sampling.
- 6.4 A HEPA-filtered vacuum cleaner should be used to pick up any fines or dust as they are generated during the cutting or drilling steps.

7.0 Reagents, Preservation Measures, and Handling

- 7.1 Samples removed for compressive strength testing should be prepared per ASTM C-617 before testing. Testing is per ASTM C-39 (1986).
- 7.2 Samples removed for TCLP testing should be handled per 40 CFR 261 before analyzing.
- 7.3 Core samples for archived storage are placed in metal cans containing packing material to keep the samples from breaking during handling.

8.0 Method

- 8.1 The selected drum is transported from the storage area (e.g., drum cell) to the containment area. The drum number and the number of cores to be taken are recorded on the data sheet for sample-tracking purposes.
- 8.2 Appropriate hoisting and rigging methods should be used to move the drum inside the containment tent. Rigging equipment that has a safe working load (SWL) of 2000 pounds or greater should be used.
- 8.3 The locations for the samples to be obtained from the drum are identified and recorded in relation to a fixed point on the drum for sample tracking purposes (Figure 2).
- 8.4 The core drill is positioned at the location selected for sampling. A 4-in.-diameter hole saw is used to cut through the drum at the place to be core drilled. The drum and polyliner are cut through, and the hole saw is removed from the drill unit. The section of drum and the polyliner cut by the hole saw are removed and placed in the radioactive waste container.

Figure 2. Square Drum with Sampling Grid (side and top views)

- 8.5** The 4-in. hole saw is removed and replaced with 3-in.-diameter core drill bits to obtain samples. The drill is operated on low speed and with very little feed (down) pressure. As the core drill heats up or binds, the drill is backed out and allowed to cool before drilling further. It may be necessary to cool and clean the bit with a small amount (1 to 2 oz) of nanopure water sprayed onto the core drill bit if the final sample analysis will allow this. The water should be allowed to drip into the cut where it will be absorbed by the concrete.
- 8.6** Drilling is to a depth of 10 to 12 in. When the appropriate depth is reached, the drill shaft should be struck with a perpendicular force to break the core; then the core drill bit (containing the drill sample) is removed and placed into the glove bag for sample removal.
- 8.7** The sample is removed into the glovebox. A saw (using a miter box) is used to cut the sample core to an appropriate length. The core is placed in the bag (the air is removed from the bag), the bag is sealed, and the following data are marked on the bag: date, drum number, core length obtained, and core location (i.e., top, middle, bottom). The planning

process should provide guidance for packaging and transporting samples, depending on the kinds of chemical analyses to be performed.

- 8.8 Reusable core drill bits (see section 8.11) are cleaned, and additional samples are drilled along the length of the drum for all sides of interest.
- 8.9 When sampling has been completed, the core-drilled drum should be wrapped in yellow herculite and sealed with tape. A radiation survey should be conducted before releasing the drum from the tent.
- 8.10 The wrapped drum is removed from the tent on a four-wheel dolly. The drum is placed onto an overpack box for storage. Cribbing material is used as necessary to ensure that the drums will not move while the box is transported. The overpack identification number should be recorded.
- 8.11 Used core drill bits are cleaned in a glove bag following established guidelines. A wire brush and/or scraper is used to remove dried cement from the core drill parts. A round (chimney type) brush attached to a variable drill motor can be used to clean the drill bit (caution should be used to not damage the teeth of the core bit).

9.0 Quality Control

- 9.1 Tracking the sample's location is critical for properly evaluating the data.
- 9.2 Bit cleaning, preparation, and materials of construction vary depending upon the end use of samples taken. For example, samples taken for TCLP metals analysis should not be taken with a steel bit, and samples taken for TCLP volatiles should not be taken with a bit cleaned with any organic solvent.

10.0 Method Performance

11.0 References

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

American Society for Testing and Materials (ASTM). 1987. "Standard Practice for Capping Cylindrical Concrete Specimens." ASTM C-617-87. Philadelphia, Pennsylvania.

American Society for Testing and Materials (ASTM). 1986. "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens." ASTM C-39-86. Philadelphia, Pennsylvania.

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), 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 (e.g., Means et al. 1978, McFadden 1980). 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 from 1 L 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

- McFadden, K. M. 1980. *Organic Components of Nuclear Wastes and Their Potential for Altering Radionuclide Distribution When Released to Soil*. PNL-2563, Pacific Northwest Laboratory, Richland, Washington.
- Means, J. L., D. A. Crerar, and J. O. Duguid. 1978. "Migration of Radioactive Wastes: Radionuclide Mobilization by Complexing Agents." *Science* 200:1477-1481.
- Tomkins, B. A., J. E. Caton, Jr., 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.
- 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.
- U.S. Environmental Protection Agency (EPA). 1991. *Contract Laboratory Program. Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration*. OLM01.8, Office of Solid Waste and Emergency Response, Washington, DC.
- U.S. Environmental Protection Agency (EPA). 1992. *Test Methods 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 National Technical Information Service, Springfield, Virginia.
- Winters, W. I., L. Jensen, L. M. Sasaki, R. L. Weiss, J. F. Keller, A. J. Schmidt, and M. G. Woodruff. 1990. *Waste Characterization Plan for the Hanford Site Single-Shell Tanks*. WHC-EP-0210, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

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.
OS060	Immunoassay for Petroleum Fuel Hydrocarbons in Soil	An immunoassay-based field screening method is used for the semiquantitative or quantitative measurement of petroleum fuel hydrocarbons (BTEX) in soils. The method is suitable for radioactively contaminated soils.
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.

Table 8.1. (contd)

Method Number	Title	Summary
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.
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.
OP040R	Reduced-Scale Zero Headspace Extraction for TCLP Volatiles in Shielded or Containment Conditions	A reduced-scale zero headspace extraction method is used for volatile organic compounds in solid wastes that are too radioactive to be handled under the conditions found in SW-846 method 1311. A prototype tumbler and syringe holder was constructed for use in a glovebox or hot cell. This method should be performed only in cases where the direct analysis suggests that TCLP regulatory limits may be exceeded.
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.

Table 8.1. (contd)

Method Number	Title	Summary
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 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.
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.
OM500R	Qualitative Analysis for Low Molecular Weight Organic Acids in Mixed Hazardous Waste Samples by Thermospray LC-MS	Low molecular weight organic acids, including formic, acetic, propionic, glyoxylic, glycolic, gluconic, citric, and tartaric acids, are qualitatively determined by thermospray liquid chromatography-mass spectrometry (LC-MS). Derivatization is not required. The method is suitable for hot cell, glovebox, or lab bench use and is applicable to tank samples. Sample radioactivity is significantly decreased by cation exchange before LC-MS.
OM510R	Determination of Chelators and their Degradation Products in Mixed Hazardous Waste Samples by Derivatization GC-MS	Methylation followed by GC-MS is used to analyze chelators and their degradation products, including EDTA, HEDTA, ED3A, NTA, citric acid, oxalic acid, and succinic acid. The method is suitable for hot cell, glovebox, or lab bench use and is applicable to tank samples.

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. (Taylor et al. 1991).

- 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 1254 (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.

Table 2. Results of Analyses for PCBs in Soil Samples using the ENSYS RISC[®] Immunoassay

Sample	PCB Conc. (µg/g)	Analyst 1	Analyst 2	Interpretation (µg/g)
1	0	5	5	5
2	2	5	5	5
3	4	5	5	5
4 ^F	4.7/2.3	5 ^F	5 ^F	5 ^F
5	5	5	5	5
6	6	5	5	5
7	8	5	5	5
8	10	5	5	5
9 ^F	11.1/11.5	5 ^F	5 ^F	5 ^F
10	20	5	5	5
11	40	5 ^F	5 ^F	5 ^F
12	50	5	5	5
13	60	5	5	5
14	80	5	5	5
15 ^F	83/72.5	5	5	5
16	100	5	5	5
17	200	5	5	5
F - indicates field sample				
FP - indicates false positive result				
Rep. 1 Rep. 2				
@ 5 µg/g				
Rep. 1 Rep. 2				
@ 50 µg/g				
Rep. 1 Rep. 2				

OS060^(a)

Immunoassay for Petroleum Fuel Hydrocarbons in Soil

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 is a field screening method for the semi-quantitative or quantitative measurement of petroleum fuels in soils. The technique is based on the specificity of an antigen/antibody reaction and is coupled with an enzyme-based color reaction for monitoring the extent of the reaction. Antibodies that are specific to the benzene, toluene, ethylbenzene, and xylenes (BTEX) components of fuels are most frequently used. Differences in kit design are primarily based on the way the analyte (antigen) is exposed to the antibody and on how the color reaction is developed and read, i.e., in solution by spectrometry or on a solid surface by reflectometry. In any format, the assay is based on the competition between the analyte and an analyte-enzyme complex (conjugate) for binding to the antibody. Less color in the assay means more analyte in the test sample.
- 1.2 Protocols and evaluations of the soil test kits manufactured by Millipore Corporation and Ohmicron Environmental Diagnostics are presented here. Kits produced by other companies may be equivalent. (Some kits are also designed to measure fuel hydrocarbons in water.)
- 1.3 As with other immunoassay-based methods, this method is suitable for screening soils that are contaminated with radioactive waste.

^(a) This method was supplied by L. C. Waters, R. A. Jenkins, R. W. Counts, and M. A. Palausky (Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee).

2.0 Summary of Method

- 2.1 Soil samples containing, or suspected of containing, fuel hydrocarbons are extracted with methanol or similar solvent. Aliquots or dilutions of the extracts are buffered and added to the "immobilized" antibody, together with a constant amount of the conjugate (a BTEX component/enzyme complex). The antibody must be "immobilized" so that unbound analyte and conjugate can be removed by rinsing. The antibody is "immobilized" in different ways by different manufacturers. Competition between analyte and conjugate for binding to the antibody is allowed to occur. The more analyte present, the less conjugate will bind. The amount of bound conjugate is determined by the addition of appropriate substrates, which are enzymatically converted to colored products. The amount of color produced is proportional to the amount of conjugate that was bound to the antibody. The assay is a typical competitive immunoassay wherein the amount of color in the final reaction is *inversely* proportional to the amount of BTEX-related components in the test sample. The fuel hydrocarbon content of the samples is usually estimated by reference to BTEX standards included in the assay. Kits that measure the reaction by relative reflectance rely on standard concentration curves programmed into the reflectometer. When a BTEX mixture is used as the standard, the amount of fuel hydrocarbons in the test soil can be expressed as BTEX equivalents. If the type of fuel contamination is known, e.g., gasoline or diesel fuel, it may be used as the standard.
- 2.2 Assay sensitivity varies depending on the kit used and the type of fuel being measured; but for total BTEX, it is usually in the range of 1 to 5 μg per gram of soil. A wide working range can be achieved via appropriate dilution of the sample extract.

3.0 Interferences

Because of the polyclonal nature of the antibodies used in this method, cross reactivity with other aromatic hydrocarbons in fuels besides the BTEX components occurs. These components include polyaromatic hydrocarbons, such as naphthalene and phenanthrene. Therefore, if a soil sample is contaminated with only one, or a few, of those reactive compounds, it would test as a false positive for petroleum fuel. Other common soil contaminants, such as chlorinated hydrocarbons, PCBs, and metals do not react with the antibody and would not be expected to interfere. Millipore has indicated that some clay samples may interfere with the test. It is appropriate to pretest for interference in a soil type by spiking and analyzing that soil.

4.0 Safety

Gloves and protective clothing should be worn to protect against unnecessary exposure to hazardous contaminants in the soil and to the methanol used to extract the soil. The handling of radioactive soil samples should follow all applicable radiochemical procedures and health physics monitoring practices.

5.0 Apparatus and Materials

(Information in this and subsequent sections is based on the use of the Millipore Extraction and BTEX Immunoassay Test Kits and the Ohmicron Soil Collector, Sample Extraction, and BTEX Assay Kits.)

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 include the following:

Millipore

- A weighing balance capable of weighing to 0.1 g
- Weighing boats and spatulas
- Polypropylene soil extraction bottles
- Extract filtration units
- Extract storage vials
- Pipettors and tips
- Timer
- Battery-powered differential photometer capable of reading absorbance at 450 nm.

Note: The methanol used to extract the soil is not included in the extraction kit.

Ohmicron

- Soil collection and extraction devices for reproducibly collecting and extracting a volume of soil (alternatively, soils may be weighed, then added to the device)
- Extract filtering caps
- Extract storage vials
- Extract diluent
- Pipettors and tips
- Timer
- Assay tubes
- Photometric analyzer.

Note: The Ohmicron RPA-IT[™] RaPID Photometric Analyzer requires 110 to 220 V AC power, which could be provided in the field by a generator or an inverter attached to a car battery. Alternatively, the test could be run in a semiquantitative mode using a battery-powered differential photometer. A soil-extraction solution is included in this kit.

6.0 Reagents

Reagents specific to this method, and included in the kits, are standard BTEX solutions, reaction buffer, analyte-specific antibody-coated assay tubes (Millipore) or antibody coupled to magnetic beads (Ohmicron), peroxidase-analyte conjugate, substrates for the peroxidase (a mixture of peroxide and a chromogen), and an acid solution to terminate the reaction. A control BTEX sample is provided in the Ohmicron kit. Unless otherwise indicated by the supplier, these reagents should be stored at 4°C when not being used.

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process. Soils, extracts, and standards should be handled as expeditiously as possible due to the volatility of the analytes being measured. Residues of soils found to contain fuel hydrocarbons should be handled and disposed of as hazardous waste.

8.0 Procedures

8.1 Millipore (Detailed instructions are provided with the Millipore EnviroGard™ Soil Extraction Bottle Kit and the Petroleum Fuels in Soil Test Kit.)

8.1.1 Soil Extraction

- 8.1.1.1 A 5 ± 0.1 -g quantity of soil is weighed onto a plastic weighing boat.
- 8.1.1.2 The soil is transferred to a 30-mL polypropylene bottle containing three mixing beads.
- 8.1.1.3 A 5-mL quantity of methanol is added to the soil sample.
- 8.1.1.4 The bottle is tightly capped and the sample extracted by vigorous shaking for 2 min.
- 8.1.1.5 The bottle filter cap and filter unit are used to filter the extract into glass storage vials for assay and/or storage.

8.1.2 Soil Extract Immunoassay

- 8.1.2.1 Reagent preparation: All reagents should be allowed to warm to ambient temperature before use. Whenever possible, the assay should be run at 18°C to 27°C. Temperatures outside this range may require extending (for lower temperatures) or reducing (for higher

temperatures) the incubation times of the assay. Reagents should be stored at 4°C when not in use.

- 8.1.2.2 Assay tube preparation: Enough antibody-coated tubes should be labeled, and placed into racks, to accommodate 1) a negative calibrator (methanol), 2) three positive calibrators, and 3) up to 16 sample extracts. To maintain precise timing, it is recommended that no more than 20 tubes be run in a single assay. Using a repeating pipettor, 0.5 mL of assay diluent is added to each tube.
- 8.1.2.3 Calibrators pipetting: Four positive calibrators with total BTEX (equal parts benzene, toluene, ethylbenzene, and 3 xylenes) concentrations of 2, 10, 50, and 300 µg/mL are provided with the kit. One of two concentration ranges is chosen by using either 50 µL of the 2, 10, and 50 calibrators (low range) or 10 µL of the 10, 50, and 300 calibrators (high range). A positive displacement pipettor is used to quickly pipet the appropriate calibrators, including the negative calibrator, to the appropriate tubes (change pipet tips between calibrators to prevent contamination).
- 8.1.2.4 Sample extract pipetting: A 10 *or* 50 µL aliquot (depending on the range of calibrators chosen - see 8.1.2.3) of each extract is pipetted into the appropriate tube, with a fresh pipet tip for each sample.
- 8.1.2.5 Conjugate addition: After calibrators and sample extracts have been added, 200 µL of the conjugate are quickly added to each tube, using a repeating pipettor. The tube rack is shaken briefly to mix the contents of the tubes.
- 8.1.2.6 Competitive binding: The tubes are allowed to incubate undisturbed at ambient temperature to allow competitive binding of the analytes and conjugate to the antibodies to occur. After 10 min, the tube contents are decanted, and the tubes are rinsed 4 times with water to remove unbound analyte and conjugate. Residual water is removed by tamping the inverted tubes on absorbent paper towels.
- 8.1.2.7 Color development: The relative amount of bound conjugate is determined by adding 500 µL of a peroxide/chromogen containing substrate to each tube. The tubes are incubated to allow the bluish-green color to develop. After 5 min, 500 µL of stop solution (1 N HCl) are added to terminate the reaction. In acidic solution, the peroxidase product is yellow.

- 8.1.2.8 Absorbance measurements: The absorbance, at 450 nm, in each tube is measured spectrophotometrically, relative to a water blank. The intensity of the color is *inversely* related to the concentration of BTEX equivalents in the samples.

8.2 Ohmicron (Detailed instructions are provided with the Ohmicron Soil Collection, Sample Extraction, and BTEX Assay Kits.)

8.2.1 Soil Extraction

- 8.2.1.1 A 10 ± 0.1 -g quantity of soil is weighed and transferred into a soil collection device. (It is simpler to use this device in the volume mode in the field and to correct the analytical result for the actual weight of soil collected.)
- 8.2.1.2 A 10-mL quantity of extraction solution is added to the soil sample.
- 8.2.1.3 The collection device is capped and shaken vigorously for 1 min (compacted clays may require longer for effective dispersion).
- 8.2.1.4 The extract is filtered into collection vials via the use of filter caps. This procedure may be facilitated by adding a bent syringe needle to the device outlet and using upward, rather than downward, pressure on the collection device plunger.

8.2.2 Soil Extract Immunoassay

- 8.2.2.1 Reagent preparation: (see section 8.1.2.1)
- 8.2.2.2 Assay tube preparation: Enough tubes are labeled and placed into the upper part of the magnetic separation rack to accommodate 1) a zero and three positive BTEX standards, in duplicate, 2) the control sample, and 3) the sample extracts. It is recommended that no more than 30 tubes be run at a time to maintain precise timing of the reaction.
- 8.2.2.3 Sample extract dilution: The sample extracts are diluted 10 fold before the assay by transferring 500 μ L to a dilution vial containing 4.5 mL of diluent. Further dilution may be made as appropriate.
- 8.2.2.4 Sample pipetting: Three BTEX standards are provided with the kit. These contain 0.09, 0.35, and 3 μ g/mL of each of the six BTEX

components. *(To be consistent with the units used by other manufacturers, these standards will be referred to as 0.54, 2.1 and 18 µg/mL of all of the six BTEX components - see section 11.0.)*

Duplicate 200-µL aliquots of the zero and three positive standards are pipetted into the appropriate tubes. The same volume, 200 µL, of the control sample (provided in the kit) and the diluted test samples are then added to the appropriate tubes.

8.2.2.5 Conjugate and antibody addition: After the standards, control, and test samples have been added, 250 µL of conjugate and then 500 µL of antibody bound to magnetic particles are quickly added to all the tubes.

8.2.2.6 Competitive binding: The tubes are quickly vortexed to mix the components and allowed to incubate at room temperature for 15 min to allow for competitive binding between analyte and conjugate to the antibody to occur. After the incubation period, the antibodies are "immobilized" on the tube walls by placing the tube rack onto the magnetized part of the rack for 2 min. The unbound analyte and conjugate are gently decanted and excess liquid removed by blotting the tubes on paper towels. Wash solution (1 mL) is added to each tube and allowed to stand for 2 min. The wash solution is decanted and the process repeated. *(Remember to keep the magnetic separator in contact with the tubes during these washes.)*

8.2.2.7 Color development: The tube rack is removed from the magnetic separator, and 500 µL of color solution are quickly added to each tube. The tubes are vortexed to resuspend the antibody/conjugate complex and incubated at room temperature to allow the color to develop. After 20 min, 500 µL of stopping solution (0.5% H₂SO₄) are added to terminate the reaction.

8.3 Estimation of BTEX Concentration in Samples

8.3.1 (Millipore) - Standards (both negative and positive calibrators) are included in each assay. The Millipore kit permits either a low, 0 to 50 µg/mL, or high, 0 to 300 µg/mL, calibrator range to be chosen. *(Note: The low range, i.e., 50 µL of 0, 2, 10, and 50 µg/mL total BTEX was used in this evaluation.)* The negative calibrator (methanol) should always produce the highest absorbance values; the positive calibrators are proportionally lower, depending on their concentrations.

Semiquantitative estimates of the concentrations of BTEX equivalents in the soil extracts are made by comparing their absorbance values with those of the negative and positive calibrators. For example, a soil sample with an absorbance greater than the 2 µg/mL positive calibrator would be estimated to contain less than 2 µg/g BTEX equivalents; samples with absorbance less than the 2 µg/mL calibrator but greater than the 10 µg/mL calibrator would be estimated to contain 2 to 10 µg/g BTEX equivalents; and so forth. Accordingly, test-sample results can be interpreted as being less than 2, 2 to 10, 10 to 50, or greater than 50 µg of BTEX equivalents per gram of soil. (Note: Because a 1-mL volume of methanol per gram of soil extraction was performed, the results obtained from soil extracts are in µg/g; results obtained from spiked methanol are in µg/mL.)

Concentrations of specific fuels may be estimated by using the equivalency tables, which are included in the instructions for the kit. For example, the calibrators used in this evaluation containing 2, 10, and 50 µg/mL total BTEX are equivalent to 2, 11, and 58 µg/mL of gasoline.

- 8.3.2 **(Ohmicron)** - A semiquantitative estimate of the BTEX concentration in the test samples can be obtained from the absorbance measurements at 450 nm as described above for the Millipore assay (see section 8.1.2.8 and 8.3.1).

The Ohmicron test system also permits a quantitative estimate of the concentration of BTEX equivalents in the test samples to be made via the use of their RPA-1™ RaPID Photometric Analyzer. This instrument automatically calculates and stores a calibration curve for BTEX based on the absorbance values obtained for the zero and positive standards. The concentration of BTEX equivalents in each test sample is determined by reference to the calibration curve.

9.0 Calculations

- 9.1 **(Millipore)** - When the assay is used as described above (section 8.3.1), calculations are not necessary to make a semiquantitative interpretation of the concentration of a test sample. However, for analysis of possible matrix effects on gasoline recovery from different types of soils (see section 11.1.5), it was necessary to make quantitative determinations of the amount of gasoline recovered. These quantitative determinations were obtained from a standard curve generated from the absorbance values of the test calibrators. The linear calibration curve was derived by a least-squares fit of the ratio $(B/B_0) \times 100$ (%) versus the log of the calibrator concentration, where B_0 = the absorbance value (A_{450}) of the negative calibrator and B = the absorbance values (A_{450}) of the positive calibrators. Estimates of the spiked soil concentrations were made using the B_0 values of both the negative calibrator and the negative soil samples.

- 9.2 (Ohmicron) - When the assay is used as described above (section 8.3.2), quantitative determinations are obtained from a standard curve generated from the absorbance values of the test standards. For BTEX, the RPA-IT[™] software automatically calculates a linear calibration line by a least-squares fit of the natural log of the ratio $(R/R_0)/(1-R/R_0)$ versus the natural log of the standard concentration, where R = the absorbance response for a positive standard and R_0 = the absorbance response for the zero standard. The calibration procedure requires that a zero-dose concentration be run as the first standard concentration. A concentration for any absorbance response greater than the average response for the zero standard cannot be calculated and is reported as "nd," none detected. The calibration procedure is described in detail in section 5 of the RPA-IT[™] RaPID Photometric Analyzer users manual. The concentration of the test samples is determined from the standard curve and is printed out as ppm ($\mu\text{g/mL}$). In this evaluation, this value was multiplied by a factor of 6 (see section 8.2.2.4) and by the dilution factor of the extract (usually 10) and is reported as $\mu\text{g/mL}$ (solvent spikes) or $\mu\text{g/g}$ (soil spikes). To assess the reproducibility of this test, the coefficient of variation $\{C.V. = (\text{standard deviation}/\text{mean}) \times 100\}$ was used.

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 Because this is a biological assay, the reactions are strongly dependent on temperature and the integrity of the reagents, and absolute absorbance values for the control samples may not be reproducible. The effects of these factors should, however, be independent of the BTEX concentration if the assay is to be valid. Therefore, appropriate BTEX standards must be included with each assay. A control of known BTEX concentration is also provided in the Ohmicron kit. It should be noted that because BTEX standards 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 absorbance units. **However, it is essential that all tubes, controls, and test samples be incubated for the same amount of time at each step of the assay.**
- 10.3 The negative controls should produce the highest absorbance; the positive controls should produce progressively less absorbance as their concentrations increase. If a blue color does not develop in the negative control within 5 min (Millipore test) or 20 min (Ohmicron test) after the addition of substrate, the test is invalid and should be repeated.

11.0 Performance

A series of spiked samples, solvents, and soils were prepared to assess the method's performance. The standards used to prepare these spiked samples were either total BTEX {Contract Laboratory Program (CLP-BTEX-10X, AccuStandard) or gasoline (API-91-01 from the American Petroleum Institute). *In this method total BTEX is defined as the sum of the concentrations of the six components, benzene, toluene, ethylbenzene, and the three isomers of xylene, in a mixture; e.g., a solution containing 10 µg/mL of each of the six components is referred to as 60 µg/mL total BTEX.* The concentration of the CLP-BTEX-10X standard was 12,000 µg/mL total BTEX. A gasoline standard, 7,180 µg/mL, was prepared in methanol. Subsequent dilutions, to prepare solvent or soil spikes, were made in either methanol (Millipore test) or in Ohmicron's extraction solution (calcium chloride in 75% methanol) as appropriate.

11.1 Millipore Test

11.1.1 Accuracy

Three experiments were performed using BTEX-spiked methanol (Table 1). A total of 22 independent samples were included in these experiments. Results were interpreted relative to calibrators of 0, 2, 12, and 60 µg/mL. In these three experiments, 19 of the samples were correctly interpreted and 3 were determined to be false positives.

A set of duplicate experiments was done using a total of 16 samples of a standard Rocky Mountain Arsenal (RMA) soil^(a) spiked with different concentrations of total BTEX (Table 2). Each experiment used an independently spiked and extracted set of 8 soil samples. The concentrations of all but one of the 16 independent samples were correctly interpreted.

Another set of experiments used RMA standard soil spiked with gasoline (Table 3). Six soil samples were spiked to gasoline levels in the range of 1 to 80 µg/g. Extracts of these soils were independently assayed twice, and the results were interpreted as BTEX and as gasoline. Two of the 12 analyses were found to be false positives when interpreted as gasoline; 10 were correctly interpreted.

Overall, the accuracy of the test is good. A total of 44 individual samples were tested, 22 spiked methanol solutions and 22 spiked soils. Six of the individual spiked soils were analyzed in duplicate (Table 3) for a total of 50 analyses. Of

(a) U.S. Army Toxic and Hazardous Materials Agency Report to U.S. Army Armament Research and Development Command Product Assurance Directorate, University of Maryland College of Agriculture; College Park, MD, 1981.

Table 1. Analysis for BTEX in Spiked Methanol Samples (Millipore)

Spiked Concentration ($\mu\text{g/mL}$)	Interpretation ($\mu\text{g/mL}$)		
	Experiment No. 1	Experiment No. 2	Experiment No. 3
0	-	<2	<2
0.2	-	<2	-
0.5	-	0 — 2	-
1	-	0 — 2	-
2	0 — 2	2 — 12	0 — 2
3	-	2 — 12	-
5	-	2 — 12	2 — 12
6	2 — 12	-	-
10	-	2 — 12	12 — 60 ^{FP}
12	> 12 ^{FP}	-	-
20	-	-	12 — 60
30	12 — 60	-	12 — 60
50	-	-	12 — 60
60	> 60 ^{FP}	-	-
100	-	-	> 60
120	> 60	-	-

— indicates concentrations not tested; FP indicates a false-positive interpretation.
Calibrators were 0, 2, 12, and 60 μg total BTEX/mL.

the 50 analyses, six (12%) were incorrectly interpreted as being false positives; no false negatives were observed. Three of the false positives were at concentrations equivalent to a calibrator. In this situation, it is unlikely that the absorbance of the test sample would exactly match that of the calibrator, and thus false positive, or false negative, interpretations would be statistically more prevalent than correct interpretations. The results obtained for samples 1 and 2 in Table 2 further illustrate this point as interpretations on either side of the target concentration were made.

11.1.2 Reproducibility

The data shown in Table 2 represent duplicate experiments in which two sets of soil samples were independently spiked and analyzed on separate days. They show good reproducibility of the method, including soil spiking, extraction, and extract analysis. The results in Table 3 also show very good reproducibility when soil extracts were independently analyzed on the same day. Duplicate

DRAFT

Table 2. Analysis for BTEX in Spiked RMA Soil Samples (Millipore)

Sample Number	Spiked Concentration ($\mu\text{g/g}$)	Interpretation ($\mu\text{g/g}$)	
		Experiment No. 1	Experiment No. 2
1	0	0 - 2	0
2	2	2 - 12	0 - 2
3	5	2 - 12	2 - 12
4	10	2 - 12	2 - 12
5	20	12 - 60	12 - 60
6	30	12 - 60	12 - 60
7	50	> 60 ^{FP}	12 - 60
8	100	> 60	> 60

FP indicates a false positive interpretation.

Calibrators were 0, 2, 12, and 60 μg total BTEX/mL.

Table 3. Analysis for Gasoline in Spiked RMA Soil Samples (Millipore)

Sample Number	Spiked Gasoline Concentration ($\mu\text{g/g}$)	Interpretation as BTEX ($\mu\text{g/g}$)		Interpretation as Gasoline ($\mu\text{g/g}$)	
		Assay No. 1	Assay No. 2	Assay No. 1	Assay No. 2
1	80	> 50	> 50	> 58	> 58
2	40	10 - 50	10 - 50	11 - 58	11 - 58
3	20	10 - 50	10 - 50	11 - 58	11 - 58
4	10	10 - 50	10 - 50	11 - 58 ^{FP}	11 - 58 ^{FP}
5	5	2 - 10	2 - 10	2 - 11	2 - 11
6	1	0 - 2	0 - 2	0 - 2	0 - 2

FP indicates a false positive interpretation.

Calibrators were 0, 2, 10, and 50 μg total BTEX/mL.

Table 4. Analysis for Gasoline in Three Types of Soils (Millipore)

Sample	Gasoline Equivalent Concentration (µg/g)	Absorbance (A ₄₅₀)	% A ₄₅₀ of Cal 0	Gasoline Content Based on % of Cal 0 (µg/g)	% A ₄₅₀ of Soil Blanks	Gasoline Content Based on % of Soil Blank (µg/g)
Cal 0	0	1.13	-	-	-	-
Cal 0	0	1.13	-	-	-	-
Cal 2	2	0.86	76.1	-	-	-
Cal 2	2	0.86	76.1	-	-	-
Cal 10	11	0.49	43.4	-	-	-
Cal 10	11	0.50	44.2	-	-	-
Cal 50	58	0.21	18.6	-	-	-
Cal 50	58	0.21	18.6	-	-	-
RMA	0	0.95	84.1	1.2	-	-
RMA	0	0.98	86.7	1.0	-	-
RMA	10	0.45	39.8	15.7	46.6	10.6
RMA	10	0.47	41.6	14.2	48.7	9.4
TN	0	1.01	89.4	0.9	-	-
TN	0	0.97	85.8	1.1	-	-
TN	10	0.42	37.2	18.3	42.4	13.5
TN	10	0.51	45.1	11.6	51.5	7.9
Clay	0	0.92	81.4	1.4	-	-
Clay	0	0.95	84.1	1.2	-	-
Clay	10	0.52	46.0	21.9	55.6	12.5
Clay	10	0.60	53.1	14.5	64.2	7.5

Calibrators were 0, 2, 10 and 50 µg total BTEX/mL

samples in the same assay also showed good reproducibility between absorbance measurements (Table 4).

11.1.3 Sensitivity. The sensitivity of the test can vary, depending on the type of fuel contaminant being measured. The results obtained in this evaluation indicate that a fuel contamination that is equivalent in immunoreactivity to 1 to 2 µg/g of total BTEX in the soil sample would be required to give a consistently positive

response. Reference tables on the relative reactivity of various fuel components are given in the Millipore kit instructions. Tables are also given to allow the user to correlate BTEX equivalents to concentrations of different types of fuel.

- 11.1.4 **Specificity.** The polyclonal antibody used in this test kit reacts to varying degrees with several components of petroleum products. A listing of these is included in the instructions provided with the kits.
- 11.1.5 **Matrix effects.** The possibility of matrix effects on the test was examined by using three different types of soil to determine the recovery of spiked gasoline. The RMA soil consists of about 7% sand, 67% silt, and 26% clay, and the Tennessee (TN) soil had very similar physical and chemical properties (Maskarinec et al. 1992). The "clay" soil was taken from an underground storage tank on the Oak Ridge Department of Energy reservation and was predominately clay. Duplicate 5-g samples of each soil type were spiked with methanol (0 μg of gasoline/g) or with gasoline in methanol (10 μg of gasoline/g) and extracted with 5 mL of methanol. Extraction of the "clay" samples required using 10 mL of methanol; test results were corrected for this dilution. Each extract was tested in duplicate along with the BTEX calibrators equivalent to 0, 2, 11, and 58 $\mu\text{g}/\text{mL}$ of gasoline. The results show that each of the extracts of blank soils produced less absorbance than the negative calibrator (Table 4). Based on percent of Cal 0, the negative calibrator, these were equivalent to 0.9 to 1.4 $\mu\text{g}/\text{g}$ of gasoline in the blank soils. On the same basis, the gasoline content of the three types of spiked soils ranged from 11.6 to 21.9 $\mu\text{g}/\text{g}$. Clearly, the level of gasoline detected in the blank soils does not account for the excess recovered in the spiked soils. (Note: Other laboratory analyses of these soils did not indicate the presence of fuel hydrocarbons.) If B_0 values based on the A_{450} values for the blank soils are used to estimate the gasoline content of the spiked soils, the results are in the expected range of 7.5 to 13.5 $\mu\text{g}/\text{g}$. Although it is impractical to run blank soil samples in the field, these data indicate that by using B_0 values based on the zero calibrator provided in the kit, the gasoline content of the soil is likely to be overestimated. With the semiquantitative use of the test, this would only be a problem when the fuel hydrocarbon content of the test soil is near that of a calibrator. In those cases, false positive interpretations could prevail.

11.2 Ohmicron Test

- 11.2.1 **Accuracy.** Three experiments were done using BTEX-spiked extraction solution. Nineteen independent spiked samples were analyzed, and 14 of these were assayed in duplicate—a total of 33 analyses. The concentrations of BTEX found by the immunoassay (IA) were plotted versus the expected concentrations. Composite results are shown in Figure 1. Statistically, the IA results gave a best-

Figure 1. Analysis for BTEX in Spiked Solvent Samples (Ohmicron)

Figure 2. Analysis for BTEX in Spiked Soil Samples (Ohmicron)

Figure 3. Analysis for Gasoline in Spiked Solvent Samples (Ohmicron)

fit straight line with an $R^2 = 0.983$ and a slope of 0.97, showing good agreement with the concentrations expected. For the individual experiments, the R^2 values ranged from 0.904 to 0.993 and the slopes from 0.97 to 1.21.

Three experiments were also done using BTEX-spiked TN soil (Maskarinec et al. 1992). Twenty five independently spiked samples were analyzed, 10 of them in duplicate. Composite results of the 35 analyses are shown in Figure 2. These results, with an $R^2 = 0.976$ and a slope of 0.94, were similar to those obtained for spiked solvent (see Figure 1) and showed good agreement with expected concentrations. The R^2 and slope values for the individual experiments ranged from 0.978 to 0.984 and from 0.89 to 1.04, respectively.

A single experiment using gasoline-spiked extraction solution was done. Four spiked samples ranging from 1 to 150 µg/mL were analyzed in duplicate. The best-fit straight line had an $R^2 = 0.987$ and a slope of 0.78. The slope is indicative of the lower immunoreactivity of gasoline relative to that of BTEX (compare Figures 1 and 3).

Two experiments using gasoline-spiked soil were done. In one experiment, soil samples were spiked in duplicate at ten concentrations (2.5 to 200 µg/g), and each extract assayed once. In the other experiment, five soil samples were spiked

Figure 4. Analysis for Gasoline in Spiked Soil Samples (Ohmicron)

(12.5 to 150 µg/g), and the extracts were assayed in duplicate. A composite of the results of all 30 analyses is shown in Figure 4. The R^2 and slope of the best-fit straight line were 0.957 and 0.76, respectively. The experiment using the extracts from the duplicate spiked soils gave an $R^2 = 0.952$ with a slope of 0.75, while the experiment involving duplicate assays of single extracts gave an $R^2 = 0.989$ and a slope = 0.78. The results shown in Figures 3 and 4 are consistent in indicating the lower immunoreactivity of the gasoline used as compared with BTEX (Figures 1 and 2).

Overall, the results show that the test accurately measured BTEX in solvent and in soil (Figures 1 and 2). They also show that the gasoline standard used, API-91-01, is measured about 75% as efficiently as BTEX, undoubtedly due to differences in immunoreactivity. After adjusting for this difference, however, gasoline is also accurately measured in this test.

11.2.2 Reproducibility. The reproducibility of the Ohmicron test was assessed by comparing the coefficient of variation (C.V.) for various parameters of the test for gasoline. These included a) duplicate assays of single, solvent spikes, b) duplicate assays of single, soil spikes, and c) single assays of duplicate, soil spikes. For this comparison, only samples with concentrations in the range of 10 to 150 µg/mL(g) were used. The average C.V. for duplicate assays of single, solvent spikes was 8.9%; for duplicate assays of single, soil spikes, 12.1%; and

for single assays of duplicate, soil spikes, 25.9%. The results show that an acceptable level of variation was obtained among repeat assays of single extracts (average C.V. of 10.5%), but that the extraction procedure may add additional variability to the test.

11.2.3 Sensitivity. The sensitivity of the test can vary, depending on the type of fuel contaminant being measured. The results obtained in this evaluation indicate that a fuel contamination that is equivalent in immunoreactivity to 1 to 2 µg/g of total BTEX in the soil sample would be required to give a consistently positive response.

11.2.4 Specificity (see section 11.1.4)

11.2.5 Matrix effects. Although a detailed evaluation of potential matrix effects on the Ohmicron test was not made, extracts of blank soils consistently produced less absorbance than the zero standard. This could lead to an overestimation of the petroleum fuel content in soil samples containing low levels of analyte (refer to section 11.1.5).

11.3 Summary of Performance

Both of the test kits used in this evaluation are rapid, easy to use, accurate, and reproducible assays for petroleum fuels in soil. Use of this field screening method could decrease both the time and cost of assessing and remediating contaminated sites.

11.3.1 (Millipore) - Millipore's EnviroGard™ Soil Extraction Bottle and Petroleum Fuels in Soil Test Kits was used in a semiquantitative mode to estimate the content of petroleum fuel hydrocarbons in solvent and soil. In this evaluation, 12% false-positive results and no false negatives were obtained. Three of the false-positive observations were for samples whose concentration were the same as that of a positive calibrator, a situation where a high frequency of false positives and false negatives would be expected on a statistical basis alone. Uncharacterized soil matrix effects may increase the frequency of false-positive test results in those test samples whose analyte concentrations are very near the concentration of one of the positive calibrators.

11.3.2 (Ohmicron) - Ohmicron's Soil Collection, Sample Extraction, and BTEX Assay Kits were used in a quantitative mode to estimate the content of petroleum fuel hydrocarbons in solvent and soil. In this evaluation, direct comparisons of the response of the Ohmicron kit and the quantity of BTEX in the solvent and soil sample spikes yielded slopes of 0.94 to 0.97, with correlation coefficients, R^2 , between 0.976 and 0.983. Gasoline in solvent and soil was consistently detected

as about 0.75 BTEX equivalents, which reflects the decreased immunoreactivity of the gasoline used in the test relative to that of BTEX.

12.0 Reference

M. P. Maskarinec, C. K. Bayne, R. A. Jenkins, L. H. Johnson, and S. K. Holladay. 1992. *Stability of Volatile Organics in Environmental Soil Samples*. ORNL/TM-12128. Oak Ridge National Laboratory. (Available from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.)

OP040R(a)

Reduced-Scale Zero Headspace Extraction for TCLP Volatiles in Shielded or Containment Conditions

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 the equipment and procedure for conducting zero headspace extraction (ZHE) of solid radioactive wastes or solids separated from liquid radioactive mixed wastes that require handling under containment or shielding. It is designed to comply with the U.S. Department of Energy (DOE) "as low as reasonably achievable" (ALARA) principle and to minimize secondary waste generation. This reduced-scale method is based upon SW-846 method 1311 (EPA 1992) (Toxicity Characteristic Leaching Procedure) and the Nuclear Regulatory Commission - U.S. Environmental Protection Agency (EPA) proposed guidance document^(b) on the testing of mixed radioactive and hazardous wastes. It involves the use of a gas-tight syringe and Teflon[®] or stainless steel valves and filter cartridges for the ZHE and leachate filtration. The scale of the leaching has been reduced, but the proportions and chemistry of the SW-846 method have been maintained. A syringe tumbler designed for glovebox or hot-cell operations is used to tumble the syringes.
- 1.2 This method is designed for ZHE of Toxicity Characteristic Leaching Procedure (TCLP) volatile organic compounds (VOCs) (Table 1), but it could also be employed for the nonvolatile leaching of metals and TCLP semivolatile organic compounds if the pH test and appropriate extraction fluid are used.
- 1.3 This method covers the ZHE only and does not include the analysis of the TCLP volatile organics. Facilities, instruments, and a procedure for the analysis of the TCLP VOCs in radioactive liquids are required to identify and measure the VOCs in the leachate.

(a) This method was supplied by R. L. Schenley, P. F. Wolfe, and W. H. Griest (Oak Ridge National Laboratory, Chemical and Analytical Sciences Division, Oak Ridge, Tennessee).

(b) Clarification of RCRA Hazardous Waste Testing Requirements for Mixed Waste," Draft Guidance, Nuclear Regulatory Commission and Environmental Protection Agency, Federal Register, 57(59), 10508 (Thursday, March 26, 1992).

DRAFT

1.4

It is recommended that a direct (or "total" as referred to in SW-846 Method 1311) analysis of the VOCs in radioactive waste be performed, and that ZHE for leachable VOCs be conducted only in cases where the direct analysis suggests that TCLP regulatory limits may be exceeded.

Table 1. TCLP Volatile Organic Compounds

Compound	Abbreviation	CAS No.
Benzene	Bz	71-43-2
Carbon tetrachloride	CCl ₄	56-23-5
Chlorobenzene	CB	108-90-7
Chloroform	CF	67-66-3
1,4-Dichlorobenzene	DCB	106-46-7
1,2-Dichloroethane	DCE	107-06-2
1,1-Dichloroethene	1,1-DCE	75-35-4
Methyl ethyl ketone	MEK	78-93-3
Tetrachloroethylene	Cl ₂ E	127-18-4
Trichloroethylene	TCE	79-01-6
Vinyl chloride	VCl	75-01-4
1,2-Dichloroethane-d ₄ ^(a)	DCE-d ₄	1868-53-7
Toluene-d ₈ ^(a)	Tol-d ₈	5203-92-9
Bromofluorobenzene ^(a)	BFB	460-00-4

(a) Denotes surrogate standards

2.0 Summary of Method

- 2.1 In a radiochemical hood, glovebox, or hot cell, waste samples (1 to 5 g) are weighed out and transferred to the gas-tight syringe. A 20-fold mass of TCLP extraction fluid No. 1, as described in SW-846 Method 1311, is introduced into the syringe, bubbles are driven out, and the syringe valve is closed.
- 2.2 The syringe is tumbled for 18 h at 30 rpm.
- 2.3 The required volume of leachate is forced into a vial using a syringe filter cartridge attached to the outlet of the syringe valve. Following facility health physics procedures, the vial is transferred to an analytical instrumentation area for the volatile organic analysis (VOA).

Caution: As required by the DOE ALARA principle to minimize radiation exposure and contamination of personnel and facilities, it is imperative to follow all radiochemistry laboratory procedures for handling radioactive samples and for health physics monitoring.

3.0 Interferences

- 3.1 The major interference is contamination from sources of volatile materials within the laboratory. Organic solvents should not be handled in the same laboratory as the ZHE. Samples suspected of being highly contaminated with solvents should be segregated from those for the ZHE.
- 3.2 This method is subject to the same losses of VOCs as those described in SW-846 Method 1311.

4.0 Safety

- 4.1 When handling radioactive samples, all applicable radiochemical handling procedures and health physics monitoring practices should be followed.
- 4.2 Because it is likely that the acidic leaching fluid will leach radionuclides from radioactive wastes, it is important that the leachate be analyzed for radioactivity before transport to the analytical laboratory.
- 4.3 Gloves and protective clothing should be worn to protect against unnecessary exposure to organic contaminants.

5.0 Apparatus and Materials

- 5.1 **Tumbling Apparatus:** The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm. Because no suitable commercial tumbler was available for use in a glovebox or hot cell, a tumbler and syringe-holder mechanism was designed, and a prototype was constructed. Figures 1 and 2 show assembled and exploded views (respectively) of the tumbler with syringes. The syringe holder (Figure 3) of the tumbler was designed with a gate into which the syringe can be placed and held while other manipulations are completed. The locking mechanism of the gate can be conveniently handled using the heavy gloves or remote manipulators in a glovebox or hot cell. A lever mechanism (Figure 4) was designed to hold the plunger of the syringe in an appropriate position and to serve as a locking system for the syringe plunger during tumbling. Since the size of the sample may vary, the lever mechanism is adjustable over the volume range of the syringe. After the leaching period is complete, the lever arm is unlocked and used to force the extraction

DRAFT

Figure 1. Tumbler and Syringes for Reduced-Scale, Modified ZHE

Figure 2. Exploded View of Tumbler and Syringes

DRAFT

Figure 3. Syringe Holder

DRAFT

Adapted/Organic

Figure 4. Syringe Holder with Lever Arm Assembly

fluid through a filter cartridge for collection and analysis. To conform with Occupational Safety and Health Administration (OSHA) safety regulations, a safety interlock stop/start switch (Figure 5) was attached to the tumbler. The start/stop switch is located away from the main body of the tumbler to prevent remote manipulators or gloves from being entangled with the rotating platform. The tumbler is mounted on a heavy (ca. 26.5 x 26.5 x 1.5 cm thick) steel base equipped with rubber-coated feet to provide a stable, non-moving foundation.

All of the parts that require remote handling are designed to either be controlled by manipulators within a hot cell or easily grasped when used with heavy gloves in a glovebox. The major structural components are easily detached to facilitate introduction of the tumbler into appropriate containment and disassembly and removal when it is no longer needed.

5.2 Zero Headspace Extractor: The zero-headspace extraction vessel is a 100-mL gas-tight glass syringe with a Teflon[®]-tipped plunger and a Luer lock fitting. Suitable sources of syringes include Unimetrics Corporation (Shorewood, Illinois), Alltech Associates, Inc. (Deerfield, Illinois), and Associated Design and Manufacturing Co. (Alexandria, Virginia). The syringe is fitted with a two- or three-way stainless steel valve with Luer lock fittings (Popper and Sons, Inc., New Hyde Park, New York, and Alltech Associates, Inc., Deerfield, Illinois).

5.3 Filter cartridge (25 mm) (Gelman Sciences, Ann Arbor, Michigan, or equivalent) with a borosilicate glass filter, pore size 0.6 to 0.8 μm , and containing no binder materials.

5.4 Glass vials of 8- to 40-mL capacity with Teflon[®]-lined screw caps.

5.5 Teflon[®] tubing, ca. 60 cm length x 5 mm ID.

6.0 Reagents

TCLP extraction fluid No. 1, prepared according to SW-846 Method 1311.

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

8.0 Procedure

8.1 To load the syringe, the plunger is pulled out, and the weighed solid or sludge is placed in the barrel of the syringe. Alternatively, the sample can be directly weighed into the syringe barrel. The sample size can vary between 1 to 5 g depending upon the amount of

DRAFT

Adapted/Organic

Figure 5. Base Plate with Lockout Start/Stop Switch

material available, the specific radioactivity of the sample, and the capacity of the syringe. The plunger is inserted and depressed to a position adjacent to the solid. The extraction fluid is drawn into the syringe, and all bubbles are removed before closing the valve by inverting the syringe, tapping the side, and depressing the plunger to expel any bubbles. The valve is closed.

- 8.2 The loaded syringe is placed on the tumbler, locked in position using the gate and lever-arm assembly, and rotated for 18 h. At the end of the tumbling cycle, the syringe is inspected for leaks and/or the presence of bubbles.
- 8.3 The syringe should be oriented in a vertical position to remove the extraction fluid with most waste samples. For wastes that easily plug the filter, orienting the syringe to point upward may minimize filter clogging. However, fine particles may be trapped between the syringe plunger and wall, causing the wall to score and the plunger to freeze. Other orientations may be required for some wastes.
- 8.4 The 25-mm filter-cartridge assembly is attached to the syringe valve, and a piece of Teflon[®] tubing is attached to the outlet of the filter cartridge to facilitate filling the collection vial.
- 8.5 The set screw on the lever-arm plunger is loosened. The extraction fluid is forced through the filter by depressing the lever arm. The fluid is collected into an appropriate vial for the VOA. An aliquot also should be taken for gross alpha/gross beta screening. The filter cartridge may be replaced during filtering if it clogs before a sufficient volume of leachate has been collected.

9.0 Quality Control

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.

10.0 Method Performance

- 10.1 The performance of the reduced-scale ZHE ("modified ZHE") was compared to the SW-846 Method 1311 protocol ZHE ("ZHE"). The ability of the ZHEs to preserve VOCs leached from wastes and to prevent contamination was compared by loading both zero headspace extractors with TCLP extraction fluid No. 1 and by spiking with the TCLP VOCs at 100 to 200 ppb. After the 18 h tumbling, samples of the fluids were spiked with VOA surrogate standards and were analyzed using SW-846 method 8260. Three standard ZHEs and three modified ZHEs were run (referred to as the three "duplicates" in

the statistical evaluation), three aliquots were withdrawn for analysis from each ZHE, and two aliquots were withdrawn from each modified ZHE. (The aliquots taken from each ZHE are the two or three "replicates" in the statistical evaluation.)

The recoveries of TCLP VOCs also were compared using spikes added to samples of Rocky Mountain Arsenal standard soil (SOIL-TCLP) and Los Alamos National Laboratory (LANL) surrogate wastewater treatment process sludge (LANL-TCLP) in TCLP extraction fluid No. 1 and tumbled for 18 h using the standard ZHE and the modified ZHE. In these experiments, two ZHEs and three modified ZHEs were run, and three aliquots were withdrawn from each ZHE and two from each modified ZHE. Spike concentrations were 100 ppb in the extraction fluid of the ZHE and modified ZHE, except for the standard soil in the modified ZHE where 200 ppb was used.

The modified ZHE was much easier to conduct than was the standard ZHE. The modified ZHE was easier to de-gas and de-bubble than the standard ZHE because of its smaller size, more convenient plunger control, and clear body. Filter plugging was a serious problem with the standard ZHE when the standard soil was leached, but was less of a problem when the LANL sludge was leached. It is possible that letting the contents of the standard ZHE settle for 30 min to 1 h might have reduced plugging problems. In contrast, the modified ZHE performed smoothly, and no filter plugging problems were experienced. The syringe in the modified ZHE also is much easier to clean than is the EPA protocol zero-headspace extractor. It also is much less expensive (\$50 to \$200, depending on supplier and model) than is the EPA protocol zero-headspace extractor (more than \$1,000) and can be simply discarded if it is badly contaminated.

The results from the experiments are listed in Tables A.1 and A.2 in Appendix A. Neither ZHE allowed external contamination of the leachates, and the total ion-current chromatograms from the VOA were almost identical to each other. In general, the recoveries of the TCLP VOCs were very close for the two ZHEs, and only small differences were apparent. A more detailed evaluation follows.

- 10.2 Statistical Analysis:** The concentrations of the 11 spiked TCLP VOCs were determined in each aliquot, and the recoveries were calculated. Table A.1 gives the 39 measured percent recovery values {i.e. $100\% \times (\text{concentration measured})/(\text{concentration spiked})$ }. A summary of the VOA surrogate standard recoveries is given in Table A.2.

The method of analysis of variances was used to estimate the significant effects for the two different ZHE methods and the three different matrices (TCLP, LANL-TCLP, and SOIL-TCLP). The linear model used to represent the percent recoveries is

$$\% \text{ Recovery} = \text{Overall Average} + \text{Method} + \text{Matrix(Method)} + \text{Experimental Error}$$

where

Method = Modified or standard ZHE method

Matrix (Method) = Matrix type nested within the ZHE method for a given day

Experimental Error = Experimental variation as measured by the different results for duplicate measurements. There are 10 degrees of freedom associated with the estimated standard deviation for this error.

Table 2 shows the average percent recoveries and the standard deviation of the experimental error. The recoveries were similar for the modified ZHE and the standard ZHE, with the exception of VCl, CCl₄, and MEK. Figure 6 shows the percent recovery difference between the modified ZHE method and the standard ZHE method. The two-sided 95% confidence intervals are included to judge significant increases or decreases in the percent recovery averages. Confidence intervals including zero indicate that the percent recoveries from the two methods cannot be distinguished. Where the lower confidence interval is above zero, the modified ZHE method performed significantly better than the standard ZHE method. Where the upper confidence interval is lower than zero, the modified ZHE method performed significantly worse than the standard ZHE method. For 10 VOCs, the modified ZHE method was comparable to or better than the standard ZHE method. For MEK, the standard ZHE method performed better than the modified ZHE method.

- 10.3 Matrix Effects.** The performance of the two ZHE methods depends on the sample matrix. Matrix effects for LANL surrogate sludge and a standard soil were compared with TCLP extraction fluid No. 1 (e.g., LANL-TCLP, or Soil-TCLP). Figure 7 shows these matrix comparisons for each ZHE method. The comparisons are made relative to the standard deviation of the differences between two matrices. Differences more than 2 standard deviations are either significant increases (positive results) or significant decreases (negative results) at about the 5% significant level. Most of the results show decreases from the TCLP extraction fluid No. 1, as is expected for sorption of the compounds by the sample matrices. The decreases are usually larger for the standard ZHE method than the modified ZHE method.

Table 2. Average Percent Recovery Values and the Standard Deviation of the Experimental Error with Associated 10 Degrees of Freedom

Volatile Organic Compounds	Symbol	ZHE Extraction Methods		Overall Average	Exp. Error Standard Deviation
		Modified N=18	Standard N=21		
Vinyl chloride	VCl	60.7	49.0	54.4	18.1
1,1-Dichloroethene	1,1-DCE	57.3	61.9	59.8	15.6
Methyl ethyl ketone	MEK	90.3	111.6	101.8	10.3
Chloroform	CHCl ₃	82.2	83.0	82.6	10.4
Carbon tetrachloride	CCl ₄	76.6	67.0	71.4	12.5
1,2-Dichloroethane	1,2-DCA	95.7	99.8	97.9	9.3
Benzene	Bz	75.0	83.2	79.4	10.5
Trichloroethene	TCE	77.7	72.0	74.6	10.2
Tetrachloroethene	Cl ₄ E	64.4	55.4	59.6	8.5
Chlorobenzene	ClBz	83.3	80.0	81.5	7.4
1,4-Dichlorobenzene	Cl ₂ Bz	74.4	61.6	67.5	5.9

N = number of samples

Figure 6. Recovery Differences Between Modified ZHE and ZHE with 95% Confidence Intervals

DRAFT

Figure 7. Matrix Effect Comparisons of Standard and Modified ZHE Methods on the Standard Soil and the LANL Surrogate (see section 10.3).

- 10.4** Variance components. Variations of the percent recoveries were examined to determine the different sources for each method. Table 3 lists the estimated standard deviations for three components of variation (matrix, duplicates, and replicates within duplicates).

Standard deviations for the modified ZHE method are lower or equivalent to those for the standard ZHE method for all sources of variation. A contributing factor to higher standard deviation values for the standard ZHE method was that the standard ZHE method is more liable to filter plugging than the modified ZHE. The modified ZHE was much easier to perform, and leachate collection proceeded more smoothly.

10.5 Conclusions

- 10.5.1** The modified ZHE is much easier to perform than is the standard ZHE, especially under shielding or containment. The operator handles less waste (reducing exposure to radioactive materials) and generates less laboratory waste.

Table 3. Standard Deviations Estimated for Different Sources of Variation of the Percent Recoveries.							
Volatile Organic Compounds	Modified ZHE Method			Standard ZHE Method			Rep/Dup
	Matrix	Duplicate	Rep/Dup	Matrix	Duplicate	Rep/Dup	
Vinyl chloride	13.4	11.8	6.2	10.7	22.2	22.7	
1,1-Dichloroethene	0	18.4	14.7	18.6	17.8	16.2	
Methyl ethyl ketone	2.4	10.4	6.5	12.3	14.3	12.1	
Chloroform	7.1	6.3	3.6	11.0	13.3	13.0	
Carbon tetrachloride	6.3	12.4	6.8	21.3	17.8	15.1	
1,2-Dichloroethane	0	8.8	3.4	9.7	13.1	11.7	
Benzene	11.4	5.1	3.5	16.1	14.0	13.2	
Trichloroethene	3.7	8.1	4.7	16.1	13.2	12.6	
Tetrachloroethene	3.9	7.7	4.4	15.4	11.0	10.3	
Chlorobenzene	2.3	6.7	3.4	14.5	10.3	9.0	
1,4-Dichlorobenzene	1.5	5.4	2.5	10.9	6.9	7.3	

10.5.2 The modified ZHE method has an accuracy equivalent to or better than the standard ZHE method for all the TCLP VOCs tested, except for MEK. The modified ZHE method is not as sensitive to matrix effects as is the standard ZHE method.

10.5.3 The modified ZHE method has a smaller standard deviation (i.e., better precision) than the standard ZHE method for the three components of variation (i.e., matrix, duplicates, and replications within duplicates).

10.5.4 Although the apparatus and method described in this protocol allow ZHE of radioactive wastes under shielding or containment, the greatest source of VOC losses is in the waste sample collection and preanalytical handling. Therefore, a direct (or "total") analysis of VOCs is recommended. Zero headspace extraction should be reserved for only those samples whose direct analysis suggests that TCLP Regulatory Limits may be exceeded.

11.0 Reference

U.S. Environmental Protection Agency (EPA). 1992. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, Third 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

Siegrist, R. L. 1992. "Volatile Organic Compounds in Contaminated Soils: The Nature and Validity of the Measurement Process." *J. Hazard. Mat.* 29:3-15.

Siegrist, R. L. and P. D. Jenssen. 1990. "Evaluation of Sampling Method Effects of Volatile Organic Compound Measurements in Contaminated Soils." *Environ. Sci. Technol.* 24:387-392.

DRAFT

Adapted/Organic

Appendix A

Experimental Results of Standard ZHE and Modified ZHE Tests

Table A.1 Percent Recovery Data from the ZHE Methods Comparison Experiment

OBS Method	Matrix	Dup	Rep	VCL	DCE	MEK	CHCl ₃	CCl ₄	DCA	Bz	TCE	Cl ₄ E	CIBz	Cl ₄ Bz
1 Mod ZHE	TCLP	1	1	59.0	42.7	79.0	80.2	62.4	87.1	62.7	69.7	55.4	75.4	69.1
2 Mod ZHE	TCLP	1	2	45.3	29.6	95.9	73.8	50.8	85.0	60.2	61.0	49.1	71.6	71.0
3 Mod ZHE	TCLP	2	1	84.5	53.9	96.5	91.5	90.3	96.2	67.2	85.8	75.2	89.3	86.0
4 Mod ZHE	TCLP	2	2	86.0	54.4	107.0	92.0	91.4	98.7	68.2	86.9	74.9	89.8	83.7
5 Mod ZHE	TCLP	3	1	84.6	96.5	88.5	92.0	92.0	97.9	68.6	86.7	74.7	87.9	77.6
6 Mod ZHE	TCLP	3	2	88.0	76.9	86.7	92.2	93.0	99.6	71.5	86.2	71.6	88.7	76.5
7 Mod ZHE	SOIL	1	1	61.5	49.5	86.6	77.5	76.7	89.9	71.4	75.2	62.4	78.2	69.2
8 Mod ZHE	SOIL	1	2	41.4	39.1	69.9	69.2	51.8	81.0	60.8	61.7	48.5	68.7	67.8
9 Mod ZHE	SOIL	2	1	35.9	32.5	97.0	67.4	60.1	94.6	66.8	67.0	56.8	77.5	75.2
10 Mod ZHE	SOIL	2	2	38.6	62.4	99.7	69.4	63.8	99.7	70.0	70.4	58.4	80.0	77.3
11 Mod ZHE	SOIL	3	1	46.7	73.5	103.0	75.8	72.9	111.0	76.4	76.2	60.4	84.2	74.8
12 Mod ZHE	SOIL	3	2	52.8	44.3	107.0	81.2	78.5	114.0	77.7	81.9	65.3	88.8	79.0
13 Mod ZHE	LANL	1	1	64.8	47.1	83.5	93.0	87.4	101.0	94.5	86.4	70.8	91.5	73.1
14 Mod ZHE	LANL	1	2	60.7	72.7	83.2	85.1	81.4	95.1	87.1	79.2	64.6	85.6	69.7
15 Mod ZHE	LANL	2	1	60.1	74.3	81.3	83.4	79.9	92.0	85.3	80.3	67.7	84.1	71.3
16 Mod ZHE	LANL	2	2	58.7	70.4	75.7	78.2	77.8	85.3	81.0	75.2	62.8	78.7	65.6
17 Mod ZHE	LANL	3	1	63.4	41.7	94.9	89.6	84.5	98.2	91.4	85.6	71.7	91.1	79.4
18 Mod ZHE	LANL	3	2	59.9	70.0	89.9	87.7	83.4	97.1	89.6	82.4	68.5	88.7	73.8
19 Std ZHE	TCLP	1	1	59.7	82.8	114.4	90.3	84.3	105.2	93.9	83.1	66.4	86.3	64.7
20 Std ZHE	TCLP	1	2	55.0	76.1	105.4	83.5	78.6	95.0	87.1	79.1	63.6	82.9	61.4
21 Std ZHE	TCLP	1	3	57.5	75.9	108.9	82.8	79.1	96.5	87.4	78.0	62.3	83.1	62.3
22 Std ZHE	TCLP	2	1	73.9	98.8	145.9	107.0	105.0	127.0	114.0	100.0	79.8	105.0	73.3
23 Std ZHE	TCLP	2	2	67.9	95.4	133.7	102.0	104.0	122.0	110.0	94.9	72.4	101.0	67.2
24 Std ZHE	TCLP	2	3	69.5	99.6	139.4	106.0	108.0	127.0	114.0	98.4	74.4	106.0	67.9
25 Std ZHE	TCLP	3	1	68.2	65.1	114.0	85.9	70.2	104.0	89.8	75.3	54.8	84.4	58.6
26 Std ZHE	TCLP	3	2	40.9	64.4	119.5	86.8	70.5	103.0	90.7	78.8	62.7	88.7	72.7
27 Std ZHE	TCLP	3	3	39.3	63.0	128.2	82.8	70.0	107.0	90.0	73.3	50.6	84.6	55.2
28 Std ZHE	SOIL	1	1	87.7	71.6	127.4	92.9	63.8	109.0	85.9	71.4	51.7	75.1	56.9
29 Std ZHE	SOIL	1	2	32.3	28.8	88.8	57.5	26.5	75.1	53.6	41.9	26.5	56.6	45.7
30 Std ZHE	SOIL	1	3	48.5	26.8	89.7	52.4	26.0	76.4	50.0	37.3	23.0	50.3	37.4
31 Std ZHE	SOIL	2	1	82.5	80.1	137.2	91.0	77.2	114.0	91.0	76.5	51.5	78.1	50.4
32 Std ZHE	SOIL	2	2	39.0	47.3	104.0	74.3	46.0	90.6	70.7	58.7	43.8	70.5	58.3
33 Std ZHE	SOIL	2	3	11.8	13.1	101.1	42.1	13.4	70.4	36.5	24.8	14.8	41.9	37.7

Table A.1 Contd

OBS Method	Matrix	Dup	Rep	VCI	DCE	MBK	CHCl ₃	CCl ₄	DCA	Bz	TCB	Cl ₂ E	ClBz	Cl ₂ Bz
34 Std ZHE	LANL	1	1	83.8	60.8	98.6	89.8	71.9	93.5	82.6	76.7	64.8	78.9	68.9
35 Std ZHE	LANL	1	2	23.5	56.6	95.4	83.2	74.4	104.0	85.5	78.4	62.6	84.1	66.8
36 Std ZHE	LANL	1	3	25.0	57.9	93.2	86.5	71.7	92.8	82.6	77.9	68.4	83.7	79.1
37 Std ZHE	LANL	2	1	30.2	49.2	104.5	89.2	57.1	96.5	80.5	73.3	58.8	80.6	73.6
38 Std ZHE	LANL	2	2	17.1	49.9	98.0	82.0	64.7	98.0	81.3	73.5	62.8	83.5	71.2
39 Std ZHE	LANL	2	3	15.7	36.6	95.7	75.7	45.4	88.8	70.0	61.4	48.4	75.3	63.9

Table A.2 Summary of VOA Surrogate Standard Recoveries from Leachates
Generated using the Standard ZHE and the Modified ZHE

Compound	Average % Recovery		Standard Deviation		% Relative Standard Deviation	
	Std ZHE	Mod ZHE	Std ZHE	Mod ZHE	Std ZHE	Mod ZHE
TCLP Extraction Fluid No. 1						
DCE-d ₄	91.7	103	3.10	5.18	3.38	5.02
Tol-d ₈	101	105	5.18	7.01	5.13	6.71
BFB	89.0	100	3.54	5.48	3.97	5.48
TCLP Extraction Fluid No. 1 + Standard Soil						
DCE-d ₄	92.8	102	4.10	5.05	4.41	4.97
Tol-d ₈	99.5	106	5.84	4.56	5.89	4.31
BFB	87.9	110	3.99	6.04	4.54	5.49
TCLP Extraction Fluid No. 1 + LANL Surrogate Sludge						
DCE-d ₄	104	105	4.88	2.56	4.68	2.45
Tol-d ₈	105	109	2.79	2.63	2.67	2.42
BFB	104	102	5.15	2.41	4.96	2.36

OM500R(a)

Qualitative Analysis for Low-Molecular-Weight Organic Acids in Mixed Hazardous Waste Samples by Thermospray LC-MS

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 the analysis of low-molecular-weight organic acids (LMWA), including formic, acetic, propionic, glyoxylic, glycolic, gluconic, citric, and tartaric acids, in mixed hazardous waste samples by thermospray liquid chromatography-mass spectrometry (LC-MS).^(b) Diglycolic acid and N-nitroso-iminodiacetic acid (NIDA) can also be determined by this method.
- 1.2 The method is applicable to wastes with radioactivity ranging from none to high. A lab bench, glovebox, or hot cell is used as appropriate, i.e., according to site-specific cutoff levels.

2.0 Summary of Method

- 2.1 Most of the radioactivity is removed from samples (pH>11) using a cation-exchange column. The pH is adjusted to 2.5 to 4, and the sample is filtered.
- 2.2 The sample is analyzed by thermospray LC-MS using an ion-exclusion column.

3.0 Interferences

- 3.1 Oxalic acid is not observed under acidic conditions with thermospray LC-MS. Under the LC conditions used here with an acid-exclusion column, oxalic acid elutes with nitrate and is masked by the strong signal of nitrate present in most waste samples. A

(a) This method was supplied by J. A. Campbell, K. L. Wahl, K. E. Grant, S. A. Clauss, G. M. Mong, R. B. Lucke, and B. D. Lerner (Pacific Northwest Laboratory, Richland, Washington).

(b) Grant, K. E., R. B. Lucke, S. A. Clauss, G. M. Mong, B. D. Lerner, and J. A. Campbell. 1994. "The Application of HPLC and Thermospray LC/MS to the Analysis of Small Organic Acids in Mixed Hazardous Wastes" has been submitted to *Anal. Chem.*

more appropriate analysis method for oxalic acid would use an ion-exchange column and atmospheric-pressure chemical-ionization MS with negative ion detection.

- 3.2 Nonvolatile inorganic species do not interfere if they are soluble in the mobile phase.
- 3.3 Under the conditions used (i.e., 0.001 N HCl as mobile phase), tartaric acid is a shoulder on the citric acid peak, and glyoxylic acid is a shoulder on the gluconic acid peak. This may not be a problem because neither tartaric acid nor gluconic acid is likely to be a constituent of a real waste sample. In addition, the ions used for qualitative analysis are different for the special problems mentioned above.
- 3.4 Glyoxylic acid is labile; the aldehyde function oxidizes readily to produce oxalic acid. A glyoxylic acid standard should be made up daily if quantitation is desired.
- 3.5 Hexanoic acid, which is not very soluble in water, cannot be detected by this method.
- 3.6 Large background effects are a persistent problem if mass spectra are scanned at mass values much less than 80. This may be the result of hydrated chloride species. An ion-suppression column for removing chloride ions would make it easier to detect lower-molecular-weight acids, such as formic acid.

4.0 Safety

- 4.1 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.
- 4.2 Radioactive components in samples may be eluted through the entire system and into the thermospray source. Radioactive components tend to concentrate at the source area where solvent degassing occurs and do not spread to other parts of the MS. Contamination of the MS system caused by using this method should be determined before instrument maintenance. Also, due to the problem of possible contamination, if the thermospray probe becomes plugged, precautions should be taken when changing the probe.

5.0 Apparatus and Materials

- 5.1 **Mass Spectrometer:** Hewlett Packard 5988A MS with thermospray interface, or equivalent

- 5.2 High-Performance Liquid Chromatograph (HPLC):** Analytical system complete with LC pump and controller with appropriate injector, valves, solvent degasser, analyte separation column, ultraviolet (UV) detector, and a printer/plotter. An autosampler is recommended so that samples can be injected from septum-sealed vials to help maintain control of radioactive samples.
- 5.2.1 HPLC column:** Bio-Rad organic acids column, Aminex Ion Exclusion, HPX-87H, 300 x 7.8 mm, or equivalent. An appropriate guard column is highly recommended.
- 5.3 Column for Sample Cleanup:** Bio-Rad analytical-grade cation-exchange column, AG 50W-X8, 50 to 100 mesh, sodium form, (or equivalent) for removing radioactivity
- 5.4 Syringe-Tip Filters:** Gelman Acrodisc LC13, 0.45- μ m pore size filters or equivalent
- 5.5 pH Meter:** with pH probe covering the pH range of at least 2 to 12
- 5.6 Volumetric Flask:** 25 mL
- 5.7 LC Vials:** compatible with autosampler
- 5.8 Solvent Filtering System**
- 5.9 Analytical Balance:** for standard preparation, to 0.01mg
- 5.10 Analytical Balance:** for sample weighing, to 0.1 mg
- 6.0 Reagents**
- 6.1 Reagent Water:** deionized water using a deionizer with an organic removal cartridge; Milli-Q (Millipore Corp., Bedford, Massachusetts) or equivalent
- 6.2 Standards:** gluconic, formic, acetic, citric, tartaric, glycolic, glyoxylic, and hexanoic acids
- 6.3 Standard:** NIDA is synthesized as follows. To a 500-mL, 4-necked flask—equipped with an overhead stirrer, an addition funnel, and a thermometer—were added 26.6 g (20 mmoles) of iminodiacetic acid and 200 mL of 1 M phosphoric acid. The contents of the flask were heated to 50°C, and a solution of 27.6 g (400 mmoles) of sodium nitrite in 60 mL of water was added dropwise. The reaction was stirred for 1 h and extracted with five 100-mL portions of diethyl ether. The ether extract was dried using MgSO_4 and

concentrated to yield a yellowish-white residue which, after recrystallization from ethyl acetate-hexane, yielded 13 g of nitroso acid.

- 6.4 **Preparation of Calibration Standards:** A series of standard solutions should be prepared with organic acid concentrations in the same range as expected in the waste samples. If glyoxylic acid is used in the standard, this solution should be made fresh each day it is used to avoid errors when this acid oxidizes to form oxalic acid.
- 6.5 **Mobile Phase Acid:** hydrochloric acid
- 6.6 **Mobile Phase:** 0.001 N HCl for LC-MS. Approximately 90 μ L of 12 N HCl is diluted to 1 L of H₂O. The resulting solution should have a pH of 2.5. The pH is adjusted with dilute NH₄OH if necessary.
- 6.7 **Polyethylene Glycol:** for MS tuning and calibration
- 6.8 **pH Standards:** commercial pH 4, 7, and 10 standards
- 6.9 **Helium:** at least 99.9% purity. Purge gas for mobile phase, 0 to 7.5 psi
- 6.10 **Compressed Air:** breathing air quality. For autosampler operation, 75 psi

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

8.0 Procedure

8.1 Sample Preparation

- 8.1.1 To remove radioactivity, a remote-handling hot cell or sample-preparation laboratory is used, depending on the level of radioactivity. The sample is flushed through a cation-exchange column (Na⁺ form) to remove most of the radioactivity caused by primary fission products in the waste. This procedure has only been tested on solutions with pH > 11 and should be performed with caution at lower pH conditions as analyte may be lost.
- 8.1.2 It should be verified that the majority of the radioactivity has been removed.
- 8.1.3 A 1-g quantity of the cation-exchanged waste sample is weighed and placed in a 25.0-mL volumetric flask.

- 8.1.4 The pH of the sample is adjusted with HCl to match the pH of the mobile phase as monitored with an extended-scale pH meter. This may require judicious dropwise addition of 0.5 M HCl to approximate the proper pH of the mobile phase. Then 0.001 N HCl mobile-phase solution is added to dilute the solution to a final volume of 25.0 mL. The final solution should be approximately pH 2.5 to 4.
- 8.1.5 An aliquot of the solution is filtered into an LC vial using a Gelman Acrodisc LC13, 0.45- μ m syringe-tip filter (or equivalent) to remove small particulates that could clog the LC column and/or the thermospray interface probe. About 20 μ L of this filtered solution are used for LC-MS analysis.

8.2 LC-MS Analysis

8.2.1 LC Conditions

Mobile phase: 0.001 N HCl, isocratic
Oven temperature: 40°C
Flow rate: 0.6 mL/min
Run time: typically, about 25 min

8.2.2 Mass Spectrometric and Thermospray Parameters

Ion source temperature: 275°C
Stem initial temperature: 100°C
Probe tip temperature: 230°C
Vapor temperature: 272°C
Multiplier voltage: 2500 V
Filament operation: both on and off modes
Scan range: 75 to 300 amu
Injection volume: 10 μ L or 20 μ L, depending on sample concentration

- 8.2.3 **Calibration and Tuning:** Polyethylene glycol (PEG) tuning solution is used to tune the thermospray interface and calibrate the MS before analysis. The standard masses of the PEG solution are in any thermospray LC-MS manual. The stability of the thermospray interface performance should be verified, and the signal intensity of PEG ions should be maximized.
- 8.2.4 Approximately 20 μ L of the filtered solution (section 8.1.5) are injected onto the LC column connected to the thermospray interface for MS detection. The data-collection procedure is described in the instrument manual.

8.2.5 Upon completion of the analysis sequence, data collection should be verified. System manuals should be consulted to obtain a printout of data and to integrate or otherwise manipulate data.

8.2.6 Final results are calculated based on sample size and all sample dilutions and other sample manipulations performed.

8.2.7 Instrument Maintenance

- Filtered deionized water should be flushed through the thermospray probe and HPLC pump at the end of each day of operation to prevent the corrosive effects of HCl on metal surfaces.
- The thermospray ion source should be cleaned at least once a week to remove nonvolatile chloride salts resulting from the use of HCl as the mobile phase.

9.0 Quality Control (QC)

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 Quantitation can be performed with this technique once a calibration curve has been established for each low-molecular-weight organic acid to be analyzed. An internal standard, such as propionic acid, should also be used during sample analysis.

10.0 Method Performance

10.1 A synthetic waste sample containing nitrate, nitrite, 2 M NaOH, ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl) ethylenediaminetetraacetic acid (HEDTA), and citrate was spiked with low-molecular-weight organic acids to determine the detection limits of the analytes. The acid standards were analyzed using both direct-flow injection (no column)-thermospray MS and thermospray LC-MS. The ions observed differed somewhat depending on whether the sample passed through the LC column (Table 1). For example, citric acid gave (M+18) as the largest peak on direct injection—(M+1) and (M+1+18) are also strong peaks; after LC-MS, 131 is the largest peak, and (M+1) is present, but neither (M+18) nor (M+1+18) are present. It appears that differing degrees of protonation and hydration may occur within the column as opposed to simply within the mobile phase. More hydration occurs on direct injection for some of these acids. The most common ions observed for the different organic acids in both techniques were $(M+1) = (M+H)^+$ and $(M+18) = (M+H_2O)^+$.

Table 1. Comparison of Ions Detected by Direct Injection vs through the Analytical Column

Acid	Direct Injection		Through Column	
	<i>m/z</i> and Assignment	Relative Intensity (%)	<i>m/z</i> and Assignment	Relative Intensity (%)
Acetic Acid (M_r 60.05)			97 (M+I+36)	100
Citric Acid (M_r 192.12)	210 (M+18)	100	131	100
	193 (M+1)	73	149	33
	211 (M+1+18)	65	147	17
	165	33	193 (M+1)	2
	147	19		
	194 (M+2)	5		
	131	5		
	149	6		
Gluconic Acid (M_r 196.16)	179 (M+1-18)	100	125 (M+1-4H ₂ O)	100
	197 (M+1)	50	179 (M+1-18)	98
	196 (M)		99	24
	214 (M+18)	4	143 (M+1-3H ₂ O)	22
	117	90	197 (M+1)	12
Glycolic Acid ^(a) (M_r 76.05)	95 (M+1+18)	100	95 (M+1+18)	100
	113 (M+1+36)	71	113 (M+1+36)	12
	94 (M+18)	26	77 (M+1)	4
	131 (M+1+3H ₂ O)	20	153	2
	153	15		
Glyoxylic Acid ^(b) (M_r 74.04)	122	100	95	100 ^(c)
	91	91	113	8 ^(c)
	121	62	92 (M+18)	2
	109	30		
	179	16		
	123	14		
	104	12		
	92 (M+18)	10		
	95	16		
Hexanoic Acid (M_r 116.06)	135 (M+1+18)	100	135 (M+1+18)	100
	153 (M+1+36)	58	99 (M+1-18)	32
	136 (M+2+18)	9	117 (M+1)	22
	233	7	153 (M+1+36)	6
	117 (M+1)	4		
Tartaric Acid (M_r 150.09)	196 (M+1+18)	100	151 (M+1)	100
	151 (M+1)	79	91	38
	168 (M+18)	55	97 (M+1-3H ₂ O)	

(a) The scan was from *m/z* 75 to 300 to see if the *m/z* 77 ion (M+1) was present.(b) (M+1) would not show since the scan range was *m/z* 80 to 300.(c) Since the *m/z* 95 and 113 ions appear at a different retention time than that observed for glycolic acid, some conversion (disproportionation) may be occurring toward the end of the column or in the spray.

DRAFT

Quantitation of low-molecular-weight organic acids using thermospray LC-MS is being explored.

- 10.2** An actual waste sample from a Hanford waste storage tank (Tank 101-SY) was analyzed using thermospray LC-MS (Figure 1). The sample consisted of a composite of several segments of waste obtained by core drilling. The material was highly radioactive. It contained a high concentration of nitrate and nitrite and a hydroxide ion concentration of 2M. The total organic carbon was 1.5 to 2.1%. Citric, glycolic, NIDA, and acetic acids were identified, and diglycolic acid was tentatively identified. The results of thermospray LC-MS studies under strictly basic conditions (using ammonium carbonate as the mobile phase at pH 10) indicate that NIDA is an artifact of the acidic conditions used to identify organic acids. Under basic conditions, the results showed that iminodiacetic acid is actually the species present in the waste sample.

(a) Total Ion Chromatogram

(b) Extracted Ion Plot m/z 193 for Citric Acid (c) Extracted Ion Plot m/z 95 for Glycolic Acid (d) Extracted Ion Plot m/z 97 for Acetic Acid

Figure 1. Thermospray LC-MS of Composite Sample

OM510R^(a)**Determination of Chelators and Their Degradation Products in Mixed Hazardous Waste Samples by Derivatization GC/MS**

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 the analysis of chelators and their degradation products in mixed hazardous waste samples by derivatization gas chromatography-mass spectrometry (GC-MS)^(b). Chelators and their degradation products that can be analyzed by this method include ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetriacetic acid (ED3A), nitriloacetic acid (NTA), citric acid, oxalic acid, and succinic acid.
- 1.2** The method is applicable to wastes with radioactivity levels ranging from none to high. A lab bench, glovebox, or hot cell is used as appropriate, i.e., according to site-specific cutoff levels.

2.0 Summary of Method

The waste samples are extracted with water, eluted through a cation ion exchange column (Na⁺ form), and then dried. The extract is derivatized with BF₃/methanol (MeOH) to form methyl esters of carboxylic acids. The derivatized extract is monitored for radioactivity and then analyzed by GC-MS, using electron-impact mode. Chemical ionization MS may be used to confirm identifications.

- (a) This method was supplied by J. A. Campbell (Pacific Northwest Laboratory, Richland, Washington), A. P. Toste (Southwest Missouri State University, Springfield, Missouri), K. L. Wahl, K. E. Grant, G. M. Mong, and R. B. Lucke (Pacific Northwest Laboratory, Richland, Washington).
- (b) K. E. Grant, R. B. Lucke, J. A. Campbell, L. J. Sears, and A. P. Toste. "Determination of Chelators and their Degradation Products in Mixed Hazardous Wastes by Derivatization GC/MS." Submitted to *Anal. Chem.*

3.0 Interferences

- 3.1 This derivatization procedure will methylate carboxylic acids, but not hydroxy groups in organic analytes. Quantitative data for HEDTA should be interpreted with caution because the HEDTA response apparently represents the lactone form and not the free hydroxide species.
- 3.2 This procedure is not reproducible for the derivatization of the symmetrical ethylenediaminediacetic acid.
- 3.3 It is difficult to dissolve NTA and its salts in water/NaOH solutions. It may be possible to dissolve NTA in strong basic solutions (pH 13) and then dilute to volume with water.
- 3.4 The product methyl ester of iminodiacetic acid (IDA) easily decomposes if the extraction solution has a pH < 7. A similar fate apparently exists for the lactone of methylated HEDTA. Both of these species must be quantitated with carefully controlled, slightly basic (pH 7.5) conditions. Multiple samples should be considered if quantitative data for IDA- or HEDTA-related analytes are to be determined. The quenching solution can be modified to pH 9 to 9.5 so that the final extraction is at pH 7 to 7.5. In typical tank waste samples, the high nitrite concentration will cause IDA, ED3A, and similar organic components with a free amine hydrogen to form nitroso compounds when derivatized under these conditions. A titration of the BF_3/MeOH reagent vs. $\text{KH}_2\text{PO}_4/\text{NaOH}$ solution is recommended to approximate the final volumes that will give the best results.

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 Mass spectrometer: Hewlett Packard 5988A mass spectrometer (or equivalent) with electron impact (EI) and chemical ionization (CI) capabilities and with GC-MS capabilities
- 5.2 Gas chromatograph: capable of splitless injection
 - 5.2.1 Fused-silica capillary column: DB-5, 30 m x 0.25-mm i.d., 0.25- μm film thickness (or equivalent)

- 5.3 Vortex mixer to stir solutions
- 5.4 Reactivial heating block
- 5.5 Reactivials (VWR Scientific or equivalent)
- 5.6 pH meter with pH probe covering the pH range of at least 2 to 12
- 5.7 Test tubes
- 5.8 Mechanical stirrer and stir bars
- 5.9 Solvent filtering system
- 5.10 Balance for sample weighing from mg to g capacity

6.0 Reagents

- 6.1 Reagent water: deionized water using a deionizer with an organic removal cartridge
- 6.2 Boron trifluoride/methanol: 12% w/v for sample derivatization (Aldrich Chemical Co. or equivalent)
- 6.3 Standards: EDTA, HEDTA, NTA, ED3A, IDA, NIDA, citric acid, succinic acid, and oxalic acid
- 6.4 Preparation of calibration standards: A stock solution is prepared containing a known amount (~5 mg/mL) in 0.1 M NaOH of the chelators that are expected in the sample, e.g., succinic acid, IDA, NIDA, citric acid, NTA, EDTA, and HEDTA. Concentrations of chelators in the standard solution should be greater than the expected concentrations in the sample solutions. A known aliquot (2 to 5 mL) of standard solution is placed in a 5-mL reactivial, blown to dryness, and derivatized simultaneously with the sample as described in section 8.1.
- 6.5 Perfluorotributylamine (PFTBA): for MS calibration and instrument performance assessment
- 6.6 Chloroform: reagent grade
- 6.7 Buffer solution of 1 M KH_2PO_4 , which has been pH adjusted to 9.0 to 9.5 with NaOH
- 6.8 NaOH for pH adjustment

- 6.9 pH standards: commercial pH 4, 7, and 10 standards
- 6.10 Helium: 99.9% or better, for GC carrier gas
- 6.11 Compressed air: breathing air quality, 75 psi, for autosampler operation
- 6.12 Methane and isobutane for CI reagent gases
- 6.13 Nitrogen: for blow-down procedure for solvent evaporation
- 6.14 Na_2SO_4 : anhydrous

7.0 Sample Collection, Preservation, and Handling

Sample collection, preservation, and handling should be addressed in the planning process.

8.0 Procedure

8.1 Sample Preparation

Caution: Depending on radioactivity levels, steps 8.1.1 through 8.1.9 may have to be performed in a hot cell or glovebox.

- 8.1.1 Two grams of the solid waste sample are weighed out, 20 mL of doubly-distilled deionized water are added, and the sample is stirred overnight in the hot cell if required.
- 8.1.2 The solution is filtered with a 0.45 μm syringe filter, or equivalent. Some solutions with high solids content may require centrifugation before filtering. The aqueous solution is then eluted through a cation exchange column (AG50-X8, or equivalent, Na^+ form) to remove the radionuclides. The radioactivity level of the aqueous solution should be low enough at this point to be removed from the hot cells {this should be verified with the radiation protection technician (RPT)}. A known aliquot of the aqueous portion (2 to 5 mL) is placed in a 5-mL reactival and evaporated to dryness with a steady stream of dry nitrogen at a temperature not greater than 70°C. To achieve complete dryness, it may be necessary to manipulate the sample; i.e., the vial may be tilted to spread out thickened salts onto the vial wall.
- 8.1.3 After the sample is completely dry, approximately 2 mL of a 12% (w/v) solution of BF_3 in methanol is added to the reactival, and the sample is heated to 100°C for 1 hour.

- 8.1.4 The sample is cooled and then 1 mL of chloroform is added.
- 8.1.5 The solution is transferred to a test tube containing 5 mL of 0.1 M KH_2PO_4 , which had been adjusted to pH 9.0 to 9.5 with NaOH.
- 8.1.6 The reactival is rinsed with another 1 mL of chloroform, which is added to the test tube.
- 8.1.7 The sample is vortexed, and the aqueous and chloroform layers are allowed to separate.
- 8.1.8 The aqueous layer is decanted from the top and discarded (it must be monitored for radioactivity before disposal). The bottom chloroform layer (~2 mL) contains the derivatized organics for analysis.
- 8.1.9 The volume of the solution should be recorded through the remainder of the sample-preparation steps. Quantification is based on the assumption that the chelators are now contained in the 2-mL chloroform layer. Any extra dilutions, concentrations, or filtering that affect this final volume must be taken into account when performing quantitative calculations.
- 8.1.10 About 100 mg to 200 mg of anhydrous Na_2SO_4 is added to collect entrained water. The dried solution should be transferred to a clean vial.
- 8.1.11 At this point, the chloroform layer should have less than 5% of the radioactivity of the original sample. This should be verified with the RPT, and then the sample should be removed from the hot cell and analyzed by GC-electron impact MS. Positive ion chemical ionization MS may be used to confirm parent ion assignment.

8.2 GC-MS Analysis

8.2.1 Chromatographic conditions

Injector port temperature:	250°C
Injection:	Splitless
Temperature program:	
Initial temperature:	50°C, hold for 1 min
Program:	50°C to 300°C at 8°C/min
Final temperature:	300°C, hold for 5 min

8.2.2 Mass spectrometric conditions

Interface temperature:	250 °C
Ion source temperature:	200 °C
Electron Impact:	
Scan range:	50 to 500 amu
Electron energy:	70 eV
Chemical Ionization:	
Reaction gas:	isobutane
Scan range:	70 to 500 amu, positive ion mode

- 8.2.3 Calibration and tuning: PFTBA is used to tune and calibrate the MS before unknown analysis. All calibration results and instrument parameters should be documented.
- 8.2.4 Once calibration and system performance have been completed and documented, response curves can be generated with the standard solution. A series of dilutions of the derivatized standard solution are made with chloroform. If concentration ranges of the chelators present in the sample solutions are unknown, at least the following dilutions of the stock solution should be made (assuming the stock-solution concentration is 2 to 5 mg/mL): 1:1, 1:5, 1:10, 1:25, 1:50 and 1:100.
- 8.2.5 Approximately 1 μ L of each of the standard dilutions should be injected onto the GC column for GC-MS analysis. Data collection is started as described in instrument manuals. If an autosampler is available, then a batch run can be set up as described in manuals.
- 8.2.6 A response curve is prepared for each analyte in the standard solution by plotting the area of the GC peak vs μ g methylated chelator injected.
- 8.2.7 Approximately 1 μ L of unknown sample is injected onto the GC column for GC-MS analysis. Data collection is started as described in instrument manuals. If an autosampler is available, then a batch run can be set up as described in the manuals.
- 8.2.8 Final results are calculated based on sample size and all sample dilutions and other sample manipulations performed. The response curve is used to obtain quantitative information.

9.0 Quality Control

- 9.1 Because of the variability in mixed-waste samples, modifications to the sample preparation and/or derivatization procedure may be necessary. 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.

10.0 Method Performance

- 10.1 A waste sample representing a composite of several segments of actual waste obtained by core drilling a waste from a double-shell storage tank was analyzed by this method. This material was highly radioactive, with a high concentration of nitrate and nitrite, a hydroxide ion concentration of 2 M, and a total organic carbon (TOC) content of 1.5 to 2.1%. Results indicate the presence of EDTA, HEDTA, ED3A, NTA, citric acid, and succinic acid (Figure 1). Table 1 identifies the peaks in Figure 1 and gives their molecular structures as determined by high resolution MS. Figure 2 gives the mass spectra of several of the peaks in Figure 1. The concentrations of the major components from the analysis of samples from a waste tank (Tank 101-SY at Hanford) are shown in Table 2.

The other minor components have been tentatively identified as chelator fragments or carboxylic acids. One component, whose structure is shown below, is thought to have formed either as a result of an interaction between the organics and the high nitrate and nitrite content in the waste tank or as an artifact of the derivatization process.

The chelators and chelator fragments constitute only 20 to 30% of the TOC.

- 10.2 Recoveries of the target organic compounds associated with Tank 101-SY wastes were determined by adding standard amounts of these materials comparable to that contained in the intermediate waste extract from ion exchange processes. Analytes chosen for the study were succinic acid, NTA, citric acid, EDTA, and HEDTA. These materials were added to the waste matrix in 0.5 to 0.8 mg/g matrix solution. In addition, a deuterated analogue of EDTA (with the deuteriums located in non-exchangeable positions on the N,N' bridge) was added (0.5 mg/g matrix solution) as a direct probe of derivatization efficiency.

Figure 1. Total Ion Chromatogram of Derivatized Waste Tank Sample (see Table 1 for identification of peaks). SC Denotes Solvent Contaminant and S Denotes Spike Components.

Table 1. Identification and Molecular Structures (underivatized) of Peaks in Figure 1 as Determined by High Resolution Mass Spectrometry

<u>Compound No.</u>	<u>Molecular Formula</u>	<u>Structure</u>	
1	$C_2H_2O_4$	HOOC—COOH	Oxalic Acid
2	$C_3H_4O_4$	HOOC—CH ₂ —COOH	
3	$C_4H_6O_4$	HOOC—CH ₂ —CH ₂ —COOH	Succinic Acid
4	$C_5H_8O_4$	$ \begin{array}{c} \text{HOOC—CH}_2\text{—CH—COOH} \\ \\ \text{CH}_3 \end{array} $	
5	$C_5H_9O_4N$	$ \begin{array}{c} \text{CH}_2\text{—COOH} \\ \diagup \\ \text{H}_3\text{C—N} \\ \diagdown \\ \text{CH}_2\text{—COOH} \end{array} $	
6	Unknown	Interference peaks, low intensity	
7	$C_5H_8O_4$	HOOC—CH ₂ —CH ₂ —CH ₂ —COOH	
8	Unknown	Interference peaks, low intensity	
9	$C_6H_{12}O_4$	HOOC(CH ₂) ₄ COOH	
10	$C_4H_7O_4N$	$ \begin{array}{c} \text{CH}_2\text{—COOH} \\ \diagup \\ \text{HN} \\ \diagdown \\ \text{CH}_2\text{—COOH} \end{array} $	IDA

Table 1. (Contd)

Compound No.	Molecular Formula	Structure
11	Unknown	Interfering peaks, low intensity
12	$C_4H_5O_5N_2$	$ \begin{array}{c} \text{CH}_2\text{---COOH} \\ \diagup \quad \diagdown \\ \text{O}=\text{N} \text{---} \text{N} \\ \diagdown \quad \diagup \\ \text{CH}_2\text{---COOH} \end{array} $ NIDA
13	$C_6H_9O_7$	$ \begin{array}{c} \text{CH}_2\text{---COOH} \\ \\ \text{OH} \text{---} \text{CH}_2\text{---COOH} \\ \\ \text{CH}_2\text{---COOH} \end{array} $ Citric Acid
14	$C_6H_9O_6N$	$ \begin{array}{c} \text{HOOC---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---COOH} \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N} \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{CH}_2\text{---COOH} \end{array} $ NTA
15	$C_7H_{13}O_5N_3$	$ \begin{array}{c} \text{CH}_3 \quad \diagdown \quad \text{CH}_2\text{---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---COOH} \\ \quad \quad \quad \diagup \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N} \quad \quad \quad \text{N} \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N}=\text{O} \quad \quad \quad \text{CH}_2\text{---COOH} \end{array} $
16	$C_8H_{12}O_5N_2$	$ \begin{array}{c} \text{HOOC---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---COOH} \\ \quad \quad \quad \diagup \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N} \quad \quad \quad \text{N} \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{C}=\text{O} \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{HOOC---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---COOH} \\ \quad \quad \quad \diagup \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N} \quad \quad \quad \text{N} \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{H} \quad \quad \quad \text{CH}_2\text{---COOH} \end{array} $ ED3A lactone
		$ \begin{array}{c} \text{HOOC---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---CH}_2 \quad \diagdown \quad \text{CH}_2\text{---COOH} \\ \quad \quad \quad \diagup \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{N} \quad \quad \quad \text{N} \\ \quad \quad \quad \diagdown \quad \quad \quad \diagup \quad \quad \quad \diagdown \\ \quad \quad \quad \text{H} \quad \quad \quad \text{CH}_2\text{---COOH} \end{array} $ ED3A

Table I. (Contd)

Compound No.	Molecular Formula	Structure	
17	$C_8H_{13}O_7N_3$		
18	$C_{10}H_{16}O_8N_2$		EDTA
19	$C_{10}H_{16}O_6N_2$		HEDTA
20	$C_7H_{11}O_6N$		

*Indicates components detected as intramolecular lactones or lactams

Figure 2. Mass Spectra (Electron Impact and Chemical Ionization) of Selected Peaks in Figure 1.

(d) Peak No. 16 Methyl Ester Lactone of ED3A (MW = 244)

(e) Peak No. 18 Methyl Ester of EDTA (MW = 348)

(f) Peak No. 19 Methyl Ester Lactone of HEDTA (MW = 288)

Figure 2. Contd

Table 2. Results of Derivatization (a) GC-MS Analyses on Tank 101-SY Window E Core Segment Samples—Concentration of Major Components (mg C/g Sample)

Sample No.	NIDA	NTA	CA	ED3A(b)	EDTA	HEDTA(c)	SA	TOC Accounted for (d)	% TOC Accounted for
R4258/C	1.30	0.40	0.44	0.19	2.00	—	0.07	4.8	44
R4259/C	.88	0.32	0.22	0.18	1.30	—	0.05	3.3	33
R4260/C	1.00	0.30	0.38	0.05	1.70	—	0.08	5.0	46
R4261/C	0.97	0.29	0.23	0.34	3.90	—	0.08	6.4	52
R4262/NC	0.24	0.06	0.14	0.32	0.81	—	0.02	2.2	20
R4263/NC	1.40	0.37	0.47	0.24	0.79	—	0.08	3.5	52
R4264/NC(e)									
(a)	Derivatization performed in fume hood								
(b)	Assuming response similar to EDTA								
(c)	HEDTA was found in window E composite samples, but not in the segment subsamples.								
(d)	Total includes minor components not included in this summary table.								
(e)	Sample analysis in progress								
C	Convective layer								
NC	Nonconvective layer								
NIDA	nitrosodiaminetetraacetic acid								
NTA	nitrilotriacetic acid								
CA	citric acid								
ED3A	ethylenediaminetriacetic acid								
EDTA	ethylenediaminetetraacetic acid								
HEDTA	N-(2-hydroxyethyl) ethylenediaminetriacetic acid								
SA	succinic acid								

The spiked samples were thoroughly dried under a gentle stream of nitrogen at 70°C. An additional unspiked sample of each representative matrix was run for comparison purposes as a basis to calculate the recovery of the added spiked materials.

The samples were derivatized in the normal fashion using BF_3/MeOH complex to methylate the acids and quenching the reaction with pH 9 phosphate buffer. The HEDTA methyl ester was found to be exceptionally sensitive to the pH of the final solution; in cases where the quenching solution was allowed to become acidic (pH 6), the amount of HEDTA methyl ester in the extracts was observed to fall dramatically.

Each sample was extracted with a known volume of chloroform and quantitated by GC-MS *versus* an internal standard (naphthalene- d_8). Each sample was quantitated twice, with the average of the two runs being determined. The recovery was determined by subtracting the calculated amount of the target materials in the unspiked samples from that found in the spiked samples. Typical recoveries were found to be essentially quantitative, within experimental error (Table 3).

Table 3. Recoveries of Target Compounds	
Target Compound	Yield %
Succinic Acid	101
Citric Acid	108
NTA	111
EDTA	117
d_4 -EDTA	85
HEDTA	27

The value obtained for d_4 -EDTA may be low because of bias introduced in experiments to determine the relative response factors (RRF) for each analyte. It is possible that the RRF determined for d_4 -EDTA was artificially high, resulting in an apparent depressed recovery amount for this analyte. To establish that d_4 -EDTA does not suffer deuterium exchange under the rather rigorous conditions of the experiment, a sample of d_4 -EDTA was derivatized in a matrix that did not contain EDTA. No diminution of signal or creation of ordinary EDTA was observed in the mass spectrum of this simulant.

The recovery of HEDTA (above) is typical for this analyte. Previous reports have indicated that only 30% of the HEDTA converts to a lactone form amenable to analysis by GC (Strachan et al. 1986).

10.3 Problems with BF_3/MeOH derivatization: HEDTA forms a lactone on derivatization with BF_3/MeOH . Because only 30% of the HEDTA forms a lactone and the remaining

70% contains an unreacted hydroxyethyl group that does not migrate on a GC column, the response factor of methylated HEDTA is 30% less on a molar basis than that of EDTA or NTA. The ED3A forms a lactam. The reaction of symmetrical ethylenediaminediacetic acid (s-EDDA) is not reproducible. Compounds similar to IDA and ED3A with free amine hydrogens will tend to form nitroso compounds under these conditions with BF_3 (Lewis acid) or when derivatized under basic conditions with dimethyl sulfate. Thermospray LC-MS studies under basic conditions have indicated that IDA is the component present in the waste samples.

11.0 Reference

Strachan, D. M., R. O. Lokken, R. D. Scheele, and A. P. Toste. 1986. "Complex Concentrate Pretreatment FY 1986 Progress Report." PNL Technical Report, PNL-7687. Pacific Northwest Laboratory, Richland, Washington.

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.

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 Reference

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

10.0 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.

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****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

Sample pretreatment with ethylenediamine and acid-form ethylenediaminetetraacetic acid is performed to ensure complete dissolution of acid-insoluble alkali nickel ferrocyanide compounds. Cyanide is then 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.

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 Cobaltcyanide complexes are known to be incompletely converted to HCN by distillation from acid.
- 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.
- 3.3 Aldehydes will convert cyanide to cyanohydrin, which will form a nitrile during distillation.

(a) This method was supplied K. H. Pool (Pacific Northwest Laboratory, Richland, Washington).

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; see Figure 1)
- Temperature controlled heating block designed to accommodate at least five micro-distillation tubes simultaneously
- Micro-distillation tube assembler/disassembler (MDTA/D; see Figure 2)
- 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

Figure 1. Micro-distillation Tube

Figure 2. Micro-distillation Tube Assembler/disassembler (MDTA/D)

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 ethylenediaminetetraacetic acid (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 Mohm/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. The concentration should correspond to 1 mg CN^-/mL .
- 6.7 A 0.25 M NaOH solution: A 10.0 ± 0.2 -g quantity of reagent grade NaOH pellets is dissolved in 1.0 L of DIW.

7.0 Sample Collection, Preservation, and Handling

In general, radioactive waste tank samples need no preservation. Once samples have been treated with pretreatment solution, however, the distillation should be performed as soon as possible (i.e., within a few days). Distillates should be analyzed within two week of their generation.

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 AgNO_3 .
- 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 AgNO_3 used should be recorded on the bench sheet.

9.0 Calculations

- 9.1 Since the titer of 0.0192 N AgNO_3 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 = $W_1 / (W_1 + W_2) = X$

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

$$\text{Spike recovery (\%)} = \frac{\left[V_{\text{SP}} - V_{\text{B}} - \frac{(W_s)(X)}{1000} \cdot \frac{A}{100} \right]}{W_{\text{SP}}} \cdot 100$$

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% warrants 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, Fourier transform infrared (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 of the results 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 the blank matrix (pretreatment solution) 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.

Chapter 10

Radiochemistry Methods

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.

References

American Society for Testing and Materials, 1993. *1993 Annual Book of ASTM Standards*, Water (I), Vol. 11.01; Water (II), Vol. 11.02; Nuclear Energy (1), Vol. 12.01; Philadelphia, Pennsylvania.

Chieco, N. A., D. C. Bogen, and E. O. Knutson, Eds. 1990. *Environmental Measurements Laboratory*

Procedures Manual, 27th Ed., HASL-300, U.S. Department of Energy, Environmental Measurement Laboratory, New York, New York.

Greenberg, A. E., L. S. Clesceri, and A. D. Eaton, Eds. 1992. *Standard Methods for the Examination of Water and Wastewater*, 18th Ed., American Public Health Association, Washington, DC.

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. Available from the National Technical Information Service, Springfield, Virginia.

Currie, L. A. 1968. "Limits for Qualitative Detection and Quantitative Determination." *Anal. Chem.* 40(3):586-693.

U.S. Environmental Protection Agency (EPA). 1980. *Upgrading Environmental Radiation Data*, Health Physics Society Committee Report HPSR-1 (1980), EPA 520/1-80-012, Washington, DC.

U.S. Nuclear Regulatory Commission (NRC). 1984. *Lower Limit of Detection: Definition and Elaboration of a Proposed Position for Radiological Effluent and Environmental Measurements*, NUREG/CR-4007, Washington, DC.

U.S. Nuclear Regulatory Commission (NRC). 1986. *Accuracy and Detection Limits for Bioassay Measurements in Radiation Protection*, Statistical Considerations, NUREG-1156, Washington, DC.

Further Reading

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

National Council on Radiation Protection (NCRP). 1985. *A Handbook of Radioactivity Measurement Procedures*, NCRP Report No. 58, Second Edition. NCRP, Bethesda, Maryland.

Currie, L. A. 1988. "Detection in Analytical Chemistry; Importance, Theory, and Practice." American Chemical Society Symposium Series 361, ACS, Washington, DC.

Keith, L.H., W. Crummett, J. Deegan, Jr., R. A. Libby, J. K. Taylor, and B. Wentler. 1983. "Principles of Environmental Analysis." *Anal. Chem.* 55:2210-2218.

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 1949(a), RP710(b)	RP710(b)
Beta		RP710(b)	900.0(c), 7110(d), D 1890(a), RP710(b), RP720(b)	RP710(b)
Tritium		RP735(b)	RP725(b), RP735(b)	RP725(b)
Actinides				
Gamma Spectrometry				
Ge(Li) or HPG	RS100(b)	RI010(b)	D 3649(a), RI010(b), 901.1(c)	
NaI(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 3365(a), RP800(b)	RP800(b)
U		C 1000(a), U-02(c)	902.0(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)	
⁵⁹ Ni, ⁶³ Ni			RE300(b)	RP300(b)
⁷⁹ Sr			RP530(b)	RP530(b)
⁸⁹ Sr, ⁹⁰ Sr		RP510(b), RP520(b)	905.0(c), Sr-01(c), RP501(b)	
⁹⁰ Sr			RP500(b), RP510(b), RP501(b)	RP501(b)
		Sr-02(c)	7500-Sr(d), Sr-02(c), RP520(b)	
⁹⁹ Tc	RS551		RP550(b), Tc-01(c), RS551(b)	
²¹⁰ Pb			Pb-01(c), RP280(b)	
²²⁸ Ra			904.0(c)	
For LEPS/Gamma Analysis				
⁹⁴ Nb, ^{93m} Nb			RE330(b)	RP330(b)
¹²⁹ I			RP230(b)	RP230(b)
¹³¹ I			D 4785(b), 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			RP710(b)	
Gross Beta Analysis			RP710(b)	
Gross Alpha Analysis			RI100(b)	
Beta Spectroscopy (LSC)				
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 .
RP450	Determination of Radium-226 in Aqueous Samples	Radium is purified by cation-exchange, selectively electrodeposited, then counted by AEA. Yield is determined with a sample duplicate spiked with ^{224}Ra .
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 ^{89}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	Pertchnetate 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.
RP570*	Radiochemical Determination of Thorium Isotopes in Aqueous Samples	Thorium is isolated by ion-exchange and a choice of liquid/liquid extraction methods. The sample is then prepared for counting by one of three methods. Thorium isotopes are determined by AEA.
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.

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.

RP450^(a)

Determination of Radium-226 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 separation of ^{226}Ra in aqueous samples (ground water, tap water, drinking water, biological samples, and dissolved soils) through ion exchange, electrodeposition, and analysis by alpha spectrometry. If ^{224}Ra is present in the sample, low levels of this isotope can also be measured. This method has been tested by a single laboratory through application to low-level samples from drinking-water sources in the Chicago vicinity.

2.0 Summary

A cation-exchange column is used to separate the analyte from other constituents in the sample (1 to 50 mL). After preconcentration and separation, the Ra is electrodeposited onto a stainless steel disc from a solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and HCl in the presence of microgram amounts of Pt. This electrodeposition method is direct, highly sensitive, and highly specific. After electrodeposition, the disc containing the analyte is placed in an alpha counter. Radium-224 is used as an internal tracer through standard additions.

The linear responses were greater than two orders of magnitude. Detection limits of the method, taken as three times the standard deviation of several reagent blank analyses, were $(1.8 \pm 0.3) \times 10^{-4}$ Bq and $(2.9 \pm 0.3) \times 10^{-4}$ Bq for ^{226}Ra and ^{224}Ra , respectively. Recoveries of ^{226}Ra and ^{224}Ra ranged from 90% to 100%, and precision was calculated to be less than 5% for the determination of ^{226}Ra .

(a) This method was supplied by J. S. Alvarado, K. A. Orlandini, and M. D. Erickson (Argonne National Laboratory, Argonne, Illinois).

3.0 Interferences

The performance studies indicated that the presence of Ba in the water sample might result in a low yield during electrodeposition.

The major interferences in the determination of the Ra isotopes by alpha spectrometry are ^{234}U and ^{230}Th . These two isotopes have major signals at 4.773 MeV and 4.684 MeV, respectively. These signals cannot be resolved from the spectral peaks of ^{226}Ra (doublet at 4.602 and 4.784 MeV). Pretreatment of the sample is needed to remove U and Th before electrodeposition.

4.0 Safety

No special safety precautions are indicated for this method.

5.0 Apparatus and Materials

- Ion-exchange column (10 cm length, 0.5 cm ID)
- Highly polished stainless steel disc (for use in alpha spectrometry)
- Electrodeposition cells for stainless steel plating {Orlandini et al. (1991) describe one example of an electrodeposition apparatus.}
- Alpha counter with standard surface barrier detector

6.0 Reagents

Reagent-grade (or better) chemicals should be used in all tests, unless otherwise indicated. Other grades may be used if it is ascertained that the reagent quality will not adversely affect the method performance. Water purity should conform to American Society for Testing and Materials (ASTM) specification D 1193, Type II (or better), unless otherwise indicated.

- 1.5 M HCl
- 6.0 M HCl
- Radium-224 standard solution (This standard may be made by using an old stock of ^{232}U . The ^{224}Ra is calibrated against a ^{236}U standard from the National Institute of Standards and Technology.)

- Cation exchange resin (AG 50W-X8), 100 to 200 mesh in hydrogen form, or equivalent
- 0.12 M H_2PtCl_6 in HCl-HNO_3
- Electroplating solution containing 0.17 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 0.14 M HCl

7.0 Sample Collection, Preservation, and Handling

Aqueous samples should be acidified to $\text{pH} < 2$ with HCl or HNO_3 . No other preservation or storage procedures are required.

8.0 Procedure

Figure 1 outlines the separation scheme for the determination of Ra.

- 8.1 To an aliquot of sample (1 to 50 mL), concentrated HCl or HNO_3 is added until $\text{pH} = 1$.

No effect has been observed on the sample uptake by the cation-exchange column when HNO_3 or HCl is used to acidify the sample.

- 8.2 A standard addition is used to monitor the quality of each analysis (assuming that the chemical yields from duplicate aliquots will be the same). Two aliquots of each sample are used. The first sample is spiked with ^{224}Ra , and the second is analyzed without spike. If ^{224}Ra is present in the sample, the signal produced in the counting process is subtracted from the signal produced by the sample containing the spike.
- 8.3 A column (10 cm length, 0.5 cm ID) is packed with 1 g of dry, analytical-grade AG 50W-X8 resin, 100 to 200 mesh in hydrogen form. The cation-exchange column is pretreated with 20 mL of 1 M HCl .
- 8.4 The sample is then poured into the column. When the sample has just loaded on the column, it is washed with 90 mL of 1.5 M HCl .
- 8.5 The Ra is eluted from the column with 45 mL of 6 M HCl .
- 8.6 The Ra solution is evaporated to dryness, and the residue is dissolved in 15 mL of electroplating solution {0.17 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and 0.14 M HCl }. The initial pH of this solution is 2.6.

Figure 1. Separation Scheme for the Determination of Radium

- 8.7 Ten microliters of 0.12 M H_2PtCl_6 (~400 μg Pt) solution are added to the electrodeposition solution.
- 8.8 The sample is then electrodeposited onto a highly polished stainless steel disk. The stainless steel is used as a cathode, and the platinum electrode near the surface is used as the anode. Each electrodeposition is carried out at 600 mA (0.2 A/cm²) for 60 min.
- 8.9 After electrodeposition, the disc containing the analyte is counted by alpha spectrometry.

9.0 Calculations

Radium-224 is used as an internal tracer through standard additions. Averages of the signals produced by ^{224}Ra (5.685 MeV, 94%) and its daughters ^{220}Rn (6.287 MeV, 100%) and ^{216}Po (6.78 MeV, 100%) are used to calculate the yield and concentration of each isotope in the standard and sample.

A correction factor is used for the decay of ^{224}Ra from the time of separation from the ^{232}U - ^{228}Th - ^{224}Ra equilibrium and during the counting period. The correction factor is calculated as follows:

$$\lambda = \frac{\ln 2}{t_{1/2}} \quad (1)$$

where

λ = decay constant
 $t_{1/2}$ = half-life (3.66 days for ^{224}Ra)

$$D = \frac{e^{\lambda \Delta t} \cdot (\lambda \cdot RT)}{1 - e^{-\lambda RT}} \quad (2)$$

where

D = decay
 Δt = decay time
RT = elapsed real time.

The activity of the ^{224}Ra tracer in the sample is calculated by using the net counts, corrected by the counts present in the sample, according to the following equation:

$$A_{^{224}\text{Ra}} = \frac{(C_a - C_s) \cdot D}{\epsilon \cdot LT \cdot V} \quad (3)$$

where

$A_{^{224}\text{Ra}}$	=	activity of ^{224}Ra
C_a	=	net counts of ^{224}Ra in tracer at separation time
C_s	=	net counts of ^{224}Ra in sample at separation time
ϵ	=	efficiency of counter
LT	=	counting time
V	=	volume added.

The chemical yield (Y) is calculated at a constant time relative to the standard.

$$Y = \frac{A_{^{224}\text{Ra}}}{A_{\text{tracer}}} \quad (4)$$

where A_{tracer} = the ^{224}Ra activity added to the sample.

Finally, the activity of ^{226}Ra in the sample is calculated using the net counts (background-corrected), according to the following equation:

$$A_{^{226}\text{Ra}} = \frac{C_s}{\epsilon \cdot LT \cdot k \cdot Q \cdot Y} \quad (5)$$

where

C_s	=	net counts of ^{226}Ra in sample
k	=	conversion factor for desired reporting units
Q	=	sample quantity (volume or mass).

10.0 Quality Control

One blank per sample batch should be run to detect contamination. Two aliquots of each sample should be used. The first sample should be spiked with ^{224}Ra , and the second sample should be analyzed without a spike to determine whether any ^{224}Ra is in the sample.

11.0 Method Performance

The method performance was developed at a single laboratory and has been previously reported (Alvarado et al., in press). An example of a Ra alpha spectrum is provided in Figure 2.

11.1 Linearity and Limits of Detection

The system produced a linear response when solutions ranging from 0.0034 Bq/mL to 0.34 Bq/mL of ^{226}Ra were used. The calibration plots had correlation coefficients (r^2) of 0.9946.

Detection limits are defined as the smallest concentration of radioactive material in a sample that will yield a net count above the system background and will be detected with 95% probability, with only 5% probability of falsely concluding that the blank observation represents a real signal. The instrument background levels were routinely measured at 0.5 counts per 1000 min. The limits of detection for a 1000-min counting period, calculated for background only, were $(2.6 \pm 0.3) \times 10^{-5}$ Bq for both ^{224}Ra and ^{226}Ra . The observed detection limits of the procedure, taken as three times the standard deviation of several reagent blank analyses, were $(1.8 \pm 0.3) \times 10^{-4}$ Bq for ^{226}Ra and $(2.9 \pm 0.3) \times 10^{-4}$ Bq for ^{224}Ra .

11.2 Matrix Effects

Nitrates of Ca, Mg, Ba, and Fe were used to study their potential effects on the separation and electrodeposition of ^{224}Ra and ^{226}Ra . Relatively low concentrations of Ca, Fe, and Mg caused a slight decrease in the Ra signal. However, the Ra signal was markedly depressed when Ba was added. The signal was reduced to 50% of the original signal when 10 μg of Ba were added. The washing step used during preconcentration and extraction was sufficient to eliminate interferences like Fe, Mg, Ca, Ba, U, Th, and Np. These results are summarized in Figure 3.

11.3 Accuracy and Precision

Precision measurements are illustrated in Figure 4. The data represent quadruplicate measurements on five consecutive days at a ^{226}Ra concentration of 3.45×10^{-3} Bq/mL in water. For 20 spike analyses, the average value obtained was 3.42×10^{-3} Bq/mL, with a relative standard deviation (RSD) of 4.6%. The error for this set of experiments was 1.1%. In a separate experiment, the recovery of ^{224}Ra was 98% with an RSD of 0.6%. For ^{226}Ra , the recovery was 93% with an RSD of 4.9%.

DRAFT

DOE Methods

Figure 2. Radium Alpha Spectrum

Figure 3. Matrix Effects on ^{224}Ra Electrodeposition with Ca, Mg, Fe, and Ba.

Figure 4. Precision of the Radium-226 Analysis

Table 1 compares Ra measurements in this work with the results obtained for ^{226}Ra by the gas-emanation technique (Method RA-03, HASL 300) (Chieco et al. 1990) and other reported values. Well water from Kimbell, Kansas, drinking water from the Illinois area, and dissolved bones were studied.

		^{226}Ra (Bq/L)	
		Measured (This Method)	Reported (Other Methods)
Well Water			
Kimbell #1		20.3 $\pm$ 0.7	21.8 $\pm$ 1.0 (a)
Drinking Water			
IL-0773-1		0.038 $\pm$ 0.004	0.039 $\pm$ 0.002 (b)
IL-0774-1		0.033 $\pm$ 0.004	0.033 $\pm$ 0.002 (b)
IL-0775-1		0.028 $\pm$ 0.003	0.028 $\pm$ 0.002 (b)
IL-0776-1		0.026 $\pm$ 0.003	0.025 $\pm$ 0.001 (b)
Dissolved Bones			
DB-116-470A		3.1 $\pm$ 0.2 (c)	2.88 $\pm$ 0.06 (b,c)
DB-116-230A		5.8 $\pm$ 0.3 (c)	7.1 $\pm$ 0.2 (b,c)
Other			
STD sample		0.36 $\pm$ 0.03	0.37 $\pm$ 0.06 (d)
(a) From Orlandini et al. 1991. (b) Measured by gas-emanation technique. (c) Value reported in Bq. (d) Round-robin reported value.			

12.0 References

Alvarado, J. S., K. A. Orlandini, and M. D. Erickson. "Rapid Determination of Radium Isotopes by Alpha Spectrometry." *J. Radioanal. Nucl. Chem.* (in press).

Chieco, N. A., D. C. Bogen, and E. O. Knutson, Eds. 1990. "Method RA-03." *Environmental Measurements Laboratory Procedures Manual*, 27th Ed., HASL-300, U.S. Department of Energy, Environmental Measurement Laboratory, New York.

Orlandini, K. A., J. S. Gaffney, and N. A. Marley. 1991. "An Improved Technique for the Rapid Assay of Radium Isotopes in Water." *Radiochim. Acta* 55, p. 205.

13.0 Further Reading

Hamilton, T. F., V. M. McRae, and J. D. Smith. 1994. "Radium Isotope Determination by Alpha-Spectrometry After Electrodeposition from Solution with Added Platinum." *J. Radioanal. Nucl. Chem.* 177, p. 365.

Roman, D. 1984. "Electrodeposition of Radium on Stainless Steel from Aqueous Solutions." *Int. J. Appl. Radiat. Isot.* 35, p. 990.

RP530(a)**Determination of Selenium-79 in Aqueous Samples****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 ^{79}Se 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 oxidation state of Se is adjusted to the neutral molecular form, H_2SeO_3 . In this form, the Se passes through a mixed-bed ion exchange column onto which most other elements are absorbed. Further purification of Se is accomplished by precipitating the elemental Se after reduction with hydroxylamine hydrochloride. The Se is dissolved in HNO_3 and prepared for LSC. 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 measurement by LSC. A flow chart (Figure 1) indicates available paths for sample preparation.

3.0 Interferences

Selenium-79 is determined by LSC; therefore, the Se fraction must be well separated from other beta emitters. This method should satisfactorily remove these interferences before counting.

4.0 Safety

Selenium is considered a highly toxic material, and the carrier and sample preparative steps should be undertaken with appropriate safety considerations.

Bromine is a relatively strong oxidizer with a reasonably low boiling point ($<100^\circ\text{C}$) and should be handled with due care.

- (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 (Dewberry 1991).

Figure 1. Pathways for Sample Preparation

5.0 Apparatus and Materials

- Beaker, appropriate sizes (e.g., 30 mL to 400 mL)
- Vials, 7 mL and 35 mL, glass, screw-cap, or equivalent (Note: 35-mL vials can be used in a centrifuge)

- Liquid scintillation vials
- Heating block (100°C), hotplate, or water bath
- 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 pipets, glass or plastic
- Filters, tared (e.g., Whatman 934AH glass microfiber filters). For the gravimetric yield determination, the filter should be small enough to lie flat on the bottom of the LSC vial. For spectrometric yield determination, filter size is not critical. Note: Some filters break apart in LSC cocktail; it is recommended filters be tested in LSC cocktail for suitability.
- Filtration unit suitable for selected filter
- Petri dishes or other suitable carriers for filters
- Centrifuge tubes (Note: 35-mL vials can be used in a centrifuge)
- 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, including temperature range of -20°C to 130°C
- N₂ gas, 2 psi (e.g., 99.99%)

6.0 Reagents

Reagent grade (or better) chemicals should be used in all tests, unless otherwise indicated. Other grades may be used if it is ascertained that the reagent quality will not adversely affect the method performance. Water purity should conform to American Society for Testing and Materials (ASTM) specification D 1193, Type II (or better), unless otherwise indicated.

Figure 2. Selenium Still

- Selenium carrier, 10 mg/mL {This may be prepared by dissolving about 1.0 g (precisely known) of gray elemental Se 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 .}
- Carbon-14 standard, National Institute for Standards and Technology (NIST) traceable
- Nitric acid, fuming, 16 M, 8 M, 0.5 M, and 0.1 M
- 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% or 9 M
- Liquid scintillation cocktail, e.g., Ultima-Gold[®]
- Hydroxylamine hydrochloride, 0.25 g/mL in H_2O (The shelf life is approximately two weeks.)
- Sodium hydroxide, 0.3 M
- Ethanol, 95% or better
- Hydrochloric acid, 9 M
- Br_2

7.0 Sample Collection, Preservation, and Handling

Water samples should be preserved to pH < 2 with HNO_3 . Refrigeration is generally not required.

8.0 Procedure

For samples containing a high-salt matrix (e.g., fused samples), an initial sample cleanup should be performed as described in step 8.1. For low-salt samples, the initial sample cleanup can be omitted 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 is transferred to an appropriately sized beaker or vial. (A 35-mL vial can be used for all of section 8.1, including centrifuging if the sample volume ≤ 10 mL). The sample volume must be recorded. A precisely known quantity (e.g., 20 mg) of Se carrier and 20 μ L 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 black Se precipitates; this takes about 45 min. The sample is then cooled.
- 8.1.4 The solution is transferred to a centrifuge tube, if necessary, and is centrifuged for about 5 min to provide a tightly-packed precipitation.
- 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, 0.5 mL concentrated HNO_3 are added.
- 8.1.9 The sample is heated until the Se dissolves.
- 8.1.10 Five milliliters of water and 50 μ L 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 beaker or 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 , and an excess of Br_2 . This HNO_3/HBr mixture has been prepared at 2 different sites as follows:

- a) 100 μL Br_2 is mixed with 15 mL 0.5 M HNO_3 ; 0.5 to 1 mL of this mixture is added to each sample
- b) 200 μL Br_2 , 500 μL 9 M HBr , and 0.5 to 1 mL 0.5 M HNO_3 are added to each sample.

The choice will depend on preference and performance on the matrix type. 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 absorb onto the column, but will collect in the elution vial. Most of the other activity will absorb onto 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.

Distillation is an excellent purification technique for Se. If sample purity is not sufficient after ion exchange and precipitation, it may be appropriate to apply distillation to the separation scheme for that matrix. Distillation may not generally be necessary, but is included as an option.

- 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 an iced-filled beaker (e.g., 400 mL). 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. When distillation is complete, the solution in the still should be pale yellow, as the red/brown Br_2 has been distilled.
- 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^{+4} to elemental Se.*
- 8.7.2 To the sample from step 8.6.8 or 8.7.1, an excess (e.g., 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^{+4} to elemental Se. The solution will turn orange or lavender.*
- 8.7.3 The solution is cooled, transferred to a centrifuge tube, if necessary, and then centrifuged. After the Se has settled, the major amount of supernate may be suctioned off with a disposable pipet.

If a second precipitation is to be performed for additional purification from other beta emitters, 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 filter small enough to fit the bottom of an LSC vial is tared, then mounted onto the filtration unit.
- 8.8.2 The black elemental Se is mounted onto the center of the filter while vacuum is applied, using a glass transfer pipet.
- 8.8.3 The vial is washed with 3 to 4 mL of ethanol, and the residual Se is transferred to the filter.

- 8.8.4 The filter is removed from the filter holder, and the filter plus the Se 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 are then cooled in a desiccator for at least 10 min.
- 8.8.6 The filter plus Se are weighed, and the mass is recorded.
- 8.8.7 The filter plus Se are transferred to a LSC vial. The filter is placed such that it lies flat on the bottom of the vial.
- 8.8.8 The Se is dissolved with 150 μL of concentrated HNO_3 .
The Se is allowed to dissolve completely before going to the next step.
- 8.8.9 To neutralize the acid, 1 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 μL HNO_3 , and adding 1 mL 0.3 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 A filter is mounted on a filtration unit. The sample is quantitatively transferred to the 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, equal to the HNO_3 volume in step 8.9.3 (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 the same volume (step 8.9.3) of fuming HNO_3 , adding the same volume (step 8.9.4) of distilled water, and removing the filter paper.
- 8.9.6 An aliquot (e.g., 100 μL) 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 (e.g., 1 mL) 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 (maximum energy 156 keV and 160 keV, respectively), which makes ^{14}C an acceptable calibration standard 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. An additional quench curve may need to be prepared to accommodate acid quenching if the standards and samples vary in acid concentration.

9.0 Calculations

9.1 Gravimetric Yield Calculation

$$Y = \frac{(\text{Mass}_{\text{gross}} - \text{Mass}_{\text{filter}})}{[\text{Se}] \cdot V} \quad (9.1)$$

Y = yield as a decimal fraction

$\text{Mass}_{\text{gross}}$ = mass of Se plus filter as milligrams from step 8.8.6

$\text{Mass}_{\text{filter}}$ = 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

$$Y = \frac{[Se]_{\text{smp}}}{[Se]_{\text{added}} \cdot CF} \quad (9.2)$$

where

[Se]_{smp} = the Se concentration found in the sample (e.g., mg/mL)

[Se]_{added} = the Se concentration of the carrier solution originally added to the sample (e.g., mg/mL)

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 of 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

$$E = \frac{CR_{\text{std}} - CR_{\text{bkg}}}{DR_{\text{std}}} \quad (9.3)$$

E = ¹⁴C and ⁷⁹Se counting efficiency

CR_{std} = Count rate of ¹⁴C standard from liquid scintillation counting data

CR_{bkg} = Count rate of the ⁷⁹Se blank

DR_{std} = Disintegration rate of ¹⁴C in the calibration standard

9.4 Quench Factor

$$F_q = \frac{CR_i}{CR_{\text{unquenched}}} \quad (9.4)$$

where

$$F_q = \text{quench factor}$$

CR_i = count rate of the quenched standard

$CR_{\text{unquenched}}$ = count rate of the unquenched standard

For Ultima-Gold™, no quench up to 20 mg of 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

$$A = \frac{CR_{\text{Se}} - CR_{\text{bkg}}}{E \cdot Q \cdot Y \cdot F_q} \cdot S \cdot C \quad (9.5)$$

where

A = sample ^{79}Se activity concentration

CR_{Se} = sample count rate obtained from the liquid scintillation counting data

CR_{bkg} = ^{79}Se background sample count rate obtained from the liquid scintillation counting data

E = ^{14}C and ^{79}Se 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:

$$A = \frac{CR_{Se} - CR_{bkg} \cdot V}{E \cdot Q \cdot Y \cdot F_q \cdot M} \cdot S \cdot C \quad (9.6)$$

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%. Use of duplicates should be considered to provide information on method precision.

11.0 Method Performance

This method was applied to four Hanford waste tank samples taken from two cores. Duplicate aliquots (nominally 0.5 g) of the tank-sludge cores were prepared by KOH fusion and diluted to 100 mL in the hot cell. The ^{79}Se analysis was performed using the initial cleanup from high-salt solutions, anion exchange, distillation, and two precipitations, followed by gravimetric yield determination. Sample ^{79}Se activities are summarized in Table 1. The RPD is relative percent difference and is a measure of the precision of the analysis, including core aliquoting. The percent uncertainty (U) includes random and systematic errors for the analysis only. Also included in the table is a summary of the major radioactive constituents measured in the tank sample matrix.

Table 1. Summary of ^{79}Se Activity in Hanford Waste Tank Samples							
Core 29				Core 30			
Sample ID	^{79}Se (Bq/g)	% U	RPD	Sample ID	^{79}Se (Bq/g)	% U	RPD
4312-1	3.6	17		4316-1	2.2	29	
4312-2	3.2	18		4316-2	2.0	29	
Average	3.4		12	Average	2.1		10
4313-1	4.1	16		4317-1	1.5	40	
4313-2	3.4	17		4317-2	1.7	38	
Average	3.8		18	Average	1.6		13
Blank	<0.7			Blank	<1.1		
Principal Radioactive Matrix							
^{137}Cs	6.3 MBq/g			^{137}Cs	5.2 MBq/g		
^{90}Sr	11 MBq/g			^{90}Sr	7.0 MBq/g		
Pu (total)	0.004 MBq/g			Pu (total)	0.004 MBq/g		
^{241}Am	0.0031 MBq/g			^{241}Am	0.0021 MBq/g		
^{99}Tc	0.0048 MBq/g			^{99}Tc	0.0037 MBq/g		
U	205 $\mu\text{g/g}$			U	190 $\mu\text{g/g}$		

No evidence of higher energy (>157 keV) beta emitters was apparent in the samples. Therefore, decontamination factors for ^{137}Cs and ^{90}Sr are better than 10^6 . Chemical yields averaged $88 \pm 4\%$ for the eight samples and two blanks.

Historically, the chemical yields average 85.4% ($n = 37$), including the set of data summarized in Table 1.

This method was tested on four defense waste processing facility (DWPF) sludge-only feed samples (and on six sludge-only glass product samples) by performing anion exchange and one precipitation process followed by ICP-OES analysis for chemical yield. The resulting decontamination factor from other beta emitters was $>10^6$. Gamma emitters were not detectable in the final product. Selenium recoveries on the 10 samples ranged from 21% to 63%. The average ^{79}Se activity in the four sludge-only feed samples was 3.3 ± 1.7 Bq/mL (200 ± 100 dpm/mL). For the six glass product samples, <20 Bq/mL (<1000 dpm/mL) ^{79}Se was observed.

12.0 References

Dewberry, R. A. 1991. "Procedure for Separation of Selenium and Determination of Selenium-79 by Liquid Scintillation Beta Counting." WSRC-RP-91-865. Savannah River Laboratory, Aiken, South Carolina.

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.

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.

Molinski, V. J. and G. W. Leddicotte. 1965. *Radiochemistry of Selenium*, NAS-NS-3030. Nuclear Science Series, National Technical Information Service, Springfield, Virginia.

RP570(a)

Radiochemical Determination of Thorium Isotopes 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

1.1 This method describes the isolation of Th in aqueous samples by ion exchange and liquid/liquid extraction followed by alpha/beta analysis using gross-beta counting and alpha spectroscopy. The methods outlined assume that an aqueous, fully solvated sample, preserved in mineral acid, has been prepared. If quantitation is desired for a non-homogeneous, non-aqueous, or solid sample, the Th tracer should be added to the sample before extraction of the actinides so that chemical recovery can be determined.

1.2 The minimum detectable concentration (MDC) of Th is 4×10^{-5} pCi/mL when analyzing a 1-L sample and counting for 1000 min on an alpha spectrometer with 20% efficiency and 0.005 cpm background over each energy region of interest. An 80% chemical recovery is normal for an aqueous sample. Assuming that most of the Th activity in the sample is due to ^{232}Th ($t_{1/2}=1.41 \times 10^{10}$ year), a reasonable assumption for most environmental samples, this MDC is equivalent to 0.37 ng/mL. The photon/electron-rejecting alpha liquid scintillation (PERALS[®]) spectrometry method, using pulse-shape discrimination and a similar count time, gives a detection threshold of 0.017 cpm, which corresponds to 69 ng/mL for ^{232}Th . The total Th determined with spectrophotometric methods has a MDL of 0.4 $\mu\text{g/mL}$ for a 50-mL sample with the complexant Arsenazo III and 3.0 $\mu\text{g/mL}$ for a 5-g sample with Thoria.

(a) This method was consolidated by K. Bower (Los Alamos National Laboratory, Los Alamos, New Mexico) from 25 submitted analytical procedures and a review of the listed Further Reading entries.

2.0 Summary of Method

The core method requires an anion exchange and aqueous-to-organic extraction to separate and concentrate the Th. The main-group-element and many transition-metal-element interferences can be eliminated with small loss in chemical recovery using base and fluoride precipitation steps before anion exchange. Alternative organic extractants used in the literature include quaternized amines such as Aliquat 336 or triisooctylamine (TiOA), primary amines such as dodecylamine (laurylamine), thenoyltrifluoroacetone (TTA), and phosphinic oxides such as trioctylphosphinic oxide (TOPO). Alternative mounting methods include coprecipitation/filtration, electrodeposition, and direct evaporation. Direct evaporation usually accompanies the use of the TTA extractant. Using liquid-scintillation alpha spectrometry has the advantage of counting the organic extractant directly with minimal sample preparation. The method described includes many optional separation and analysis steps that may improve the quality of the data under various sampling conditions and with various sample types. Figure 1 summarizes the various analytical pathways available for Th analysis.

3.0 Interferences

- 3.1 Good separation from other alpha emitters, such as U and Pu, is necessary for optimal isotopic determination. Since mass abundant U is usually associated with Th in the environment and in nuclear applications, the organic extraction following anion exchange is recommended.
- 3.2 As a general rule, the amount of self-attenuation in an alpha-spectroscopy determination is minimized, and the spectral quality is best, when the mass of the sample matrix in front of the alpha detector is minimized. Comparable spectral resolution is reported for direct deposition, electrodeposition, and coprecipitation/filtration when chemical separations are adequate.

4.0 Safety

The CRC Handbook of Radiation Measurement and Protection, 1982, classifies ^{232}Th and natural abundance Th (primarily ^{232}Th) as Group IV, low toxicity. Group I, high toxicity, includes ^{227}Th , ^{228}Th , and ^{230}Th , and ^{234}Th is of medium toxicity. The specific activity, radiation type (alpha, beta, and gamma), and mass amounts of Th isotopes are all considerations in determining radiation-exposure hazard. It is relevant to point out that non-Th fractions after separation may contain significant activity and should be handled appropriately. The principle of "as low as reasonably achievable" (ALARA) is a helpful goal when sample radiation levels are of concern.

Figure 1. Analytical Pathways for Th Analysis (Bold Text - Critical; Italics - Optional)

The organic solvents and extractants used in these procedures are not generally considered dangerous to use. Flammability is a concern when using organic solvents. It is recommended that open flames not be used near organic reagents.

5.0 Apparatus and Materials

- Hot plate
- Centrifuge
- Centrifuge cones (50-mL capacity is one useful size.)
- Extraction vials (50-mL capacity with plastic closures is one useful kind.)
- pH meter with combination electrode
- Alpha-counting planchets
- Gross beta counter
- Ion-exchange column (e.g., plastic 0.5 to 0.75 cm ID x 20 cm, fitted with reservoir)
- Assorted glass beakers for sample evaporation
- Pipets suitable for tracer, control standard, and sample deposition use
- Transfer pipettes
- Filter membrane (e.g., Nuclepore, 25 mm dia, 0.1 to 0.2 μm or equivalent)
- Alpha spectrometer consisting of a multichannel analyzer, biasing electronics, a vacuum pump, and silicon barrier or passivated ion-implanted silicon detectors operated in vacuum chambers. For alpha liquid-scintillation measurements, a photon-measurement instrument, such as the PERALS[®] spectrometer, can be used.

6.0 Reagents (List not inclusive, depending on preparation steps used)

Reagent grade (or better) chemicals should be used in all tests, unless otherwise indicated. Other grades may be used if it is ascertained that the reagent quality will not adversely affect the method performance. Water purity should conform to American Society for Testing and Materials (ASTM) specification D 1193, Type II (or better), unless otherwise indicated.

- TTA-Methyl Benzoate: 11.1 g of TTA is dissolved in 50 mL of methyl benzoate and diluted to 100 mL with methyl benzoate in a glass bottle to make a 0.25 M solution of the extractant.
- Cerium Solution: (1000 $\mu\text{g/mL}$) - 0.266 g of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ is dissolved in 100 mL of 0.65 M HCl.
- Concentrated Hydrofluoric Acid: (HF)
- Anion exchange resin (AG1X8 Cl^- form) or equivalent 100 to 200 mesh
- Nitric Acid: 1 M, 2 M
- Hydrochloric Acid: 10 M, 4 M, 0.65 M, and 0.1 M
- Ammonium Iodide in Hydrochloric Acid: 0.1 M NH_4I in 10 M HCl (This may be prepared by dissolving 1.45 g of NH_4I in 10 mL of deionized water, adding 80.6 mL of concentrated HCl, and diluting to 100 mL with deionized water.)
- Hydrofluoric Acid in Hydrochloric Acid: 0.1 M HF in 4 M HCl
- Aluminum Nitrate: 2 M $\text{Al}(\text{NO}_3)_3$ (This may be prepared by dissolving 213.0 g $\text{Al}(\text{NO}_3)_3$ in 500 mL of deionized water.)
- Sodium Hydroxide: 6 M NaOH
- Lanthanum Carrier: 0.1 mg La^{+3}/mL . (This may be prepared by dissolving 0.0779 g of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 250 mL of 1 M HCl.)
- Cerium Carrier: 1 mg Ce^{+3}/mL (This may be prepared by dissolving 0.266 g $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in 100 mL of 2% HCl.)
- URAEX™ and THOREX™ are mixtures of selective extractants, scintillators, and organic solvents. They are available directly from ETRAC, Inc., Knoxville, Tennessee.

7.0 Sample Collection, Preservation, and Handling

Aqueous samples collected in the field may need to be acidified to reduce adherence to plastic-container surfaces. Teflon® is a preferred vessel material for low-level samples, although high-density polyethylene will be adequate for most purposes. Sample volatility is not a concern, although analyte-concentration determinations assume no solvent evaporation. Slight evaporation

can actually be measured from polyethylene vials. Sample toxicity is not normally a problem at nanocurie radiation levels.

8.0 Procedure

- 8.1 Volume Adjustment.** Dilution of a concentrated sample or evaporation of a dilute sample in a glass beaker on a hot plate to a useful starting volume such as 25.0 mL.
- 8.2 Internal Tracer and Control Standard.** Addition and equilibration with an internal tracer if one was not added during sample dissolution. Various analysts have used ^{228}Th , ^{229}Th , and ^{234}Th . Thorium-234 is a beta emitter of high activity and would simplify the alpha spectra at the cost of running a separate gross beta count. The quantity of the tracer should not exceed the expected total-Th activity to be measured, especially where isotopic impurities in the tracer may be misinterpreted as sample. An equilibration time of 1 day is common. A control standard containing the internal tracer and ^{232}Th as the internal standard could be run in parallel to a sample set, but is not essential for most analyses.
- 8.3 Fluoride Precipitation.** If the sample contains excessive salt, a fluoride and base precipitation can be performed. The fluoride precipitation uses a Ce carrier ($\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in 2% HCl) and concentrated HF. For example, a typical environmental sample may have 1 mL of concentrated HF and 50 μL of 1000 $\mu\text{g/mL}$ Ce solution added after quantitative transfer to a 50-mL centrifuge cone. After centrifugation, the supernatant can be discarded, and the precipitate can be dissolved in 1M HNO_3 with 0.5 mL 2 M $\text{Al}(\text{NO}_3)_3$.
- 8.4 Base Precipitation.** The pH is then adjusted above 9 using 6 M NaOH. After the sample is centrifuged and the supernatant is discarded, the precipitate can be dissolved with a small amount (such as 1 mL) of 10 M HCl.
- 8.5 TOPO Extraction.** The sample is converted to the nitrate form with sequential evaporations followed by dissolution in concentrated HNO_3 . The final evaporated salt is dissolved in 2 N HNO_3 to which an excess of oxalic acid and the extractant in an organic phase has been added. A 25-mL sample, for example, would have 0.1 g of oxalic acid added and 10 mL of 2% TOPO in cyclohexane. The organic layer is centrifuged and removed to another tube containing 1 M HF for back extraction. After shaking for 3 min, the aqueous layer is separated (centrifuged) and evaporated. The salt, which contains both Th and U, is dissolved in a small volume of 10 M HCl. Anion exchange using the chloride counterion is recommended to further separate U and Th. Alternatively, a U extraction into scintillation solvent, such as URAEXTM, can be followed with Th extraction in a scintillation solvent, such as THOREXTM, and counted directly in a spectrometer, such as the PERALS[®] spectrometer.

- 8.5.1 **TiOA extraction:** The sample in 10 M HCl is warmed to 50°C and mixed with 1/3 volume equivalents of 10% TiOA in p-xylene equilibrated with 10 M HCl. The aqueous phase, which contains the Th, is further purified with anion exchange.
- 8.5.2 **Anion exchange using chloride counterion:** The dissolved precipitate is quantitatively loaded on an anion exchange column such as BioRad AG1X8 (100 to 200 mesh), which has been equilibrated with 10 M HCl. A typical ion-exchange column may contain 5 mL of resin in a 0.5- to 1.0-cm diameter plastic tube. The Th is directly eluted with 10 M HCl while Pu, U, and other actinides are not. If Pu, Np, and U fractions are required for separate analysis, they can be eluted with 0.1 M NH_4I in 10 M HCl, 4 M HCl/0.1 M HF, and 0.1 M HCl eluents respectively. At least five bed volumes are recommended for each elution. Eluent may be collected in extraction vials with plastic closures.
- 8.6 **TTA Extraction.** The pH of the Th eluent is adjusted between 1.4 and 1.5 with dilute ammonium hydroxide. Two milliliters of 0.25 M TTA in methyl benzoate are added. The organic phase is shaken and separated. The extraction is repeated using 2 mL of fresh TTA solution. The organic fractions are combined and scrubbed with two 4-mL aliquots of 2 M HNO_3 .
- 8.6.1 **Spectrophotometric analysis:** A measured fraction of the Th eluent may be prepared for spectrophotometric analysis using Thorin or Arsenazo III colorimetric reagents if total Th using corroborative data is needed. If Fe (III), Zr, or Ti continue to show interferences as evidenced by overlapping absorption bands to the E_{max} of the Th complexes (545 nm for Thorin-Th and 660 nm for Arsenazo III-Th), liquid/liquid extraction using Aliquat 336 is recommended as an additional separation step.
- 8.6.2 **Aliquat 336 extraction:** Aliquat 336 in toluene is added to the anion-exchange eluent containing Th in equal volume in a separatory funnel and mixed for 1 min. The aqueous layer is drained through Whatman 41 paper into a glass beaker. The paper is washed with a few mL of 10 M HCl. The organic fraction is discarded and the aqueous fraction is evaporated to dryness. A small volume of 50% HCl (for example, 0.5 mL) is added to dissolve the salt, followed by 1 mL of 10% hydroxylamine hydrochloride. The solution is warmed briefly.
- 8.6.3 **Anion exchange using nitrate counterion:** A second ion-exchange stage may be useful where Pu is inadequately separated in the first stage. The Th chloride is converted to Th nitrate through triple evaporation and addition of concentrated HNO_3 . The sample solution is finally adjusted to about 8 M HNO_3 , and an excess of NaNO_2 is added to the sample after several equivalents of ferrous

sulfamate have been added with warming to adjust the Pu oxidation state to +4. The sample is loaded on an anion-exchange column with resin such as BioRad AG1X8 (100-200 mesh), which has been equilibrated with 8 M HNO₃. After washing with 8 volumes of 8 M HNO₃, the Th fraction can be eluted with 7 to 8 volumes of 10 M HCl. If the Pu is needed, it can be eluted with 10 volumes of 10 M HCl to which ammonium iodide (0.032 M) has been freshly added. Alternatively, the Np and Pu can be eluted with 8 volumes of 0.5 M HCl/0.5 M H₂SO₄.

- 8.7 Direct Deposition and Counting.** A known fraction or all of the organic phase is evaporated on a glass cover slip or counting planchet for alpha spectrometry (and gross beta counting, if needed).
- 8.7.1 Coprecipitation:** A small amount (e.g., 50 µL) of 1 mg/mL Ce solution is added to the HCl effluent from ion exchange. Alternatively, a small quantity of 0.1 mg/mL La carrier (e.g., 1 mL) can be added. A small amount of concentrated HF (e.g., 1 mL) is added to the solution. The solution is cooled for 25 min. A 0.1-µm polycarbonate, or appropriate, filter is wetted with ethanol, and the sample is filtered using water and ethanol as wash solutions. The filter is dried and counted in the alpha chamber.
- 8.7.2 Electrodeposition:** The sample is evaporated to near dryness, and a few mL of concentrated HNO₃ are added several times. The residue is dissolved in a few mL of 12 M HCl and evaporated. The residue is dissolved in a small amount of plating solution and transferred to the plating cells loaded with the counting disks. The solution is plated for 20 min at 3 amp, adding distilled water as necessary to replace evaporation electrolysis loss. After draining the electrolyte, the cells are rinsed with water and then isopropyl alcohol. The counting disks are calcined for 5 min at 425°C. The sample disks can then be counted on the alpha spectrometer.
- 8.7.3 Alpha Scintillation Counting:** A known volume of the scintillator extractant is placed in a 10- by 75-mm culture tube and counted in an appropriate detector, such as the PERALS[®] spectrometer. A spectrum is collected for a time sufficient to give the required accuracy and counting statistics.

9.0 Calculations

The activity of the unknown Th isotope in pCi/g is X_{Th} , which equals the net count rate in the unknown isotope peak, C_1 times the activity in the Th tracer added in pCi, A_t , over the net count rate in the tracer peak, C_t , times the original sample mass, W_t . If beta counting of a ²³⁴Th tracer

is used, the ratio of instrument counting efficiencies, $\text{Eff}_{\text{beta}}/\text{Eff}_{\text{alpha}}$ should be multiplied by the result.

$$X_{Th} = \frac{C_i \cdot A_i}{C_r \cdot W_i}$$

To achieve a reporting limit of 0.5 pCi/g, routine samples normally require 24-h count times.

10.0 Quality Control

Control standards should be prepared periodically to verify tracer purity and method execution. Spectra should be maintained with all calculation sheets so that result verification would be possible by an independent inspector.

11.0 Method Performance

To be completed.

12.0 Further Reading

Bernabee, R. P., D. R. Percival, and F. D. Hindman. 1980. "Liquid-Liquid Extraction Separation and Determination of Plutonium and Americium," *Anal. Chem.*, 52: 2351-2353.

Bock, R. 1979. *Handbook of Decomposition Methods in Analytical Chemistry*, International Textbook Company, pp. 86-94.

Brits, R. J. N. 1975. "A Routine Method for the Determination of $^{234}\text{U}/^{238}\text{U}$ Ratio in Natural Water," *Chem. Geol.*, 25:347-354.

Burney, G. A., and R. M. Hasbous. 1974. "Radiochemistry of Neptunium," Prepared for Subcommittee of Radiochemistry, National Academy of Sciences - National Research Council, Technical Information Center, U.S. Atomic Energy Commission, Oak Ridge, Tennessee (NAS-NS-3060).

Casella, V. R., C. T. Bishop, A. A. Glosby, and C. A. Phillips. 1981. "Anion Exchange Method for the Determination of Uranium, Thorium, and Lead-210 in Coal and Coal Ash," *J. Radioanal. Chem.*, 62(1-2):257-266.

Corley, J. P., et al. 1977. *A Guide for Environmental Radiological Surveillance at ERDA*

Installations, ERDA 77-24, Energy Research and Development Administration, Division of Safety, Standards and Compliance.

Goldin, A. S. 1983. "Internal Quality Control for Radiobioassay, Office of Radiation Programs," U.S. Environmental Protection Agency.

Hashimoto, T., H. Taniguchi, H. Sugiyama, and T. Sotobayashi. 1979. "Simultaneous Determination of Uranium and Plutonium in Soils by Means of Single Alpha Spectrometry," *J. Radioanal. Chem.*, 52(1):133-142.

Hindman, F. D. 1983. "Neodymium Fluoride Mounting for Alpha Spectrometric Determination of Uranium, Plutonium, and Americium," *Anal. Chem.*, 55:2460-2461.

Hindman, F. D. 1986. "Actinide Separations for Alpha Spectrometry Using Neodymium Fluoride Coprecipitation," *Anal. Chem.*, 58:1238-1241.

Hyde, E. K. 1960. "The Radiochemistry of Thorium," U.S. Atomic Energy Commission Report NAS-NS 3004.

Johns, F. B., P. B. Hahn, D. J. Thome, and E. W. Bretthauer (Eds.). 1979. *Radiochemical Analytical Procedures for Analysis of Environmental Samples*, EMSL-LV-0539-17.

Kanipe, L. G. 1977. *Handbook for Analytical Quality Control in Radioanalytical Laboratories*, EPA-600/7-77-088, U.S. Environmental Protection Agency.

Khandekar, R. N. 1976. "Determination of Transuranium Elements in Nuclear Weapon Debris," *Radiochemical, Radioanalytical Letters*, Volume 25 (2), pp. 77-86 (Th not discussed).

Kressin, I. K. 1977. "Electrodeposition of Plutonium and Americium for High Resolution Alpha-Spectrometry," *Anal. Chem.*, 49(6):842-846.

Krishnaswami, S., and M. M. Sarin. 1976. "The Simultaneous Determination of Th, Pu, Ra Isotopes, ^{210}Pb , ^{55}Fe , ^{32}Si , and ^{14}C in Marine Suspended Phases," *Anal. Chim. Acta*, 83:143-156.

Lieberman, R., and A. Moghissi. 1968. *Health Physics*, 8:359.

McDowell, W. J., and B. L. McDowell. 1994. *Liquid Scintillation Alpha Spectrometry*, CRC Press, Boca Raton, Florida, pp. 137-142.

Moore, F. L. 1958. "Liquid-Liquid Extraction of Uranium and Plutonium from Hydrochloric Acid Solution with Tri(iso-octyl)amine," *Anal. Chem.*, 30:908-911.

- Moore, F. L. 1958. "Radiochemical Determination of Ionium [thorium-230] in Uranium Fluorination Ash," *Anal. Chem.*, 30:1020-1021.
- Osmond, J. K., and J. B. Cowart. 1976. "The Theory and Uses of Natural Uranium Isotopic Variations in Hydrology," *At. Energy Rev.*, 144:621-679.
- Roman, D. 1980. "The Electrodeposition of Thorium in Natural Materials for Alpha Spectrometry," *J. Radioanal. Chem.*, 60:317-322.
- Samuelson, O. 1963. *Ion Exchange Separations in Analytical Chemistry*, John Wiley and Sons, Inc. New York.
- Sill, C. W. 1977. "Determination of Thorium and Uranium Isotopes in Ores and Mill Tailings by Alpha Spectrometry," *Anal. Chem.*, 49, (4):618-621.
- Sill, C. W., and R. L. Williams. 1981. "Preparation of Actinides for Alpha Spectrometry without Electrodeposition," *Anal. Chem.*, 53:412-415.
- Talvitie, N. A. 1972. "Electrodeposition of Actinides for Alpha Spectrometric Determination," *Anal. Chem.*, 44:280-283.
- White, J. C., and W. J. Ross. 1961. "Separations by Solvent Extraction with Tri-n-octylphosphine Oxide," NAS-NS-3102.
- Wrenn, M. E., N. P. Singh, S. A. Ibrahim, and N. Cohen. 1978. "Thorium-229 as an Isotopic Tracer for the Radiochemical Determination of Thorium Isotopes in Biological Samples," *Anal. Chem.*, 50(12):1712-1713.
- Sill, C. W., K. W. Puphal, and F. D. Hindman. "Simultaneous Determination of Alpha-Emitting Nuclides of Radium through Californium in Soil," Health Services Laboratory, U.S. Atomic Energy Commission, Idaho Falls, Idaho.
- Volchok, H. L., and G. dePlanque, (Eds.). *EML Procedures Manual*, 25th Edition, Environmental Measurement Laboratory, U.S. Department of Energy, New York.

13.0 Thorium Isotope Reference Data

<u>Isotope</u>	<u>Atomic Mass</u>	<u>Half-life</u>	<u>Specific Activity (Ci/g)</u>	<u>Decay Mode and Energy (MeV)</u>
²²⁷ Th	227.02770	18.72 day	3.073×10^4	α (6.04, 5.98, 5.76)
²²⁸ Th	228.02872	1.913 yr	819.6	α (5.42, 5.34)
²²⁹ Th	229.03176	7340 yr	0.213	α (4.85, 4.90, 4.97)
²³⁰ Th	230.03313	7.54×10^4 yr	0.02062	α (4.69, 4.62)
²³¹ Th	231.1082	1.0633 day	5.316×10^5	β (0.318); γ
²³² Th	232.03805	1.41×10^{10} yr	1.09×10^{-7}	α (4.01, 3.95)
²³³ Th	233.1138	22.3 min	3.62×10^7	β (1.244); γ
²³⁴ Th	234.0436	24.1 day	2.315×10^4	β (0.273); γ

RP580^(a)**Water Distillation from Soil and Aqueous Matrices Using a Micro-Distillation System for Tritium Determination****1.0 Scope and Application**

This method describes the distillation of tritiated water from large (5 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

For the analysis of soil samples, 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 fraction of water actually distilled is determined. 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.

3.0 Interferences

- Other volatile radionuclides may be distilled with the water. This problem is minimized by distilling water samples from a basic solution or by placing activated charcoal above the soil samples.

^(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).

- Organically bound ^3H in soil may not be distilled, resulting in a potentially low bias.
- Organics that contact the Gortex[®] membrane will wet the hydrophobic membrane, causing it to lose hydrophobicity. The membrane will then not function properly.

4.0 Safety

After the distillation, the MICRO DIST[®] should be broken along the breakage ring with the break directed into the fume hood. This will minimize the possibility of hot liquid or contamination spattering onto the analyst.

5.0 Apparatus and Materials

- Round bottom flask, e.g., 25 mL (for > 5 g 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) reference Figure 1, or equivalent
- 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)
- Liquid scintillation counting (LSC) vials, plastic

6.0 Reagents

Reagent grade (or better) chemicals should be used in all tests, unless otherwise indicated. Other grades may be used if it is ascertained that the reagent quality will not adversely affect the method performance. Water purity should conform to ASTM specification D 1193, Type II (or better), unless otherwise indicated.

- "Dead" water - low-tritiated water (the ^3H -level tolerance in the dead water will depend on the data quality objectives)
- 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 Water Fraction 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.

Figure 1. MICRO DIST® Distillation Apparatus

- 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 (up to 50 g) is added to the flask, and the gross mass is determined.
- 8.2.3 A precisely known volume (e.g., 10 mL of "dead water") is added to the sample as a carrier.

To prepare a spike sample, 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 above the Gortex[®] membrane 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 "dead 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 (up to 5 g) is added to the MICRO DIST[®] tube sample section, and the gross mass is determined.

8.3.4 A precisely known volume (e.g., 5 mL of "dead" water) is added to the sample as a carrier.

To prepare a spike sample, 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 "dead" 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 (e.g., 1/4 pellet) of solid NaOH. A small amount (a few milligrams) to give a light purple color) of solid KMnO_4 is added to oxidize organics, or a few milligrams 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 Fraction in Soil

$$\frac{m_w - m_d}{m_w} = F_w$$

where

m_w = wet soil mass

m_d = dry soil mass

F_w = mass fraction of water in soil

9.2 Determination of Soil Sample Activity

$$A_{\text{soil}} = \frac{(CR_{\text{smp}} - CR_{\text{bkg}})}{E \cdot M} \cdot \frac{[(M \cdot F_w) + m_c]}{m_s} \cdot C$$

where:

A_{soil} = sample activity

CR_{smp} = sample count rate

CR_{bkg} = background count rate

E = detection efficiency {e.g., (standard count rate)/(standard disintegration rate)}

M = sample aliquot analyzed for ^3H , g (wet mass)

m_c = mass of "dead" 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

$$A_{\text{soil}} = \frac{(CR_{\text{smp}} - CR_{\text{bkg}})}{E \cdot V_s} \cdot C$$

where:

A_{water} = sample activity

V_s = sample volume prepared for LSC

The activity calculations are based on samples and standards with similar quench characteristics and therefore, constant counting efficiency. In this case, the generation of a quench curve is not necessary. If the quench characteristic will differ between samples and standards such that the counting efficiency will be affected, a quench curve will need to be generated and the quenching factor applied to the samples. A discussion of the quench curve generation and application to sample activity calculations is provided in Method RI100, Liquid Scintillation Instrumentation Method.

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 accuracy 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 ^3H region.
- The external standard measurement should be evaluated to verify that the samples and standards have consistent quench factors.

11.0 Method Performance

Results of the water distillation method applied to two EMSL performance evaluation (PE) samples are presented in Table 1.

Table 1. Results on EMSL PE Samples

Known Value (Bq/L)	Analytical Result (Bq/L)	Bias	n (*)
364.2 ± 36.4	371.3 ± 58.9	+1.9%	3
273.7 ± 27.4	272.8 ± 6.2	-0.3%	3
368.2 ± 36.8	360.0 ± 5.0	-2.2%	3

(*) n = number of replicates

12.0 Source Procedures

Callow, S. 1992. *Tritium by Lachar Micro-Dist™ and Liquid Scintillation Counting*. LA-218-114, Westinghouse Hanford Company, Richland, Washington.

Fadett, S. K., and R. S. Stebin, Jr. 1993. *Tritium Determination in Soil and Water Using a Lachar Micro-Dist™ System*. PNL-MA-599, PNL-ALO-418, Pacific Northwest Laboratory, Richland, Washington.

Los Alamos National Laboratory (LANL). "Extraction of Tritiated 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.}

- 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 (Krieger and Whitaker 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.

Table 4. Compilation of Fissionable Nuclide Data

Nuclide	SF (%)	Neutron Yield per fission	Ratio to ²³⁵ U fission	Neutron Yield per fission by thermal n	Ratio to ²³⁵ U fission by thermal n
²³² Th	2.37	0.6(a), 0.496(b)	33	0.527(c)	3.2
²³³ U	1.3E-10	0.077(b), 0.0779(d), 0.07(b)	47	0.074(c), 0.066(a,b)	43
²³⁵ U	WEAK	0.165(b), 0.164(e)	10	0.158(b), 0.167(c)	1.0
²³⁸ U	WEAK	0.49(a), 0.412(b), 0.439(c)	2.7	0.46(f)	2.8
²³⁶ Np	N	(0.077)(b)	(47)	(0.0648)(b)	(40)
²³⁷ Np	N	0.122(d), (0.11)(b)	74	0.107(c)	66
²³⁸ Pu	1.84E-7	0.0406(d), (0.053)(b)	25	0.046(c)	28
²³⁹ Pu	4.4E-10	0.069(a), 0.063(b), 0.0598(e)	40	0.061(a,b), 0.065(c)	39
²⁴⁰ Pu	N	0.0911(b), 0.088(b)	54	0.090(c)	55
²⁴¹ Pu	N	0.160(d)	97	0.157(c)	96
²⁴¹ Am	4.1E-10	0.0394(d), (0.053)(b)	24	0.044(c)	27
²⁴² Am	WEAK	(0.077)(b)	(47)	(0.0648)(b), 0.069(c)	42
²⁴³ Cm	N	(0.077)(b)	(47)	(0.0648)(b)	(16)
²⁴⁴ Cm	1.347E-4	(0.053)(b)	(32)	(0.0267)(b)	(36)
²⁴⁵ Cm	WEAK	(0.077)(b)	(47)	(0.0648)(b), 0.059(c)	(96)
²⁴⁷ Cm	N	(0.158)(b)	(96)	(0.0157)(b)	(96)
²⁴⁹ Cf	2.5E-7	(0.037)(b)	(22)	(0.0267)(b), 0.027(c)	16
²⁵¹ Cf	N	(0.077)(b)	(47)	(0.0648)(b)	(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) Walden, et al., 1981
(d) Benedetti, et al., 1982
(e) Bersant, et al., 1977
(f) Romen, 1989

12.0 References

- Argonne National Laboratory (ANL). 1963. *Reactor Physics Constants*, ANL-5800, 2nd edition, Section 1, "Fission Properties." Argonne, Illinois.
- Benedetti, G., A. Cesana, V. Sangiust, and M. Tarrani. 1982. "Delayed Neutron Yields from Fission of Uranium-233, Neptunium-237, Plutonium-238, -240, -241, and Americium-241." *Nucl. Sci. Eng.*, 80:379-387.
- Bersant, C., P. J. Challen, M. H. McTaggart, P. Taoulidis, and J. G. Williams. 1977. "Absolute Yields and Group Constants of Delayed Neutrons in the Fast Fission of Uranium-235, -238, and Plutonium-239." *J. Br. Nucl. Energy Soc.*, 16(2):161-176.
- Keepin, R. G. 1972. "Physics of Delayed Neutrons - Recent Experimental Results." *Nucl. Techn.* 13:53-58.

Ronen, Y. 1989. "Prediction of the Delayed Neutron Yields for Actinide Nuclides." *Ann. Nucl. Energ.* 16(12):647-648.

Waldo, R. W., R. A. Karam, and R. A. Meyer. 1981. "Delayed Neutron Yields: Time Dependent Measurements and a Predictive Model." *Physical Rev. C.* 23(3):1113-1127.

13.0 Further Reading

Dyer, F. F., J. F. Emery, and G. W. Leddicotte. 1962. *A Comprehensive Study of Neutron Activation Analysis of Uranium by Delayed Neutron Counting*. ORNL-3342, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

De Soetse, D., R. Gijbels, and J. Hoste. 1972. *Neutron Activation Analysis*. Wiley-Interscience, London, England.

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.

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) (discussed in Chapter 1). 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 ensure 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 addressed during the DQO planning process and specified in the QAPP. In keeping with the concept of performance based methods, however, all methods should be run with appropriate QC samples to demonstrate 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 documents performance parameters (e.g., detection limit, accuracy, and precision) 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. Accuracy and precision should be evaluated with at least three samples; 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 establish 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-duplicate or sample-duplicate 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 Evaluating Methods to Ensure Generation of Qualified Analytical Data: A Performance-Based Approach

Introduction and Purpose

This appendix provides guidance for selecting and qualifying analytical methods to help ensure that those methods will provide qualified data. Qualified data are those data that meet quality requirements determined during the data quality objective planning process (DQOPP) and documented in the quality assurance project plan (QAPP).

A recommended method selection and qualification process is described below and depicted in Figure 1.

Method Selection

Analytical methods from two general source types can be identified:

- Methods that have been published as consensus or regulatory methods
- New methods or modified consensus/regulatory methods.

Examples of consensus/regulatory methods are methods that have been published as American Society for Testing and Materials standards (ASTM 1986) or as U.S. Environmental Protection Agency (EPA) or state-agency regulatory methods (e.g., some EPA SW-846 methods). Examples of new

methods or modified consensus/regulatory methods are analytical methodologies taken from journal articles, laboratory-developed methodology, and consensus/regulatory methods that have been substantively modified in ways that could effect the chemistry being performed.

Frequently, new or modified methods have limited or no quality control (QC) data associated with them, but most consensus/regulatory methods have been thoroughly evaluated, and method performance has been well documented in the form of QC data that relate to specific matrices. Where available, performance data associated with a method should be carefully examined and used as a tool in the method-selection process. However, matrix-specific QC data supplied with a method do not provide any guarantee that the method will produce identical QC data for other matrices.

When review of QC documentation for a consensus/regulatory method indicates that the method should produce data meeting project DQOs, and no other constraining issues such as safety or high levels of radioactivity apply, use of the consensus/regulatory method is appropriate. If, however, a consensus/regulatory method is not appropriate for the scope of analytical testing defined in the DQOPP or if a

Figure 1. Method Selection and Qualification Process to Produce Qualified Data

new method or modified consensus/regulatory methods would result in added safety, faster analysis times, or reduction in the amount of waste produced, staff are encouraged to select a method from another source, modify the consensus/regulatory method, or develop a new method.

Method and Laboratory Qualification

The nature and extent of method evaluation will depend on the intended use(s) of the data. It will also depend on the source from which the method was selected, on method-specific technical details (e.g., use of tracers in radiochemical analyses), and on managing the risks of failure to meet analytical DQOs. The applicability of the following guidance should be evaluated and, where appropriate, tests should be performed and documented.

At a minimum, a laboratory should establish confidence that the analyst(s) and instrumentation are able to perform the method and produce data that meet QC criteria documented in the QAPP. The laboratory may only need to analyze control spike and blank samples to demonstrate that bias, precision, and sensitivity DQOs should be met. Greater confidence in the laboratory's ability to meet DQOs would be established by analyzing spikes and blanks of the test-sample matrices. Analyzing project-related spikes and blanks can yield better understanding of interferences and limitations as they apply to the matrix of interest. However, analysis of project-related spikes and blanks is not always possible or appropriate. Judgment must be used and agreement with stakeholders obtained in determining appropriate method-qualification activities.

Some considerations in method qualification are indicated below and should be used as appropriate:

- detection limits {e.g., minimum detection limit (MDL) study in 40 CFR, Ch I, Appt. B to Part 136 for organic and inorganic analyses}
- working range
- bias
- precision
- chemical yields
- potential interferences (e.g., purity of separated analyte)
- other data-quality issues (e.g., chromatographic or spectroscopic resolution)
- comparability to other methods (inter- or intra-laboratory testing)
- application of statistical methodology such as that presented in Youden and Steiner (1975) to evaluate the ruggedness of the method.

Method and Laboratory Requalification

Requalification should be considered if a specified period of time has elapsed during which the method was not used, and no control standards were analyzed. Requalification should also be considered by the laboratory when different analysts assume responsibility for the performance of the method or when new instrumentation is placed into service. Documentation of an analyst's proficiency also serves to demonstrate method requalification. Methods that are modified following initial qualification should also be requalified.

Data Qualification

After a method is evaluated, selected, and qualified, it is then available for use on a project, as agreed in the DQOPP (Chapter 1). It should be understood that

a method may provide adequate QC data for blank and blank spike samples, but that sample-matrix variations may have tremendous effects on performance of the method on actual samples. It is important to remember that final qualification of data must be based on actual performance of the method for the samples of interest (i.e., batch-QC data). Therefore, appropriate batch QC must be applied to properly qualify analytical data relative to the project DQOs. Batch QC may include one or more of the following, depending on the method or analyte:

- sample or matrix-spike duplicates to evaluate data for precision
- matrix spikes to evaluate data for bias
- carriers/tracers/surrogates to evaluate and/or correct data for chemical yields
- blanks to evaluate data for contamination

Some data qualification may also entail looking at specific sample parameters such as spectral resolution, presence of interferences, or purity of the separated, analyzed sample fraction.

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

BTEX - benzene, toluene, ethylbenzene, and xylenes

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

CI - chemical ionization

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

DQOP - data quality objectives 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

EI - electron impact	ft - foot
EIC - electret ionization chamber	FTIR - Fourier transform infrared
EM - Environmental Restoration and Waste Management	FRF - field record form
EML - Environmental Measuring Laboratory	FWHM - full width half maximum
EMSL - Environmental Monitoring System Laboratory	g - gram
EMV - electron multiplier voltage	gain shift - new channel position of a peak (PHA systems) of specific energy relative to a previous channel location
END - endrin	gal - gallon
EPA - U. S. Environmental Protection Agency	GBq - giga becquerel
EQL - estimated quantitation limit	GC - gas chromatography
ER - environmental restoration	GC-ECD - gas chromatography - electron capture detector
ER - external ratio	GC-MS - gas chromatography-mass spectrometry
ERR - error display	GFAA - graphite furnace atomic absorption
ES&H - environment, safety, and health	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.
eV - electron volt	GM - Geiger Müller
F - Fahrenheit	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.
FCV - free-column volumes	
FI - flow injection	
FIAS - flow-injection analysis system	
FID - flame ionization detection	
FM - Factory Mutual	

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

ICV - initial calibration verification

ID - identification

ID - inner diameter

ID - inside diameter

ID - isotope dilution

IDA - iminodiacetic acid

IDL - instrument detection limit

IDLH - immediately dangerous to life and health

in. - inch

INEL - Idaho National Engineering Laboratory

internal standard - a known quantity of one or more known compound(s) added to a sample for quantitation purposes.

IPL - Isotope Products Laboratory

IR - infrared spectroscopy

IR - isotope ratio

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.

Kg - kilogram

L - liter

LANL - Los Alamos National Laboratory

lb - pound

LCD - liquid crystal display

LCL - lower control limit

LC-MS - liquid chromatography-mass spectrometry

LCS - laboratory control sample

LDPE - low-density polyethylene

LED - light-emitting diode

LEP - low energy photon

LEPS - low energy photon spectroscopy

LFL - lower flammability limit

LIN - lindane

LMD - Laboratory Management Division

LLW - low-level radioactive waste	MDTA/D - micro-distillation tube assembler/ disassembler
LMWA - low-molecular-weight organic acids	MEK - methyl ethyl ketone
LSC - liquid scintillation counting	MEM - memory display
LSGAECF - Liquid Scintillation Gross Alpha Efficiency Calibration Form	method - a document describing an operation in sufficient detail that a knowledgeable analyst or sampler can perform that operation successfully.
LSTECF - Liquid Scintillation Tritium Efficiency Calibration Form	MeV - million electron volts
LWDF - Liquid Waste Disposal Facility	µg/g - microgram per gram (parts per million)
M - molar	µGy - microgray
MAX - maximum	M-gM - multi-gas monitor
mbar - millibar	mg - milligram
MBC - mass bias correction	MIBK - methyl isobutyl ketone
MBq - megabecquerel	mil - .0254 millimeter (10^{-3} inch)
MC - methoxychlor	min - minute
MCA - multichannel analyzer	mis - membrane inlet system
µCi - microcurie	µL - microliter
MCL - maximum contaminant levels	mL - milliliter
MDA - minimum detectable activity	µm - micrometer
MDC - minimum detectable concentration	mm - millimeter
MDL - method detection limit	mR - milliroentgen
MDL - minimum detection limit	mRad - millirad
MDR - minimum detectable count rate	mrem - millirem

MS - mass spectrometry	nm - nanometer
MS-DOS - Microsoft disk operating system	NNEDDC - N-[naphtyl(1)]-ethylenediamine
MSDS - material safety data sheet	NPDES - National Pollutant Discharge Elimination System
μSv - microsievert	NPH - normal paraffin hydrocarbons
mSV - milli sievert	NTA - nitriloacetic acid
MUST - Melton Valley Storage and the Evaporatory Concentrate Storage Tank, located at Oak Ridge National Laboratory	NPT - national pipe thread
mV - millivolt	NRC - U. S. Nuclear Regulatory Commission
MV - molar volume	OD - optical density
NAA - neutron activation analysis	OD - outside diameter
NaK - sodium-potassium alloy	OES - optical emission spectroscopy
NAREL - National Air and Radiation Environmental Laboratory	ORNL - Oak Ridge National Laboratory
NBL - New Brunswick Laboratory	ORD - optical rotatory dispersion
NBz - nitrobenzene	OSHA - Occupational Safety and Health Administration
NCRP - National Council on Radiation Protection and Measurements	OVA - organic vapor analyzer
NFPA - National Fire Protection Association	OVS - OSHA versatile sampler
ng - nanogram	PAH - polycyclic aromatic hydrocarbons
NIDA - N-nitroso-iminodiacetic acid	PAH - polynuclear aromatic hydrocarbons
NIOSH - National Institute Occupational Safety and Health	PAM - portable alpha monitor
NIST - National Institute of Standards and Technology	PARCC - precision, accuracy, representativeness, completeness, comparability
	PC - personal computer

PCB - polychlorinated biphenyls

PCE - perchloroethene

pCi - picocurie

PCP - pentachlorophenol

PE - performance evaluation

PEEK - poly ether ether ketone

PEG - polyethylene glycol

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.

PFTBA - perfluorotributylamine

PHA - pulse height analyzer

plateau curves - A function of count rate vs. voltage setting

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.

psi - pounds per square inch

psig - pounds per square inch gauge

PTFE - polytetrafluoroethylene

PUF - polyurethane foam

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.

REL - recommended exposure limit

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

RTD - resistance temperature device

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.

ST - small tubes

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

TiOA - triisocotylamine

TLD - thermoluminescent dosimeter

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

TTA - thenoyltrifluoroacetone

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

ZHE - zero headspace extraction

Index

A

- absorbed inorganic liquids, 5-3
- acceptance criteria, 2-7, 3-6
 - for field activities, 3-6
- acceptance testing, 2-7
- accuracy
 - defined, 3-2
 - assessed by, 3-2
- administrative approval, 4-8
- administrative dose, 4-8
- adsorbents, 8-5
- air sampling, equipment for, 7-6
- ALARA, 3-1, 4-1, 4-4, 4-6, 4-7
 - principles, 4-6
 - philosophy, 4-6
- aliquots, 4-4
- alkali metals (see metals)
- alpha spectrometry (see separation of ^{226}Ra), RP450-1
- alpha spectroscopy (see isolation of Th), RP570-1
- alpha track detectors, RA020-1
 - apparatus, RA020-3
 - indoor surfaces, contaminated, RA020-1
 - method performance, RA020-8
 - procedure, RA020-3
- alternative apparatus/reagents, 6-5
- alternative methods, 6-3
- analytes (see identification)
- analytical
 - data, 3-6
 - data, estimated uncertainty of, 3-7
 - methods, considerations for selection, 6-2
 - method tables, 6-3
 - objective, 6-2
 - instrumentation, 3-7
 - results, 3-7
- analyzing, RMW, 4-1
- anion-exchange filter membranes, RS551-1
 - apparatus, RS551-2
 - method performance, RS551-5
 - procedure, RS551-2
 - rapid isolation and measurement of ^{99}Tc , RS551-1
- anion exchange (see isolation of Th), RP570-2
- aqueous matrices, group actinide screening RP725-1
 - apparatus, RP725-2
 - method performance, RP725-6
 - procedure, RP725-3
- aqueous matrices, tritium determination (see soil and aqueous matrices)

- aqueous radioactive mixed wastes (see radioactive mixed wastes, aqueous)
- aqueous radioactive samples (see radioactive samples, aqueous)
- aqueous samples (see separation of ^{226}Ra), RP450-1
- aqueous samples, determination of ^{79}Se , RP530-1
apparatus, RP530-3
method performance, RP530-14
procedure, RP530-6
- aqueous samples, determination of ^{99}Tc , RP550-1
apparatus, RP550-1
extraction chromatography, RP550-1
method performance, RP550-7
procedure, RP550-3
- aqueous samples, HLW, total radioactive Sr
RP501-1
apparatus, RP501-4
extraction chromatography, RP501-1
method performance, RP501-11
procedure, RP501-5
- aqueous samples, ^{59}N and ^{63}N determination, RP300-1
apparatus, RP300-2
method performance, RP300-12
procedure, RP300-4
- aqueous samples, rapid isolation of TcO_4^- (see anion-exchange filter membranes)
- aqueous samples, sequential separation of Am and Pu, RP800-1
apparatus, RP800-2
method performance, RP800-6
procedure, RP800-3
- aqueous solutions, ^{29}I analysis, RP230-1
apparatus, RP230-2
method performance, RP230-12
procedure, RP230-4
- aqueous solutions, separation of Nb, RP330-1
apparatus, RP330-2
determination of $^{93\text{m}}\text{Nb}$, ^{94}Nb
method performance, RP330-10
procedure, RP330-3
- aqueous-to-organic extraction (see isolation of Th), RP570-2
- Argentometric titration, MU012R-1
- Aroclors, OG100R-1, OP100R-1, OS010-1, OS020-1
- asbestos, 5-3
- assessments
management (see management assessments)
independent, 2-8
scheduling, 2-8
results, 2-8
- auger sampler, ST011R-3
- B**
- background counts, 10-3
- background subtraction (see GC/MS system)
- bacon-bomb sampler, ST011R-1
- batch
defined, 3-2
samples in, 3-2

benchtop work, defined, 4-9

bias

defined, 3-2

net, 3-2

BioNebraska BiMelyze™ Mercury Assay Kit,
MB100-1 to -2

borehole logging, RS100-1

apparatus, RS100-3

gamma-ray-emitting radionuclides,
RS100-1

in situ analysis, RS100-1

method performance, RS100-8

procedure, RS100-4

blind sample

defined, 3-2

QC, 3-8

C

caution(s), 4-11

calibration, 8-5, 9-3, 10-4

cans, safety (see safety precautions)

capillary gas chromatography (see soils,
supercritical fluid extraction)

carbon, organic (see organic methods)

carcinogen, defined, 4-4

cement solidified low-level liquid waste,
SW010R-1

chain-of-custody

documentation, 1-10

form, 1-14

chain-of-possession form, 1-14

check sample, defined, 3-2

chelating resin, RP510-1

chelators (see mixed hazardous waste samples,
determination of chelators and their degradation
products)

chemical handling, 4-12, 5-6

chemicals, organic, volatile, 8-4

chemicals, storage, 4-16, 4-18, 5-6

chemicals, toxic, 4-15

choosing methods, factors in, 6-1

chromate ions, test for, MS110-1

chronic freshwater toxicity levels, 5-8

chromatography, extraction

MP110R-1

RP280-1

RP501-1

RP550-1

RP725-1

RP800-1

chromatography, gas, 8-1

derivatization GC-MS, OM510R-1

chromatography, ion, 9-4

cleanup QC, 8-5

CMPO {see octyl(phenyl)...}

- colorimetric test, indicator strip, chromate, MS110-1
 - apparatus, MS110-2
 - method performance, MS110-4
 - procedure, MS110-3
- colorimetric test, indicator strip, lead, MS210-1
 - apparatus, MS210-2
 - method performance, MS210-4
 - procedure, MS210-3
- colorimetric test, indicator strip, nickel, MS410-1
 - apparatus, MS410-2
 - method performance, MS410-4
 - procedure, MS410-3
- colorimetric test, indicator strip, nitrate ions, MS310-1
 - apparatus, MS310-2
 - method performance, MS310-4
 - procedure, MS310-3
- colorimetric test strips, instrument for, MS100-1
 - apparatus, MS100-2
 - method performance, MS100-7
 - procedure, MS100-4
 - reflectrometry-based instrument, MS100-1
- column bleed (see GC/MS system)
- column, cation exchange, RP450-2
- comparability defined, 3-2
- completeness defined, 3-2
- component concentrations, 6-3
- compound confirmation, 8-6
- computer software, 2-6 (also see software)
 - controls for, 2-6
- results, 2-6
- security policies and procedures, 2-7
- constant air monitor (CAM), 4-7
 - criteria for using, 4-7
- containers
 - recommendations, 5-2, 5-4
 - size of, 4-16, 4-17
- contaminant concentration level (see action level)
- contaminated clothing, 4-11
- contaminated indoor surfaces, RA010-1
 - apparatus, RA010-3
 - Electret ionization chambers, RA010-1
 - method performance, RA010-11
 - procedure, RA010-4
- contamination, potential for, 4-4
- contamination, prevention of, 5-6 to 5-8
- continuous-mode sampling, 7-8
- control (s), 4-10
 - chart, 3-2, 3-6
 - measures, 2-5
 - limits, 3-2, 3-6
 - laboratory samples, 3-6
 - levels, administrative, 4-7, 4-8
 - benchtop work, 4-9
- control sample, 3-2, 3-8
 - radionuclides, 3-8
 - organic and inorganic analytes, 3-8.
- controlled documents, 2-5
- converter, analog to digital, 10-5

core samples, sampling method, SW010R-1

corrective actions, 2-4

criteria

- acceptance, 3-6
- quality control, 3-6

criticality, defined, 4-4

cyanide, MU012R-1

- apparatus, MU012R-2
- Argentometric titration, MU012R-1
- method performance, MU012R-8
- procedure, MU012R-3
- remote microdistillation, MU012R-1

cryogenics, 4-22

D

data , 2-8

- project, assessing, 1-1
- quality (see data quality)
- summary, 1-9
- management (see data management)
- review, 1-10
- reporting formats, 1-10
- reporting requirements, 3-7
- collection operations, 2-6
- acceptability, 2-7
- analytical, 3-1, 3-6
- out-of-control, 3-6
- reporting, 7-13, 8-6, 9-4, 10-5
- traceability of, 3-7

database, DOE procedures

- access to, Intro-3
- assembly of, Intro-3
- external access, Intro-3
- goal of, Intro-2
- maintenance of, Intro-2

methods consolidation, 10-1

procedures in, Intro-2

searches in, Intro-3

updates to, Intro-3

data management, 1-10

records-control requirements, 1-10

data quality

- establishing, 1-2

- assessment (DQA) (see data quality assessment)

data quality assessment, 1-11

- when to perform, 1-11

- defined, 1-11

- requirements of, 1-11

- six steps of, 1-11

data quality objectives (DQOs), 1-1

dead time, 10-5

decision-level concentration, 10-3

decision-level count rate, 10-2

dead time, 10-5

Determination of Radium-226, RP450-1

- apparatus, RP450-2

- method performance, RP450-7

- procedure, RP450-3

Determination of Th Isotopes, RP570-1

- apparatus, RP570-4

- method performance, RP570-9

- procedure, RP570-6

determination of VOCs in water and soil, OS040-1

dip sample, ST011R-1

direct aqueous injection gas chromatography,
OG015R-1

direct-purge mass spectrometry (see water and
soils, rapid determination)

dispensing and transfer, 4-15

dispersible conditions, 4-2, 4-10

limited, 4-2, 4-10

highly or readily, 4-2, 4-10

dispersibility, defined, 4-2

dispersibility of radioactive or hazardous material,
4-2

disposal of radioactive and hazardous waste, 5-1

low-level radioactive waste, 5-2

high-level radioactive waste, 5-3

transuranic waste, 5-4

documentation

changes to entries, 2-5

requirements, 3-7, 5-3

dodecylamine, RP570-2

DOE enhancement, 1-1

DOE Methods

assembly of, Intro-3

comments on, send to, Intro-4

contents of, Intro-3

development of, Intro-2

focus of, Intro-2

goal of, Intro-3

intent of, Intro-1, Intro-2

intent of editors, Intro-2

maintenance of, Intro-2

revisions to, Intro-1

DOE Order(s)

5700.6C, 2-1, 2-2

DOE Procedures Database (see database)

dose

effective equivalent, 4-7

equivalent levels, 4-9

dose limits

annual, guidelines, 4-7

occupational, equivalent, 4-7

radiological worker, 4-7

summary of, 4-8

dose rate, 4-6

abnormal, protection from, 4-7

dosimeters, 4-8

double blind

defined, 3-3

QC, 3-8

DQOP

defined, 1-4

description of, 1-2

final goal, 1-3

focus of, 1-2

iterative process, 1-3

stakeholder involvement, 1-3

steps, 1-4 to 1-8

vs. traditional data quality, 1-2

DQO process

training videos on, 1-2

basic tenant of, 1-3

recent applications, 1-3

example of flexibility, 1-3

draft method(s)

approval of, Intro-3

- defined, Intro-2
 - inclusion in *DOE Methods*, Intro-3
 - nonverified, Intro-2
- drains, French, 5-8
- drilling, 7-2
- drum sampling, equipment for, 7-4
- drums, all wastes, headspace sampling, SA011R-1
apparatus, SUMMA™ canister, SA011R-2
2
cleaning SUMMA™ canister apparatus, SA011R-6
collection, field blanks, SA011R-9
collection, field duplicates, SA011R-9
collection, field reference standards, SA011R-12
collection, headspace gas, SA011R-8
collection, equipment blanks, SA011R-10
headspace gas, poly bags, SA011R-1
- drums, 71 gal, square, core samples, SW010R-1
apparatus, SW010R-2
cement solidified low-level liquid waste, SW010R-1
- drums, TRU wastes, headspace sampling, SA010R-1
equipment cleaning, sampling manifold, SA010R-9
equipment cleaning, needle assembly, SA010R-14
equipment, components, SA010R-2
equipment-blank collection, SA010R-18
field-blank collection, SA010R-17
field-duplicate collection, SA010R-17
field-reference-standard collection, SA010R-19
sample collection, SA010R-16
- duplicate, defined, 3-3
- E
- effluents, liquid
radioactive, 5-6
nonradioactive, 5-7
- EiChroM™ pre-filter column, MP110R-1
- Electret ionization chambers, RA010-1
- electrodeposition (see separation of ²²⁶Ra), RP450-1
- emergency washing facilities, 4-12
design and provision of, 4-12
drench hoses, 4-12
personal eyewash units, 4-12
- environmental matrices, group actinide screening, RP730-1
apparatus, RP730-2
method performance, RP730-7
procedure, RP730-3
- environmental restoration and waste management (EM)
project(s) objective and scope, flexibility of, 1-2
- environmental samples, determination of ⁹⁰Sr, RP510-1
apparatus, RP510-2
chelating resin, RP510-1
method performance, RP510-12
procedure, RP510-4
- environmental sampling and analysis
goals of, 3-5
- environment, safety, and health (ES&H), standards, 4-1

EPA data quality objective planning process (see DQOP)

EPA test methods, 6-1, 7-1, 8-1

equipment

core-sampling, 7-9

types, performance of work, 2-6

error(s), 1-6

decision, 1-6

probabilities, 1-8

analysis, 1-12

estimate of uncertainty, 8-6

exposure

risk of, 4-1

personnel, controlling, 4-6

control during a job, 4-6

rates, nonuniform external, 4-6, 4-7

skin, 4-7

to ionizing radiation, occupational, 4-7

planned variances, 4-9

extraction chromatography (see chromatography, extraction)

extraction, filter membrane, ⁹⁹Tc analysis, RS551-1

extractions, organics, 8-5

F

face shields, 4-6

facilities guidelines, TRU waste, 5-5

field screening, 4-4, 9-1

field duplicate, defined, 3-3

filter samples, determination of ⁹⁰Sr (see soil, water, and filter samples)

fire blankets, 4-12

fissile content, total, RP735-1

apparatus, RP735-2

delayed neutron counting, RP735-1

method performance, RP735-4

neutron activation, RP735-1

procedure, RP735-3

flammable and combustible liquids, 4-15

fume hoods, limits, 4-10

G

gamma-ray-emitting radionuclides (see borehole logging)

gamma-ray spectrometry, RI010-1

gain shift, 10-5

gas chromatography (see chromatography, gas)

gases, compressed, 4-16, 4-19

GC/MS system, 8-1

glassware, organic analysis, 8-2, 8-3

glovebox, 4-11

graphite furnace atomic absorption (GFAA), MP100R-1

gross alpha and beta determination, RP710-1
apparatus, RP710-2

- method performance, RP710-12
- procedure, RP710-4
- gross alpha, beta, and tritium rapid determination, RP720-1
- gross alpha emission, RA010-1, RA020-1
- gross-beta counting (see isolation of Th), RP570-1
- gross gamma screening, RP730-1
- groundwater sampling, 7-6
- guidelines for sampling of RMW, 7-2 to 7-6
- H**- halogens, organic (see organic compounds)
- handling, 2-5, 2-6
 - RMW, 4-1
- hazard communication, requirements, 4-1
- hazardous chemicals
 - air concentrations of, 4-12
- hazardous wastes
 - minimization, 5-1
- high-efficiency particulate air filters (HEPA), 4-4, 4-6
- high-level radioactive wastes, analysis for VOCs, OP010R-1
 - apparatus, OP010R-4
 - method performance, OP010R-11
 - procedure, OP010R-9
 - remote purge and trap GC, OP010R-1
- high-level wastes
 - disposal of, 5-4
 - other wastes managed as, 5-4
- high-level waste storage tanks (see sampling liquids and solids)
- high-performance liquid chromatography (HPLC)
- holding times, 9-5
- hood, approved (see safety precautions)
- hot cell, OP150R-1, OG015R-1, OG100R-1
- housekeeping, 4-24
- HPLC with UV absorbance detection, OH100R-1
- hydrocarbon samples, preparation and cleanup, for VOCs, OC010R-1
 - apparatus, OC010R-2
 - method performance, OC010R-7
 - procedure, OC010R-3
- I**- ICP-MS determination for specific radionuclides, MM100-1
 - apparatus, MM100-3
 - procedure, MM100-5
- ICP-MS determination for U, MM800-1
 - apparatus, MM800-2
 - groundwater and drinking water, MM800-1
 - method performance, MM800-13
 - procedure, MM800-4
- ICP-MS determination, flow injection preconcentration, MM210-1
 - apparatus, MM210-4
 - method performance, MM210-13
 - procedure, MM210-8

- identification, 2-5
- immunoassay for petroleum fuel hydrocarbons in soil, OS060-1
 - apparatus, OS060-3
 - method performance, OS060-18
 - procedure, OS060-3
- immunoassay QC, 8-5
- independent assessments, 2-8
- indicator strip-based colorimetric test for lead, MS210-1
- indicator strip-based colorimetric test for nitrate ions, MS310-1
- inductively coupled plasma (ICP), MP100R-1
- information quality, 3-1
- inorganic analysis, 9-1
- in situ* analysis (see borehole logging)
- iodine-129 analysis, RP230-1
- inspection(s), 2-7
 - and acceptance testing, 2-7
 - level of, 2-7
 - degree of independence, 2-7
- inspection testing, 2-7
- instrumentation, organic, 8-1
- instrumental QC, 8-5
- instrument background (see GC/MS system)
- instrument quality control chart, 10-4
- instrument reliability tests, 10-5
- intercomparison programs, 3-8
- interferences, potential, 6-3
- ion exchange (see isolation of Th), RP570-1
- ion exchange (see separation of ²²⁶Ra), RP450-1
- isolation of Th in aqueous samples, RP570-1
- J**
- K**
- L**
- laboratories, RMW, 4-4
- laboratory control sample, 3-7
 - defined, 3-3
 - spiked, 3-7
 - results from, 3-7
- laboratory types,
 - A, 4-4, 4-5
 - B, 4-4, 4-5
 - C, 4-4, 4-5
 - D, 4-4, 4-5
- lead ions, test for, MS210-1
- limitations resulting from radioactivity safety constraints, 7-1
- liquid effluent samples (see sampling liquids, effluent monitoring)

- liquid/liquid extraction (see isolation of Th),
RP570-1
- liquid-liquid extraction (see radioactive samples,
aqueous)
- liquid sampler, automated, refrigerated, SO010R-2
- liquid scintillation counting, RI100-1
apparatus, RI100-4
matrices, aqueous radioactive samples,
RI100-1
method performance, RI100-10
procedure, RI100-5
- liquid scintillation counting, (LSC) system, RI100-
1, RP720-1, RP300-2, RP510-1
- liquids, radioactive aqueous, OG015R-1
apparatus, OG015R-2
direct aqueous injection gas chromatogra-
phy, OG015R-1
method performance, OG015R-13
nonhalogenated volatile organics,
OG015R-1
procedure, OG015R-6
- liquids, radioactive, or leachates, OH100R-1
apparatus, OH100R-2
HPLC with UV absorbance detection,
OH100R-1
method performance, OH100R-7
procedure, OH100R-4
TCLP acidic semivolatile compounds,
OH100R-1
- liquids, radioactive, solvent extraction, MP100R-1
apparatus, MP100R-2
for U and Th, MP100R-1
method performance, MP100R-4
procedure, MP100R-3
- liquids, TRU, MP110R-1
apparatus, MP110R-3
extraction chromatography, MP110R-1
method performance, MP110R-4
procedure, MP110R-3
- logging, borehole, RS100-1
- M**
- management, 2-4, 2-5, 4-6
- management assessments, 2-7, 2-8
process for performing and documenting,
2-7
results of, 2-7
- material safety data sheets (MSDS), 4-1
- matrix, 3-2
defined, 3-3
spike duplicates, defined, 3-3
spike, defined, 3-3
duplicate, defined, 3-3
duplicate analysis, 3-5
effects, organics, 8-3
- matrix blank, 3-7
defined, 3-3
- matrix-specific
bias, 3-7
precision, 3-7
detection limit, 3-7
- matrix effects
on method performance, 3-7
- maximum dose equivalent, 4-8
- measurement process, proficiency of, 3-2

- mercury, immunoassay for, MB100-1
- metals, alkali, 4-20, 4-21
- methanolic extraction, OG010R-1
- method(s), Intro-3
 - analytical, guidance on, 1-10
 - blank, defined, 3-3
 - chemicals required, 4-1
 - consolidation of, Intro-3
 - defined, Intro-1
 - demonstrating, Intro-3
 - detection limit (MDL), defined, 3-3
 - DOE (see *DOE Methods*)
 - draft (see draft methods)
 - field sampling, Intro-1
 - frequently used, Intro-1
 - generation of, Intro-3
 - inclusion in *DOE Methods*, Intro-3
 - new (see new methods)
 - nonverified (see draft methods)
 - numbering system (see numbering system for methods)
 - performance requirements for, Intro-3
 - preparation of, Intro-3
 - protection, 4-1
 - selection of (see method selection)
 - standard, required modifications to 4-4
 - using and modifying, Intro-3
 - verification, Intro-1, Intro-3
 - verified (see verified methods)
- method selection
 - guidelines for, Intro-1
 - performance requirements for, Intro-3
 - sampling QA/QC controls for, 1-10
 - acceptance criteria, 1-10
- micro-distillation system (see soil and aqueous matrices)
- minimum detectable count rate, 10-3
- minimum detectable concentration, 10-3
- mixed hazardous waste samples, determination of chelators and their degradation products, OM510R-1
 - apparatus, OM510R-2
 - method performance, OM510R-7
 - procedure, OM510R-4
- mixed hazardous waste samples, qualitative analysis for low-molecular-weight organic acids, OM500R-1
 - apparatus, OM500R-2
 - method performance, OM500R-6
 - procedure, OM500R-4
- mixed-waste samples at DOE sites, 8-1
- modification
 - of method(s), 8-1, 8-5
 - of procedures, Intro-2
- monitoring and data collection equipment
 - calibration of, 2-5
 - maintenance of, 2-5
- monitor, 4-9
- N
- neutron activation (see fissile content, total)
- new methods
 - development, reasons for, Intro-1
 - need for, Intro-2
- nickel ions, test for, MS410-1
- niobium, separation of, RP330-1

- nitrate ions, test for, MS310-1
- nitrite reactions (see matrix-specific effects)
- no-fault attitude, 2-4
- nondispersible conditions, 4-2, 4-10
- nonhalogenated volatile organics, OG015R-1
- normal paraffin hydrocarbons (NPH), OC010R-1
- nonvolatile compounds (see organic compounds and organic methods)
- normal paraffin hydrocarbons (NPH)
- numbering system for methods, Intro-4
example of, Intro-4
- O**
- octyl(phenyl)-N-N-diisobutyl-carbamoyl-methylphosphine oxide (CMPO)
- organic acids, low molecular weight, OM500R-1
- organic compounds
nonvolatile, 8-4
semivolatile, 8-4
thermally labile, 8-4
volatile, 8-4
- organic methods
total organic carbon, 8-1
total organic halides, 8-1
chlorine, OS010-1
nonvolatile (or thermally labile), 8-1, 8-3
semivolatile, 8-1
standards, 8-5
volatile, 8-1, OP010R-1, OG015R-1,
OG015R-1, OC010R-1, OP020R-1
- out-of-control data, 3-6
- P**
- PCB (see polychlorinated biphenyls)
- performance data, Intro-3
- peroxides, organic, 4-19
- pesticides (see sludges, radioactive mixed wastes)
- personnel exposure, 3-1
- petroleum fuel hydrocarbons in soil, OS060-1
apparatus, OS060-3
method performance, OS060-10
procedure, OS060-4
- photoacoustic infrared method (see water, detection of chlorinated VOCs)
- plan(s)
project {see project plan(s)}
for assessing data quality, 1-1
- plutonium, MP100R-1
- Poisson uncertainty statistic, 10-5
- polychlorinated biphenyls (PCBs)
analysis of as Aroclors, OG100R-1,
OP100R-1
concentration by chlorine content,
OS010-1
immunoassay for, OS020-1
- practical quantitation limits, defined, 3-4
- precautions, 4-1, 4-6, 8-2
- precautions needed when analyzing for trace organics, 8-2

- precipitates, 5-8
 - precision, defined, 3-4
 - preparation, hydrocarbon samples, for VOCs (see hydrocarbon samples)
 - procedure(s), 3-6, 3-7
 - combination of, Intro-3
 - database, DOE (see database)
 - defined, Intro-1
 - in *DOE Methods*, Intro-2
 - modification of, Intro-2
 - searching for, Intro-3
 - selection of, Intro-3
 - identifying, 2-5
 - emergency, 4-1
 - procurement, 2-7
 - project personnel, 3-5
 - project plan(s)
 - contents of, 1-1, 1-2, 1-9
 - defined, 1-1, 1-4
 - implementing, 1-1, 1-10
 - quality assurance (see QAPP)
 - guidance for, 1-9
 - purpose of, 1-9
 - schedule, 1-10
 - review and approval, 1-11
 - project planning
 - guidance for, 1-1
 - protective clothing, 4-6, 4-7
 - requirements, 4-9
 - hand protection (gloves), 4-12
 - foot protection (shoes), 4-12
 - eye and face protection, 4-12
 - safety goggles, 4-12
 - splash goggles and face shields, 4-12
 - protection of unborn child, 4-7
 - protocols, 3-6, 3-7
 - laboratory control, 3-6, 8-4, 9-2, 10-2
 - hazard communication, 4-1
 - pulse pileups, 10-5
 - purgable organics, 5-7
 - purge and trap methods, 8-5, OP030R-1
 - in a glovebox, off-line, OP030R-3
 - remote, OP010R-4
 - purgewater, disposal of, 5-8
- Q**
- QA (see quality assurance)
 - QA requirements, 2-1, 2-3
 - failure to meet, 2-3
 - QAMP
 - defined, 2-2, 3-4
 - QAPP, 2-5, 2-8, 3-5, 3-6
 - primary objectives, 3-6
 - framework for writing, 1-2
 - defined, 1-1, 1-3
 - development of, 2-1, 2-2
 - contents of, 2-2, 2-3
 - management approval, 2-3
 - vocabulary, 2-3
 - quality levels, 2-3
 - deviations from, 2-5
 - purchased items and services, 2-7
 - procedures, 2-7
 - QA program, 2-1
 - defined, 2-1
 - goal of, 2-1

- management role, 2-1
 - contents of, 2-2
 - criteria, 2-2
 - documented by, 2-2
- QC program, 3-6
- components, 3-1
 - goal of, 3-1
 - defined, 3-1
- qualifications, 2-4
- documentation of, 2-4
- quality
- defined, 2-1
 - assurance (see quality assurance)
 - levels, 2-3
 - considerations, 2-3
 - improvement (see quality improvement)
 - project requirements, 2-4
 - goals, 2-4
 - of data, 2-4
 - information, 3-1
- quality assurance (QA)
- project plan (see QAPP)
 - specifications, 2-1
 - program (see QA program)
 - topics, 2-2
 - management plan (see QAMP)
 - requirements (see QA requirements)
 - deficiencies, 2-4
 - nonconformances, 2-4
 - allocation of resources, 2-8
- quality control (QC), 3-1
- program (see QC program)
 - analysis, 3-1
 - inorganics, 9-2
 - instrument, 9-3
 - levels of, 3-1
 - organics, 8-4
- radiochemistry, 10-4
- reduced levels, 3-1
 - criteria, 3-5
 - sampling activities, 3-5, 7-13
 - samples, 3-6, 3-8
- quality improvement, 2-4
- basic goal of, 2-4
- quality problems
- management system, 2-4
 - preventing, 2-4
 - detecting, 2-4
- quantification limit, 8-5
- R
- radiation, DOE protection policies, 4-7
- radiation area monitor (RAM), 4-7
- criteria for using, 4-7
- radiation dose limits, 4-7
- radiation measurement, 10-5
- radiation protection
- standards, 4-1
 - practices, 4-1
 - policy, DOE, 4-6
- radiation work permit (RWP), 4-9
- radioactive mixed waste and hazardous waste, 5-2, 7-8
- radioactive liquid waste system, 5-7
- radioactive materials
- physical containment/confinement, degree of, 4-2

- engineered safeguards, 4-2
- administrative controls, 4-2
- maximum allowable quantity, 4-9, 4-10
4-11
- dispersible or potentially dispersible, 4-10
- radioactive mixed wastes, aqueous, for PCBs, OP100R-1
 - apparatus, OP100R-2
 - GC-ECD, OP100R-1
 - method performance, OP100R-6
 - procedure, OP100R-3
 - solid-phase extraction disks, OP100R-1
- radioactive mixed wastes (RMW)
 - very low-activity, 4-1
 - laboratory (see RMW laboratory)
 - samples, operating guide for, 4-5
- radioactive samples, aqueous, for semivolatile organics, OP120R-1
 - apparatus, OP120R-2
 - liquid-liquid extraction, reduced-scale, OP120R-1
 - method performance, OP120R-7
 - procedure, OP120R-2
- radioactive samples, for VOCs, OP030R-1
 - apparatus, OP030R-1
 - method performance, OP030R-5
 - procedure, OP030R-2
 - purge and trap in glovebox, OP030R-1
- radioactivity
 - dispersibility, 4-2
 - samples (see matrix-specific effects)
- radiological controls, guidelines for, 4-4
- radiological work, guidelines for, 4-9
- radionuclides, 4-2
 - radionuclides, gamma ray emitting, RS100-1
 - radionuclide toxicity, classification of, 4-3
 - radiotoxicity, defined, 4-2
- readiness reviews, 2-3
- reagents (see matrix-specific effects)
- reagent
 - blank (see method blank)
 - grade, 3-5
 - preparation of, 6-5
- records, maintenance of, 2-5
- recycling program, 5-2
- reference material(s), defined, 3-5
- reflectrometry-based instrument, MS100-1
- refrigeration, 9-1
- refrigerators and freezers, 4-16
- relative dispersibility, conditions of, 4-2
- remote microdistillation, MU012R-1
- remote purge and trap GC (see high-level radioactive waste)
- replicate sample, defined, 3-5
- Resource Conservation and Recovery Act, SD010R-1
- respirators, 4-6
- repository protection, 4-9
 - equipment, 4-6

- representativeness, defined, 3-5
- respirator (see safety precautions)
- restrictions, offsite shipping, 7-11
- revision of Compendium, Intro-1
- RMW laboratory
 - requirements, 4-4
 - selection, guidelines for, 4-4
- roughing pumps, 8-4
- run log, 9-5
- S**
- safe handling and storage of chemicals, 4-11
- safe operations, guidance for, 4-1
- safe practices, 4-12
- safety, Chapter 4
 - equipment, 1-9
 - precautions, 4-16, 4-23
 - considerations, 1-9, 2-3, 4-6, 8-3
 - controls, 3-5
 - sampling methods, 7-12
- samplers, hard sludge, ST010R-14
- sample(s), 3-1
 - analysis, 1-10 (see also, SOPs)
 - collecting, 1-9 (see also, sample collection)
 - container(s), 1-10
 - field-duplicate, 3-5
 - handling, 4-6
 - hazardous waste, analysis of, 4-2
 - identification, 1-13
 - laboratory control, 3-6
 - labeling, 1-10, 5-6
 - maintenance requirements, 1-10
 - preparation, 10-4
 - preparation, guidance on, 1-10
 - preservation, 1-10 (see also, SOPs)
 - radioactive, analysis of, 4-2
 - RMW, 4-4
 - samples of, 3-6
 - size, 1-10
 - split, defined, 3-5
 - container types, 1-12
- sample collection
 - selection of SOPs or methods for, 1-10
- sampling (see drums, all wastes; drums, TRU wastes; tanks, liquids and sludge) and analytical activities (see sampling and analysis)
 - accuracy, 3-6
 - considerations, 8-4
 - evaluation of, Intro-2
 - screening requirements for, 1-9
 - equipment, 1-10
 - maintenance requirements, 1-10
 - methods, 6-1
 - contingency approaches, 1-9
 - QA/QC controls, acceptance criteria, 1-10
 - QC activities, 3-5
 - strategies, 1-12
 - primary approaches to, 1-12
 - plan, 1-12
 - soil/sediment, 7-2
 - tank waste, 7-8
 - waste and environmental, 7-1
 - waste form, 7-9
- sampling and analysis
 - data resulting from, 2-1
 - scope of activities, 3-1
 - waste requirements, 4-1

- hazardous waste, 4-1
- radioactive mixed waste (RMW), 4-1
- sampling and transport, 6-3
- sampling and analysis plan (S&AP)
- sampling liquids and solids, ST011R-1
 - apparatus, ST011R-4
 - method performance, ST011R-21
 - procedure, ST011R-13
- sampling liquids, effluent monitoring, SO010R-1
 - apparatus, SO010R-5
 - method performance, SO010R-14
 - procedure, SO010R-8
 - protective clothing, SO010R-5
 - sewers, facility process, and retention process, SO010R-1
- sanitary sewer, 5-8
- screening, radiological, 6-5
- SEARCHmate, Intro-3
- selenium-79, determination of, RP530-1
- semivolatile compounds (see organic compounds and organic methods)
- separation of ^{226}Ra in aqueous samples, RP450-1
- shielding, 4-7
- shipping, 2-5
- sinks, 5-8
- size of samples limited, 8-1
- sludge collector
 - 3-L, ST011R-5
 - 25-L, ST011R-5
- sludge (defined), SD010R-1
 - sludge, hard, SD010R-4
 - sludge, soft, SD010R-4
- sludges, radioactive mixed wastes, analysis of, OP130R-1
 - apparatus, OP130R-3
 - method performance, OP130R-7
 - pesticides, OP130R-1
 - procedure, OP130R-5
 - TCLP semivolatiles, OP130R-1
- software
 - computer (see computer software)
 - configuration management methods, 2-6
- soil and aqueous matrices, tritium determination, RP580-1
 - apparatus, RP580-2
 - method performance, RP580-10
 - procedure, RP580-3
 - water distillation, RP580-1
- soil sampling, 7-8
- soil/sediment sampling, equipment for, 7-2
- soils, immunoassay for mercury, MB100-1
 - Part 1, using microplates, MB100-1
 - apparatus, MB100-2
 - method performance, MB100-8
 - procedure, MB100-4
 - Part 2, using test tubes, MB100-12
 - apparatus, MB100-12
 - method performance, MB100-15
 - procedure, MB100-14
- soils, immunoassay for PCBs, OS020-1
 - apparatus, OS020-2

- method performance, OS020-12
- procedures, OS020-4
- soils, for semivolatile organic compounds, OS050-1
 - apparatus, OS050-2
 - method performance, OS050-10
 - procedure, OS050-7
 - supercritical fluid extraction, OS050-1
- soil, water, and filter samples, determination of ^{90}Sr , RP520-1
 - apparatus, RP520-2
 - method performance, RP520-13
 - procedure, RP520-4
- solid phase extraction, OP100R-1
- solid radioactive mixed wastes, for PCBs, OG100R-1
 - apparatus, OG100R-2
 - method performance, OG100R-6
 - PCBs as Aroclors, OG100R-1
 - procedure, OG100R-3
- solid radioactive mixed wastes, for VOCs, OP020R-1
 - apparatus, OP020R-2
 - method performance, OP020R-4
 - procedure, OP020R-3
 - ultrasonic solvent extraction for, OP020R-1
- solid radioactive wastes, zero headspace extraction, OP040R-1
 - apparatus, OP040R-3
 - method performance, OP040R-10
 - procedure, OP040R-8
- solids, extracting nonvolatile and semivolatile organic compounds, OP150-1
 - apparatus, OP150-1
 - method performance, OP150-2
 - procedure, OP150-2
 - ultrasonic extraction, glovebox or hot cell, OP150-1
- solvent extraction, MP100R-1
- SOPs, 1-10
 - deviations from, 2-5
- spectrometry
 - inductively coupled plasma, mass, 9-1
 - inductively coupled plasma, optical emission, 9-1
- spectrometry, gamma ray, RI010-1
 - apparatus, RI010-3
 - matrices, variety, RI010-1
 - method performance, RI010-11
 - procedure, RI010-7
- spectroscopy, gamma ray, RP230-1
- spike, level of, 3-2
- split samples, 3-5
- standard addition, defined, 3-5
- standard operating procedures (see SOPs)
- standard reference material, defined, 3-5
- stop work order, 2-3
- storage
 - general considerations, 5-5
 - temporary, TRU, 5-4
- storing, 2-5
- strontium-90, determination of, RP510-1, RP520-1

- strontium, purification of, RP500-1
- strontium, radioactive, determination of, RP501-1
- SUMMA™ canisters, 7-4
- supercritical fluid extraction, OS050
- surface water sampling, 7-8
- surfaces, indoor, contaminated
 - alpha track detectors, RA020-1
 - Electret ionization chambers, RA010-1
- surrogates, defined, 3-5
- survey,
 - self, requirements, 4-9
 - whole body, 4-9
- SW-846, 3-1
- T**
- tanks, storage of, 5-8
- tanks, liquid and sludge sampling, low-level waste, ST010R-1
 - apparatus, ST010R-4
 - equipment, decontamination of, ST010R-16
 - hard sludge, ST010R-13
 - liquids, ST010R-10
 - sample packaging, ST010R-15
 - soft sludge, ST010R-12
 - thin organic layer, ST010R-11
- task/milestone chart, 1-10
- TCLP acidic semivolatile compounds, analysis of, OH100R-1
- TCLP semivolatiles and pesticides, analysis of (see sludges, radioactive mixed wastes)
- technetium-99, analysis, RP550-1
- thenoyltrifluoroacetone, RP570-2
- thermally labile compounds (see nonvolatile compounds)
- thermospray LC-MS, OM500R-1
- thorium, solvent extraction of, MP100R-1
- TOPO (see tri-n-octylphosphine oxide)
- total fissile content, determination of, RP735-1
- total quality management (TQM), 2-1
- toxic chemical, defined, 4-4
- traceability , defined, 3-5
- training, 4-2, 4-9
 - personnel, 2-4
 - requirements (see training requirements)
 - needs, identifying, 2-4
 - priorities, assigning to needs, 2-4
 - instructors, qualified, 2-4
 - required, 4-1
 - protective clothing, 4-2
 - spill handling, 4-2
 - chemical compatibility, 4-2
 - radiation safety, 4-2
- training requirements, 4-9
 - establishing, 2-4
 - satisfying, 2-4
- transuranic waste, 5-4
 - contact-handled, 5-4

- drum (see drum, transuranic waste)
 - liquid, MP110R-1
 - packaging, storing, and disposing of, 5-4
 - remote-handled, 5-4
- triisooctylamine (TiOA), RP570-2
- tri-n-octylphosphine oxide (TOPO), MP100R-1
- trioctylphosphinic oxide, RP570-2
- tritium, determination of, RP580-1
- TRU•Spec column, MP100R-1
- TRU waste (see drums), SD010R-1
- tune of (see GC/MS)
- U
- ultrasonic disrupter, remote, OP150R-1
- ultrasonic extraction, OP150R-1, OP020R-1
- uncertainty, defined, 3-5
- updates to compendium, Intro-1
- uranium, solvent extraction of, MP100R-1
- U.S. Environmental Protection Agency (EPA) (see EPA)
- U.S. Department of Energy (DOE) (see DOE)
- V
- vacuum pumps, 9-2
- validation requirements
 - .analytical data, 1-10
- venting system (see roughing pumps and safety precautions)
- verification testing, 2-6
- verified method(s)
 - defined, Intro-2
 - inclusion in *DOE Methods*, Intro-3
- volatile
 - compounds (see organic compounds and organic methods)
 - nonhalogenated organics, analysis of, OG015R-1
 - organic compounds (VOCs), 7-2, 7-3, OC010R-1
- W
- warning devices, 4-7
- waste disposal sites, 7-2
- waste handling, 1-9
- Waste Isolation Pilot Plant, SD010R-1
- waste stream (defined), SD010R-1
- wastes, underground, repository, 7-10
- water and soils, rapid determination of VOCs, OS040-1
 - apparatus, OS040-4
 - procedure, OS040-9
 - method performance, OS040-14
- water, detection of chlorinated VOCs, OS030-1
 - apparatus, OS030-4
 - method performance, OS030-10
 - procedure, OS030-5

water, determination of ^{210}Pb , RP280-1
 apparatus, RP280-1
 method performance, RP280-4
 procedure, RP280-2

water, groundwater and drinking water (see ICP-
 MS determination for U)

water, purification of Sr, RP500-1
 apparatus, RP500-2
 determination of ^{89}Sr , ^{90}Sr
 method performance, RP500-10
 procedure, RP500-3

water samples, determination of gross alpha, gross
 beta, and gross tritium, RP720-1
 apparatus, RP720-2
 method performance, RP720-9
 procedure, RP720-3

water samples, determination of ^{90}Sr (see soil,
 water, and filter samples)

water sampling, equipment for, 7-6

windows (daily retention time), 8-6

work performance, 2-5
 acceptance criteria for, 2-5

X

Y

Z

zero headspace extraction, OP040R-1

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>		
1	Keith Abel	PNL P8-08	P. O. Box 999	Richland , WA 99352
1	Dr. Harry Babad	WHC R2-78	P. O. Box 1970	Richland, WA 99352
2	Becky Bechtold	WHC H6-01	P O Box 1970	Richland, WA 99352
1	Will Becraft	Northwest Instruments	3100 Geo. Washington Way	Richland , WA 99352
1	Marsha L. Bell	WHC, T6-16	P. O. Box 999	Richland, WA 99352
1	Roger C. Bowman	WHC, H6-24	P. O. Box 1970	Richland, WA 99352
1	Stanley O. Branch	DOE-RL, R3-72	P. O. Box 550	Richland, WA 99352
1	Barbara Broomfield	WHC, N3-13	P.O. Box 1970	Richland, WA 99352
1	Michael J Brown	WHC R3-45	P. O. Box 1970	Richland, WA 99352
1	Tom Brun	WHC N1-06	P. O. Box 1970	Richland, WA 99352
1	Dr. James Campbell	PNL P8-08	P. O. Box 999	Richland, WA 99352
1	Paul Carter	DOE-RL, R3-80	P. O. Box 550	Richland, WA 99352
1	John Cavanaugh	Department of Energy, A5-52	P. O. Box 550	Richland, WA 99352
1	Timothy E. Chapman	PNL, B1-34	P. O. Box 999	Richland, WA 99352
1	Charissa J. Chou	WHC, H6-06	P O Box 1970	Richland, WA 99352
1	Donald E Clark	WHC H6-05	P. O. Box 1970	Richland, WA 99352
1	Paula K. Clark	U. S. DOE, R3-80	P. O. Box 550	Richland, WA 99352
1	Steven W Clark	WHC H6-01	P. O. Box 1970	Richland, WA 99352
1	Mike Cline	WHC, H6-24	P. O. Box 1970	Richland, WA 99352
1	Julie M. Colby	WHC, G6-16	P. O. Box 1970	Richland , WA 99352
1	Wayne C. Cosby	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	Beverly A. Crawford	WHC, T6-50	P O Box 1970	Richland, WA 99352
1	Gloria Cummins	WHC, H6-24	P. O. Box 1970	Richland, WA 99352
1	Asok K. Dasgupta	WHC MS S3-28	P. O. Box 1970	Richland, WA 99352
1	Roger L Dirkes	PNL, K6-81	P. O. Box 999	Richland, WA 99352
1	David Dodd	WHC T6-50	P. O. Box 1970	Richland, WA 99352
1	John J. Dorian	WHC, H6-39	P. O. Box 1970	Richland, WA 99352
1	Joel A Eacker	WHC, R2-50	P. O. Box 1970	Richland , WA 99352
1	Susan Eberlein	WHC, L5-55	P. O. Box 1970	Richland, WA 99352
1	Daniel L. Edwards	WHC, S3-90	P. O. Box 1970	Richland, WA 99352
1	Monte R. Elmore	PNL, P8-30	P. O. Box 999	Richland, WA 99352
1	Sandy K. Fadeff	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	O. Thomas Farmer	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	Ms. Gay E. Fitzgibbon	WHC H6-07	P. O. Box 1970	Richland, WA 99352
1	Cynthia L. George	WHC, L5-55	P. O. Box 1970	Richland, WA 99352
1	Ron Gerton	DOE-RL, R3-72		Richland, WA 99352
12	Steve C. Goheen	PNL P8-08	P. O. Box 999	Richland, WA 98352
1	Robert M. Gough	PNL, P7-79	P. O. Box 999	Richland, WA 99352
1	Dale Halgren	WHC, S6-70	P. O. Box 1970	Richland, WA 99352
1	Dan Hansen	WHC, T6-50	P. O. Box 1970	Richland, WA 99352
1	Denise J Hert	WHC H6-04	P O Box 1970	Richland, WA 99352
1	David Hetzer	WHC S6-30	P O Box 1970	Richland, WA 99352
1	Julian G. Hill	WHC, R2-12	P. O. Box 1970	Richland, WA 99352
1	Eric W. Hoppe	PNL P7-22	P. O. Box 999	Richland, WA 99352
2	Jim Huckaby	WHC, R2-78	P. O. Box 1970	Richland, WA 99352
1	Jeanette Hyattt	WHC, H4-19	P. O. Box 1970	Richland, WA 99352
1	Richard Jaquish	PNL,B1-34	P. O. Box 999	Richland, WA 99352
1	Mary F. Jarvis	U. S. Department of Energy	P. O. Box 550	Richland, WA 99352

<u>No. of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>		
1	Dr John R. Johnson	PNL, K3-53	P. O. Box 999	Richland , WA 99352
1	Bruce Killand	PNL,P7-68	P. O. Box 999	Richland, WA 99352
1	A. Gaylord King	PNL, P7-22	P. O. Box 999	Richland, WA 99352
1	David Koppenaal	PNL, P7-07	P. O. Box 999	Richland, WA 99352
1	Chris Kramer	WHC, H6-04	P. O. Box 1970	Richland, WA 99352
1	Kris Kuhl-Klinger	PNL, P7-27	P. O. Box 999	Richland, WA 99352
1	Elwood Lepel	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	Fred Leung	PNL, K4-13	P. O. Box 999	Richland, WA 99352
1	Chung-King Liu	U. S. Department of Energy	P. O. Box 550, A5-52	Richland, WA 99352
1	Rich Lucke	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	Dennis Mahlum	PNL,P7-56	P. O. Box 999	Richland, WA 99352
1	Tapas Maiti	PNL,P7-07	P. O. Box 999	Richland, WA 99352
1	Robert P. Marshall	WHC, T6-14	P. O. Box 1970	Richland, WA 99352
1	Bernie Mayancsik	WHC, T3-01	P. O. Box 1970, T3-01	Richland, WA 99352
1	Richard G. McCain	WHC, H6-06	P. O. Box 1970	Richland, WA 99352
1	Margaret McCulloch	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	Charles E McDonald	WHC H1-60	P. O. Box 1970	Richland, WA 99352
1	Kent M. McDonald	WHC, T4-03	P. O. Box 1970	Richland, WA 99352
1	Norton G. McDuffie	WHC, R2-78	P. O. Box 1970	Richland, WA 99352
1	Padmanabhan K. Melethil	PNL, P7-22	P. O. Box 999	Richland, WA 99352
1	Pete Mellinger	PNL, B1-40	P. O. Box 999	Richland, WA 99352
1	Heui K. Mezmarich	WHC, T6-16	P. O. Box 1970	Richland, WA 99352
1	Tony Miskho	WHC, H6-30	P. O. Box 1970	Richland, WA 99352
1	Gary M. Mong	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	Carol D. Morrison-Beyer	WHC, S3-90	P O Box 1970	Richland , WA 99352
1	Samuel T. Murff	MACTC, R3-82		Richland, WA 99352
1	Clifford Narquis	WHC, T4-16	P. O. Box 1970	Richland, WA 99352
1	Ms. Jacquie Noble-Dial	DOE-RL, R3-72	P. O. Box 550	Richland, WA 99352
1	Al F. Noonan	Pacific Northwest Laboratory	P. O. Box 999 K9-81	Richland, WA 99352
1	Jerry Osborne	WHC, R2-78	P. O. Box 1970	Richland, WA 99352
1	Gert Patello	PNL, P7-14	P. O. Box 999	Richland, WA 99352
1	Marsha Patridge	PNL K7-94	P. O. Box 999	Richland, WA 99352
1	Thomas R Pauley	WHC, G6-46	P. O. Box 1970	Richland, WA 99352
1	Scott W. Petersen	WHC, H6-23	P O Box 1970	Richland, WA 99352
1	Richard D Pierce	WHC, N3-13	P O Box 1970	Richland, WA 99352
1	Kathy A. Poston	PNL,P8-01	P. O. Box 999	Richland, WA 99352
1	Kenneth S. Redus	Mactec	P. O. Box 1427, R3-82	Richland, WA 99352
1	Fred R. Reich	WHC, L5-55	P O Box 1970	Richland, WA 99352
1	Dr. Fred Riedel	WHC, T6-31	P. O. Box 1970	Richland, WA 99352
1	Bob Riley	PNL, K6-96	P. O. Box 999	Richland, WA 99352
1	James M. Robbins	PNL P7-22	P. O. Box 999	Richland, WA 99352
1	Randal J. Roberts	WHC, N3-13	P. O. Box 1970	Richland, WA 99352
1	Tom Rudolph	WHC, R3-54	P. O. Box 1970	Richland, WA 99352
1	Dr. Joseph K. Samuels	HEHF, B1-61		Richland, WA 99352
1	Leela M. Sasaki	WHC, R2-12	P. O. Box 1970	Richland, WA 99352
1	John W. Schmidt	WHC, H6-30	P. O. Box 1970	Richland, WA 99352
1	Mike Schwab	Bechtel Haford Company,		Richland, WA 99352
4	Cary Seidel	WHC H1-61	P O Box 1970	Richland, WA 99352

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>		
1	Deb S. Sklarew	PNL, K6-96	P. O. Box 999	Richland, WA 99352
1	Ed Smith	HEHF, H1-78		Richland, WA 99352
1	Gary Smith	PNL, P7-14	P. O. Box 999	Richland, WA 99352
1	Scott Somers	NISI, B2-75		Richland, WA 99352
1	Dr. Paul S. Stansbury	PNL, K3-62	P. O. Box 999	Richland, WA 99352
1	Dave L. Stanton	A5-20	P. O. Box 550	Richland, WA 99352
1	Marc Stevenson	WHC, B2-35	P. O. Box 1970	Richland, WA 99352
1	Dr. Ted Stram	DOE-RL, S7-55	P. O. Box 550	Richland, WA 99352
1	Curtis Stroup	WHC B2-23	P. O. Box 1970	Richland, WA 99352
1	Mike Sutey	WHC, R1-49	P. O. Box 1970	Richland, WA 99352
1	Berta Thomas	PNL, B1-34	P. O. Box 999	Richland, WA 99352
1	Bill Thomas	PNL, P8-08	P. O. Box 999	Richland, WA 99352
1	Chris J. Thompson	PNL, K6-96	P. O. Box 999	Richland, WA 99352
1	Wendy Thompson	WHC, N3-05	P. O. Box 1970	Richland, WA 99352
1	Glenn T. Thornton	PNL P7-68	P. O. Box 999	Richland, WA 99352
1	John H. Tillman	WHC, H4-23	P. O. Box 1970	Richland, WA 99352
1	Sebastian Tindall	Bechtel Hanford Inc., H4-80	P. O. Box 969	Richland, WA 99352
1	Wayne Toebe	WHC, H6-22	P. O. Box 1970	Richland, WA 99352
1	Richard L. Weiss	WHC, H4-23	P. O. Box 1970	Richland, WA 99352
1	Betty Jo Westergard	PNL, K6-79	P. O. Box 999	Richland, WA 99352
1	Paul D. Whitney, Ph.D.	PNL, K5-12	P. O. Box 999	Richland, WA 99352
1	Joyce E. Widrig	Pacific Northwest Laboratory	P. O. Box 999, K8-04	Richland, WA 99352
1	W. I. (Bill) Winters	WHC, T6-50	P. O. Box 1970	Richland, WA 99352
1	Marc Wood	WHC, N3-13	P. O. Box 1970	Richland, WA 99352
1	Tom W. Wood	PNL, K6-47	P. O. Box 999	Richland, WA 99352
1	Judy Work	WHC H6-28	P. O. Box 1970	Richland, WA 99352
1	Eric Wyse	PNL, P8-08	P. O. Box 999	Richland, WA 99352

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1		US EPA Library	2890 Woodbridge Avenue	Building 209, MS-245	Edison, NJ 08837-3679
1	Charles S. Abrams	1987 Virginia Avenue			Idaho Falls, ID 83404
2	Mary Adamic	Argonne National Lab - West		P. O. Box 2528	Idaho Falls, ID 83403
1	Bruce Adams	Building 785	P. O. Box 2528	Argonne National Lab West	Idaho Falls, ID 83415
1	Linda Adams	CELS-Coming Inc.		HP-ME-03-078	Coming, NY 14895
1	Ted Adams	B. Koh and Associates Inc.		11 W. Main Street	Springville, NY 14141
1	Stephen F. Agnew, Ph.D.	Los Alamos National		Group INC-4, MS C346	Los Alamos, NM 87545
1	Faizy Ahmed, Ph.D.	Phenomenex		2320 West 205th Street	Torrance, CA 90501
1	Hop B. Aiken	Westinghouse SRC	Mail Stop Building 773A	P. O. Box 616	Aiken, SC 29802
1	Souhail R. Al-Abed	University of Cincinnati		5995 Center Hill Road	Cincinnati, OH 45224
1	A. J. Aldridge	BNFL Springfield C&MS		Salwick, PRESTON	ENGLAND, PR40XJ
1	Booz Allen			20201 Century Blvd	Germantown, MD 20874
1	Marcus Allen	DOE, EM-24		Forrestal Building	Washington, DC 20545
1	Phillip Allen	Clemson University		P. O. Box 709	Pendleton, SC 29670
1	Ildikó Almási	Electr. Engineer	H-1147 Budapest	MicroVacuum Ltd.	Kerékgyártó u 10, Hungary
1	Rich Amano	LDC		7750 Camino Road Suite	Carlsbad, CA 92009
1	Clarine Anderson	Adams and Hobart		46732 Fremont Boulevard	Fremont, CA 94538
1	Fred Anderson	Analytical Standards		2307 Camden Avenue	Parkersburg, WV 26101
1	Isabel Anderson	EG&G Idaho	P. O. Box 1625		Idaho Falls, ID 83415-1406
1	James Anderson	Department of Chemistry		University of Georgia	Athens, GA 30602
1	Michael P. Anderson	ELMC Chemistry Lab		P.O. Box 491	Vancouver, WA 98666-0491
1	Rusty Anderson	120 Ashley Lane			Powell, TN 37849
1	Ken Angelos	Golder Associates Inc.		4104 148th Avenue NE	Redmond, WA 98052
1	Richard J. Antepenko	Martin Marietta Specialty		P. O. Box 2908	Largo, FL 34649-2908
1	J. A. Applegate	Martin Marietta Energy	P. O. Box 628		Piketon, OH 45661
1	Aruna Arakali	West Valley Nuclear		MS 307	West Valley, NY 14171-0191
1	Dennis Armstrong	Los Alamos National		P. O. Box 1663, MS K490	Los Alamos, NM 87545
1	Kathleen Aspell	EG&G Idaho		P. O. Box 1625	Idaho Falls, ID 83415-2420
1	Mike Ault	U. S. Ecology		P. O. Box 638	Richland, WA 99352
1	Dr. D. C. Aumann	Institute fur Physikalische	Wegelerstrabe 12	Der Universitat Bonn	53115 Bonn, Germany
1	Prof. Dr. C. Aumann	Institut fur Physikalische	Abt Nuklearchemie,	Der Universitate Bonn	53115 Bonn, Germany
1	John Austin	USEPA OSW- (OS-333)		401 M Street S.W.	Washington, DC 20460
1	Halil Avci	Argonne National Laboratory	Building 900	9700 South Cass Avenue	Argonne, IL 60439
1	Jeanne Bagan	Lawrence Livermore Nat.		P. O. Box 808	Livermore, CA 94550
1	Ellen Bailey	Alpha Analytical		8 Walk Up Drive	Westboro, MD 01581
1	N. Ruth Bailey	Laboratory Division	P. O. Box 1060	Health Protection Branch	Dartmouth, Nova Scotia,
1	Robert Bailey	The Ohio State University	1080 Carmack Road	216 Bevis Hall	Columbus, OH 43210-1002
1	Stan Bajic	Ames Laboratory		7 Stedding Hall	Ames, IA 50011
1	Cheryl Baker	Public Health Laboratory		221 State Street, Station No.	Augusta, ME 04333
1	John Baker	WMX-EML		2100 Cleanwater Drive	General, IL 60134
1	Steven N. Bakhtiar	Reynolds Electrical & Eng.		P O Box 98521, MS 772	Las Vegas, NV 89193-8521
1	Dr. Jim Balk	Nebraska State Health Dept.		3701 S. 14th Street	Lincoln, NE 68502
1	Edmond J. Baratta	FDA	109 Holton Street	Winchester Eng. & Anal. Lab	Winchester, MA 01890
1	D. Barcelo	CRD-CSIC, Dept.		c/Jordi Girona 18-26	08034 Barcelona, Spain
1	J. E. Barefield	Los Alamos National Lab		MS J567	Los Alamos, NM 87545
1	Brad Barkey	ACZ Laboratories Inc.		30400 Downhill Drive	Steamboat Springs, CO
1	Sue Barkey	ACZ Laboratories Inc.		30400 Downhill Drive	Steamboat Springs, CO
1	Jodie Barr	Analytical Technologies Inc.		225 Commerce Drive	Fort Collins, CO 80524

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Kris W. Barrett	Jacobs Engineering Group		251 South Lake Avenue	Pasadena, CA 91101
1	Harry Barrick	Env. Technologies Group	P. O. 1x 9840	1400 Taylor Avenue	Baltimore, MD 21284-9840
1	Dean A. Bass	Argonne National Laboratory		9700 South Cass Ave.	Argonne, IL 60439-4831
1	Ray Bath	Waste Policy Institute		555 Quince Orchard Road,	Gaithersburg, MD
1	Linda Bauer	MOUND	P. O. Box 3000		Miamisburg, OH 45343
	William F. Bauer	Analytical Chemistry Unit	P. O. Box 1625	EG&G Idaho Inc.	Idaho Falls, ID 83415
1	Charles K. Bayne	ORNL	P O Box 2008	Bldg 6011, MS 6370	Oak Ridge, TN 37830-6370
1	Ellyn Beary	NIST		Building 222, Room A341	Gaithersburg, MD 20899
1	Rosa Beas	Roy F. Weston, Inc.		212 Frank West Circle A	Stockton, CA 95206
1	Dan Beasley	c/o A. T. Kearney Inc.		2952 George Washington	Richland, WA 99352
1	Dick Beaver	Babcock and Wilcox	P. O. Box 1469	Idaho Inc. , Mail Stop 0206	Idaho Falls, ID 83403
1	Annette Begin	TriWaste Treatment		4 Km. North Box 311	Big Valley, Alberta, Canada
1	Robert G. Belmer	S-Cubed		3398 Carmel Mountain Road	San Diego, CA 92121
1	Uwe Beinlich	Isotrak	Gieselweg 1	Amersham Buchler GmbH &	D38110, Braunschweig
1	Devin Belleau	ALCOA - Massena		P. O. Box 150	Massena, NY 13662
1	Joe Bennett	P. O. Box 1625			Idaho Falls, ID 83415-4123
1	Walter J. Berger	Enseco • CRL		7440 Lincoln Way	Garden Grove, CA 92641
1	Nicole Bernholz	Brookhaven National		Building 535A	Upton, NY 11973
3	Mark Bernick	c/o Roy F. Weston Inc.	2890 Woodbridge Avenue	GSA Raritin Depot	Edison, NJ 00837
1	Michel Bernon, Ph.D.	MB Associates		6225 Rockhurst Road	Bethesda, MD 20817
1	Tegwyn Bery	Y-12 Plant	P. O. Box 2001	Oak Ridge	Oak Ridge, TN 37831
1	David Best	Westinghouse SRC		DWPT 704-IT, Rm 231	Aiken, SC 29808
1	D. C. Bhatnagar	Algonquin College		200 Lees Avenue	Ottawa Ontario, Canada
1	Dr Arun K. Bhattacharya	ATEC Associates, Inc		8665 Bash St	Indianapolis, IN 46256-1202
1	Joe Bianconi	CWM Federal	2309 Renard Place SE Suite	UMTRA Project Office	Albuquerque, NM 87106
1	Dottie Biggs	US EPA NEIC Library		Box 25227	Denver, CO 80225
1	Dr. Larry A. Birchfield	Oak Ridge Analytical		1345 Oak Ridge Turnpike,	Oak Ridge, TN 37830
1	Detlef Birkholz	ETL Enviro-Test		9936 67th Avenue	Edmonton, Alberta, Canada
1	John Birri	US EPA		2890 Woodbridge Avenue	Edison, NJ 08837
1	Allison Blackman	DOE	Box A		Aiken, SC 29802
1	Robert P. Blauvelt	Dames & Moore		One Blue Hill Plaza Suite 530	Pearl River, NY 10965-1668
1	Sophie J. Bobrowski	ORNL	P. O. Box 2008		Oak Ridge, TN 37831-6131
1	Joe Boda	USDOE Office of Waste	EM-322	Trevion II 12800	Germantown, MD 20874
1	Ecaterina Bodor	Institute of Public Health and	C. P. 93	Str. Pasteur No. 6	R-3400 Cluj Napoca,
1	Don Bogen	USDOE/EML		376 Hudson Street	New York, NY 10014-3621
1	Bill Boivin	Whiteshell Labs		AECL	Pinawa, Manitoba, ROE 1L0
1	Izabela Bojakowska	Patstwowy Institut	00-975 Warszana	ul. Rakowiecka 4	Poland,
1	Rainer F. Bokelmann	Siemens AG, KWU BP		P. O. Box 101063	D-63010, Offenbach a Main
1	Kevin B. Bolger	USEPA ESD/MQAB		77 West Jackson Blvd.,	Chicago, IL 60604-3590
1	P. Ch. Alvaro Bollati	AgipRaffinazione	20017 Rho Mi	Sede Secondaria Raffineria	SS 33 del Sempione, Italy
1	Mark Bollinger	Argonne National Laboratory		9800 S. Cass Avenue	Argonne, IL 60439
1	Pat Boone	US EPA, Region V		77 West Jackson Blvd.,	Chicago, IL 60604
1	Amrit Boparai	Argonne National Lab		9700 S. Cass Ave	Argonne, IL 60439-4837
1	W. D. Bostick	Martin Marietta Energy	P.O. Box 2008	Oak Ridge K25 Plant	Oak Ridge, TN 37831
1	Dave Bottrell	U. S. DOE	656 Quince Orchard Road	Analytical Services Division	Gaithersburg, MD 20878
1	J. L. Botts	Oak Ridge National		P. O. Box 2008	Oak Ridge, TN 37831-6384
1	Ken Bower	MS G740		Los Alamos National	Los Alamos, NM 87545
1	Amy Bowman	FERMCO	P. O. Box 398704		Cincinnati, OH 45239

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>				
1	Ted Bowman	ARS Inc.		3945 Holcomb Bridge Road	Norcross, GA	30092
1	Bill Boyce	Westinghouse SRS		SRTC 773A, B147	Aiken, SC	29801
1	Allen Bradley	IT Corporation		312 Directors Drive	Knoxville, TN	37923
1	Cheryl Bradley	290 Metal Development	Ames Laboratory	Iowa State University	Ames, IA	50011
1	Chuck D. Brady	Westinghouse SRC		P. O. Box 616	Aiken, SC	29802
1	Christine Brannon	Lawrence Livermore	P. O. Box 808, Mail Stop	7000 East Avenue	Livermore, CA	94550
1	Susan Breneman	Martin Marietta	Box 1072	Knolls Atomic Power	Schenectady, NY	12301
1	Thomas P. Brennan	Martin Marietta Energy	P. O. Box 2003		Oak Ridge, TN	37831-7606
1	Anne Briggs	Acujrex Environmental	P. O. Box 7044		Mountain View, CA	94039
1	Mike Brisson	Westinghouse SRC	MS Building 703-11C	P. O. Box 616	Aiken, SC	29802
1	Frazier L. Bronson	Canberra Industries Inc.		800 Research Parkway	Meriden, CT	06450
1	Bruce Brown	NET Inc.		1700 Harmon Road	Auburn Hills, MI	48326
1	Don Brown	Texas Dept. of Health		1100 West 49th Street	Austin, TX	73756
1	Judith M. Brown	JANOS Technology Inc.		HCR #33 Box 25, Route 35	Townshend, VT	05353-7702
1	Norman Brown	Sandia National Lab		Detp. 6624, Mail Stop 0734	Albuquerque, NM	
1	Randy Brown	ATEC		1300 Williams Drive	Marietta, GA	30066
1	Neil R. Brown, Ph.D.	Chemical Technology	9700 South Cass Avenue No.	Argonne National Laboratory	Argonne, IL	60439
1	Dr. Patrick Brug	CST-1, MS G740	LANL		Los Alamos, NM	87545
1	Melton F. Bryant	Westinghouse - Savannah	P. O. Box 616	Savannah River Laboratory	Aiken, SC	29808
1	Mark Brynildson	Sandia National Laboratory	P.O. Box 969	Dept. 8642	Livermore, CA	94551-0969
1	Lisa Buchan	Bechtel	P O Box 350		Oak Ridge, TN	37831
1	Norman P. Buddin	Martin Marietta Energy	P. O. Box 2003	Blair Rd	Oak Ridge, TN	37830-7446
1	Jim Burger	Auxier and Associates, Inc.		412 Executive Tower Drive,	Knoxville, TN	37923
1	Jack Bum	ORNL ER CSL	151 Lafayette	Bechtel Env.	Oak Ridge, TN	37831-0350
1	Kerry I. Burns	AECL-Research	Chalk River Lab.	General Chemistry Branch	Chalk River, Ontario,	
1	Tony Burns	Quality Assurance Lab		P. O. Box 22567	San Diego, CA	92192
1	Richard Burrows	Enseco IRMAL		4955 Yarrow Street	Arvada, CO	80002
1	Debbie Busch	Argonne National laboratory		9700 S Cass Ave Bldg 203,	Argonne, IL	60439
1	Gregory A. Busch	EMS Heritage Laboratories,		7901 West Morris Street	Indianapolis, IN	46231
1	Rickie Byrd	Martin Marietta	P. O. Box 1410	5600 Hobbs Road	Paducah, KY	42001
1	Marguetta Cain	Ohio EPA		P. O. Box 163669	Columbus, OH	43216-3669
1	Matt Cain	EM-521		U. S. DOE	Washington, DC	20585
1	Donald J. Cameron, Ph.D.	AECL Research	Chalk River Ontario	Chalk River Laboratories	Ontario, Canada	K0J 1J0
1	Katherine Campbell	A-1m MS F600	LANL		Los Alamos, NM	87545
1	Peggy J. Campbell	MMES	Bldg. 1054-B MS 6404	P. O. Box 2008,	Oak Ridge, TN	37831-6404
1	Dr. Nada Canak	The Institute for the	Palmoticeva 30	Plaating of the City of	11000 Belgrade, Yugoslavia	
1	Robert P. Cannon	EBASCO		2211 West Meadowview	Greensboro, NC	27407-3488
1	Linda Cardenes	IT-Las Vegas		4330 South Valley View,	Las Vegas, NV	89103-4047
1	Daniel B. Cardin	ENTECH Laboratory		950 Enchanted Way No. 101	Simi Valley, CA	93065
1	David M. Cardin	Oak Ridge Field Office	P. O. Box 2001		Oak Ridge, TN	37831
5	Terri Carstenson	Bio-Nebraska		3820 NW 46th Street	Lincoln, NE	68524-1637
1	Charles Carter	Lockheed		975 Kelly Johnson Drive	Las Vegas, NV	89119
1	Mike Carter	US DOE	656 Quince Orchard Road	Analytical Services Division	Gaithersburg, MD	20878
1	Doug Cartwright	Energetics		19800 Apple Ridge Place	Gaithersburg, MD	20879
1	Steve Castellano	FGL Environmental	P. O. Box 272		Santa Paula, CA	93061
1	John R. Celeste	Lawrence Livermore		P. O. Box 808	Livermore, CA	94550
1	Seshu Chalasani	Brookhaven National	P. O. Box 5000	Building No. 535A	Upton, NY	11973
1	Al Chambers	Martin Marietta Energy		P. O. Box 2009	Oak Ridge, TN	37831-8189

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Bill Chambers	Sandia Labs	P. O. Box 5800	Department 01824, MS 0342	Albuquerque, NM 87185
1	Susan D. Chapnick	Gradient Corporation		44 Brattle Street	Cambridge, MA 02138
1	Carolyn Childress	Sandia National Laboratory	P O Box 969	Dept 8642	Livermore, CA 94551-0969
1	Matt Chisum	Mason & Hanger	P. O. Box 30020	Pantex Plant	Amarillo, TX 79177
1	Aaron Christ	Olin Ordnance		Route 148	Marion, IL 62959
1	Stan Christensen	ICF Kaiser Engineers		165 South Union Blvd., Ste	Lakewood, CO 80228-2213
1	Virgene Church	EG&G Rocky Flats	P. O. Box 464	Bldg 051	Golden, CO 80402
1	Frank W. Clark	Aquaterra	Newton Road	Newton House	Leeds, LS7 4DN UK
1	Glen Clark	REECO, MS 713	P.O. Box 98521		Las Vegas, NV 89193-8521
1	James S. Clark	NIST	Building 235, Room A132	Health Physics Div. 354.02	Gaithersburg, MD 20899
1	John P. Clark	Westinghouse, SRC	P. O. Box 616	703-10C	Aiken, SC 29802
1	Mary Clark	Environmental Studies	1504 Avenue A	National Air & Rad. Env. Lab	Montgomery, AL 36115-2601
1	Tom Clark	IT Corp		11499 Chester road	Cincinnati, OH 45246
1	Kevin Coates	Army Corps pf Engineers.		12565 W. Center Rd	Omaha, NE 68144
1	Linnea M. Coffey	Enseco - CRL		7440 Lincoln Way	Garden Grove, CA 92641
1	Tom Colandrea	12988 Angosto Way			San Diego, CA 92128
1	Beth A. Cole	ORNL	Bldg. 4500S MS 6131	P. O. Box 2008	Oak Ridge, TN 37831
1	Charles J. Coleman	Westinghouse Savannah		Building 773-A	Aiken, SC 29808
1	Jlm Collell	5966 Cleveland Avenue			Columbus, OH 43231
1	Ana Concalves	Instituto de Tecnologia	1699 Lisboa Codex	Estrada do Paco do Lumiar	Portugal,
1	Edward J. Conley	New England Regional		60 Westview Street	Lexington, MA 02173
1	Joan Connolly	EG&G Idaho	P.O. Box 1625		Idaho Falls, ID 83415-3930
1	Michael Connolly, Ph.D	EG&G Idaho Inc	P. O. Box 1625		Idaho Falls, ID 83415-3930
1	Ron Conrad	Los Alamos National	MS K 490	P. O. Box 1663	Los Alamos, NM 87545
1	Marcus Cooke, Ph.D.	IT Corporation, Regional		312 Directors Drive	Knoxville, TN 37923
1	Carl Cooley	Battelle, Oak Ridge		1093 Commercial Park Rd,	Oak Ridge, TN 37830
1	Gail Cooley	Battelle, Oak Ridge		151 Lafayette Drive, Suite	Oak Ridge, TN 37830
1	Monika Corleanca	FERMCO		P. O. Box 398704	Cincinnati, OH 45239-8704
1	Morton Corn	Johns Hopkins University	615 N. Wolfe Street	School of Hygiene & Public	Baltimore, MD 21205
1	B. Rod Corrigan	Environmental Consultants		391 Newman Avenue	Clarksville, IN 47129
1	Dan Costley	DIAL		P. O. Box Drawer MM	Mississippi State , MS
1	W. Cottrell	Oak Ridge National	P. O. Box 2008	Bethel Valley Rd.	Oak Ridge , TN 37831-6384
1	Robert G. Courson	Dir., Environmental Services	1200 Sixth Avenue	EPA Region 10	Seattle, WA 98101
1	John C. Courtney	10326 Hackberry Court			Baton Rouge, LA 70809
1	Clinton Cox	USEPA/NAREL		1504 Avenue A	Montgomery, AL 36115-2401
1	Jeffrey Crain	Argonne National Laboratory	9700 S. Cass Avenue	Building 200	Argonne, IL 60439
1	Barb Crocker	EG&G Rocky Flats	P. O. Box 464	Environmental Library	Golden, CO 80402-0464
1	Alan Crockett	Idaho National Engineering	P. O. Box 1625	EG&G Idaho, Inc.	Idaho Falls, ID 83415
1	June Crowe	IT Corporation		312 Directors Drive	Knoxville, TN 37923
1	Raymond Crowley	Millepore Corporation		34 Maple St	Milford, MA 01757
1	Dr. Stephen Crump	Westinghouse SRC		Building 773-A	Aiken, SC 29802
1	Jody Cruse	Dade, Moeller, and		1905 Terminal Drive	Richland, WA 99352
1	Greg Csullog	EACL Research	Chalk River	Chalk River Laboratories	Ontario, Canaca K0J 1J0
1	James P. Culp	Environmental Engineer		1125 Cresthaven Drive	Silver Spring, MD 20903
1	Robert U. Curl	EG&G		P. O. Box 1625	Idaho Falls, ID 83402
1	Ewa Dabek	ETC Environmenta Canada		3439 River Road	Ottawa, Ontario, Canada
1	Tanya Dagliyan	Phenomenex		2320 West 205th Street	Torrance, CA 90501
1	Dr. Joseph N. Daka	Medical Devices Bureau		775 Brookfield Road	Ottawa, Ontario, Canada

<u>No. of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Dennis G. Dalga	FERMCO		P. O. Box 398704	Cincinnati, OH 45239-8704
1	Swati Damle	NIH	Building 13, Room 2E63	9000 Rockville Pike	Bethesda, MA 20892
1	Ray Daniels	SAIC		20300 Century Blvd.	Germantown, MD 20874
1	R. Allan Danielson	Department of Health	2 South 45th Avenue	Division of Radiation	Yakima, WA 98908
1	Andrew J. Danzig	Environmental Engineer	1101 Market Street PSC 1E	Tennessee Valley Authority	Chattanooga, TN 37402
1	Rajesh V. Dave	Laboratory Resources		158 Tices Lake	East Brunswick, NJ 08816
1	Dr. Michael H. Davis	ATEL	P.O. Box 76	6878 S. State Route 100	Melmore, OH 44845-9999
1	Ronnie H. Davis	Analytical Chemist	P. O. Box 2530	1560 Bear Creek Road	Oak Ridge, TN 37831-2530
1	John Dawson	Chem Labs Inc		P. O. Box 1711	Brentwood, TN 37027
1	Richard D. Dayvault	Geotech, Inc.	P.O. Box 14000		Grand Junction, CO 81502
1	Mario Mastrolilli de Angelis	AgipPetroli	Via Laurentine, 449	00142 Rome	Italy,
1	Michael W Deegan	Power Systems Group		2111 Wilson Blvd, Suite 1100	Arlington, VA 22201
2	Stan Defillipis	Ecotech		3342 International Park	Atlanta, GA 30316
1	Gail DeRuzzo	Weston, Inc.	Pickering Creek Industrial	208 Welsh Pool Road	Lionville, PA 19341-1313
1	Lata Desai	Westinghouse Electric		P. O. Box 2078	Carlsbad, NM 88221
1	Darlene M. DeSinho	DOE GJPO		Rust Geotech. Waste Mgmt	Grand Junction, CO 81502
1	Dr. Mary A. O. Dettelsen	Bureau of Haz Waste		50 Wolf Road	Albany, NY 12233-7252
1	John Deuble	Ogden Env & Energy		5510 Morehouse Drive	San Diego, CA 92121
1	Terry Devine	Conf. of Rad. Ctrl Progm.		205 Capital Avenue	Frankfurt, KY 40601
1	Thomas A. Devito	Knolls Atomic Power Lab	P. O. Box 1062		Schenectady, NY 12301
1	Ray Dewberry	Westinghouse SRS		SRTC 773-A	Aiken, SC 29801
2	John R. Dick	EG&G Rocky Flats		P. O. Box 464	Golden, CO 80402-0464
1	James W. Dillard	IT Corporation		5815 Middlebrook Pike	Knoxville, TN 37921-5947
3	Stuart Dinwinddie	New Mexico Environment	525 Camino de los Marquez,	Hazardous Radioactive	Santa Fe, NM 87502
1	Pete Dirknamt	DOE-ID	785 DOE Place	RESL Building 690	Idaho Falls, ID 83402
1	Rick DiSalvo	US DOE	P. O. Box 928	Rocky Flats Field Office	Golden, CO 80402
1	Dr. Mara Djukanovic	Department for Landscape	Kneza Viseslava Street No. 1	University of Belgrade	11000 Beograd, Yugoslavia
1	Fred Doern	AECL Research		Whiteshall Laboratories	Pinawa, Manitoba, Canada
1	Robert Dolenc	REECO		P. O. Box 98521	Las Vegas, NV 89193
1	Steve Donovan	CN Geotech, Inc.	P.O. Box 14000		Grand Junction, CO 81502
1	Jesse Donnan	Westinghouse - Savannah	P. O. Box 616	Savannah River Laboratory	Aiken, SC 29808
1	Julie Dorsey	P. O. Box 2009			Oak Ridge, TN 37831
1	Kris Downs	Hydrometrics Inc.		2727 Airport Road	Helena, MT 59601
1	Barton Draper, Ph.D.	Bechtel	P.O. Box 193965	50 Beale Street	San Francisco, CA
1	Wayne A. Drown	Westinghouse SRC		P. O. Box 616	Aiken, SC 29802
1	Sharon Duboise	Texas Department of Health		1100 West 49th	Austin, TX 78756
1	Renee DuBose	Building 241-84H		Westinghouse Savannah	Aiken, SC 29801
1	W. Stephan Dubyk	H+GCL		505 Marquette NW Suite	Albuquerque, NM 87192
1	Douglas C. Duckworth	ORNL		P. O. Box 2008, MS-6375	Oak Ridge, TN 37831-6375
1	Stan Dudka	Trent University ERS			Peterborough Ontario,
1	Dr. Charles S. Dudley	Martin Marietta Energy		P. O. Box 2008	Oak Ridge, TN 37831-6113
1	Pam Dukes	Bureau of Radiological	2600 Bull Street	Dept. of Health & Env.	Columbia, SC 29201
1	David S. Duncan	Argonne West		P. O. Box 2528	Idaho Falls, ID 93403
1	Jan W. Dunker	U.S. Army Corps of		12565 West Center Road	Omaha, NE 68144-3869
1	David L. Dunn	Westinghouse SRC	Mail Stop Building 735A	P. O. Box 616	Aiken, SC 29802
1	Donald E. Dunning, Jr.	Argonne-OR		P. O. Box 6974	Oak Ridge, TN 37831-6974
5	Ken Duvall	U.S. Department of Energy		1000 Independence Avenue	Washington, DC 20585
1	James A. Ealy	MMES		P. O. Box 2003	Oak Ridge, TN 7831-7169

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Laurie Easterling	Radian Corporation		120 S. Jefferson Circle	Oak Ridge, TN 37830
1	Martha A. Ebra	Westinghouse SRC		P. O. Box 616	Aiken, SC 29802
1	Martin C. Edelson, Ph.D.	Ames Laboratory		Iowa State University	Ames, IA 50011
1	Richard Ediger	The Perkin-Elmer Corporation		761 Main Avenue	Norwalk, CT 06859-0215
1	Chuck Edrington	Fisher Scientific	P. O. Box 4829	2775 Pacific Drive	Norcross, GA 30091
1	Chip Edwards	Lawrence Livermore		P. O. Box 808	Livermore, CA 94550
1	Philip Edwards	Environmental Syntectics Inc.		P. O. Box 953	Rancho Murieta, CA 95683
1	Lance Eggenberger	DataChem Laboratories		960 W. Levoy Drive	Salt Lake City, UT 84123
1	Prof. Gilbert Eggemont	Vrije Universiteit Brussel	Laarbeeklaan 103	AZ-Cyclotron	B-1090 Brussels, Belgium
1	Katherine Eidam	Battelle - Pantex	Building 12-100	P. O. Box 30020	Amarillo, TX 79177
1	Karla R. Elam, Ph.D.	Oak Ridge National		P. O. Box 2008	Oak Ridge, TN 37831-6495
1	Rosemary J. Ellersick	CDM Federal Programs		13135 Lee Jackson Mem	Fairfax, VA 22033
1	John Elling	LANL		MS J580	Los Alamos, NM 87545
1	Carol Ann. M. Elliott	National Research Council		Montreal Road	Ottawa, Ontario, Canada
1	Geneva Ellis	DOE		EM-44	Washington, DC 20585
1	Tim H. Elmont	EG&G Rocky Flats	P. O. Box 464		Golden, CO 80402-0464
1	Tom Emenhiser	CH2M Hill, Inc.	P. O. Box 1647		Gainesville, FL 32602
1	Janice L. Engels	Martin Marietta Energy		P. O. Box 2003	Oak Ridge, TN 37831-7606
1	Margie English	Idaho Div. of Environmental		1410 North Hilton	Boise, ID 83706
1	Patrick M. Epperson	LLNL	P. O. Box 808	L-310	Livermore, CA 94550
1	Dr. Mitchell D Erickson	Argonne National Laboratory		9700 South Cass Ave	Argonne, IL 60439-4843
1	John Erickson	Env. Rad. Section, State of	P. O. box 47827	Department of Health, Div. of	Olympia, WA 98504-7827
1	Dr. Fabio Ermolli	Aquater	61047 S. Lorenzo In Campo	Hydrogeology Dept.	Pesaro, Italy
1	Kenneth U. Erondy	ESE, Inc.		P. O. Box 1703	Gainesville, FL 32602-1703
1	Lola Estes	RAPIC	P. O. Box 2003	Building K-1210 MS7256	Oak Ridge, TN 37831-7256
1	Joan Etheridge	Etheridge Associates	2262 Marine Drive	Chemical & Waste	Oakville, Ontario, Canada
1	Hideo Ezure	RANDEC		821-100 Funaishikawa Tokai	Ibaraki 319-11, Japan
1	Louis Fadel	Environ Services of Ohio Inc.	P. O. Box 167571	4350 Naverri Avenue	Oregon, OH 43616
1	Michael P. Failey	Battelle Columbus		505 King Avenue	Columbus, OH 43201-2653
1	Billy J. Fairless	EPA- Region VII		25 Funston Road	Kansas City, KS 66115
1	Gary J. Fallick	Millipore Corporation,		34 Maple st	Milford, MA 01757-3696
1	Darryl Farber	The Pennsylvania State		133 Willard Building	University Park, PA
1	Bruce S. Ferguson	Immuno Systems Inc.		4 Washington Avenue	Scarborough, ME 04074
1	Michael J. Fern	EIChrom		8205 S. Cass Avenue, Suite	Darien, IL 60559
1	Amadeo R. Fernandez Alba	Universidad De Almeria	Facultad de Ciencias	Dept. de Ciencia Analytica	Almeria, Spain 0407
1	Daro Ferrara	P. O. Box 616		Westinghouse Savannah	Aiken, SC 29083
1	D. Figg	Los Alamos National Lab		MS G740	Los Alamos, NM 87545
1	James A. Finger	Director Environmental		College Station Road	Athens, GA 30613
1	Bob Finnigan			125 Los Altos Ave	Los Altos, CA 94022
1	Isabel Fisenne	DOE Environmental		376 Hudson Street	New York, NY 10014-3621
1	Joan Fisk	Los Alamos National Lab		P. O. Box 1663, K-484	Los Alamos, NM 87544
1	Patricia Fitzpatrick	Lockheed		980 Kelly Johnson Drive	Las Vegas, NV 89119
1	Dr. Robert A. Fjeld	Clemson University		Clemson Research Park	Clemson, SC 29634-0919
1	Nanette Fladung	Microbial Environmental		11280 Aurora Ave	Des Moines, IA 50322
1	Dr. Robert J. Floran	Sandia National Laboratories		P. O. Box 5800	Albuquerque, NM
1	Charles R. P. Flynn	CHEMRAD		1055 Commerce Park Drive,	Oak Ridge, TN 37830
1	Norman Flynn	Quanterra		5010 Gadwall Circle	Stockton, CA 95207
1	Oliver Ford	USEPA OSW-Methods		401 M St., S.W., OS-331	Washington, DC 20460

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	G. R. Fountain	KAPL, Inc.	Building G-1	P. O. Box 1072- Room 289	Schenectady, NY 12301
1	Linda Fowler	Compu Chem.	P. O. Box 14998	3308 Chapel Hill/Nelson	Research Triangle Park, NC
1	Veryl Frahm	V SL, Hannan Hall Room 307	Cardinal Station	The Catholic University of	Washington, DC 20064
1	Mary W. Francis	ORNL	BLDG 2001	P O Box 2008	Oak Ridge, TN 37831-6050
1	Mike Franz	Enseco		2544 Industrial Boulevard	West Sacramento, CA
1	Dorris Frazier	P. O. Box 2008		Bethel Valley Road	Oak Ridge, TN 37831-6198
1	Nancy Freeman	SCM-Chemical		3901 Armistead Road	Baltimore, MD 21226
1	Dr. Jed Freudenthal	Environmental Consultancy	3720 AE	P. O. Box 202	Bilthoven, The Netherlands
1	S. Fu	Hannan Hall	Catholic University	Vitreous State Laboratory	Washington, DC 20064
1	Dr. Roswitha Gail-Eller	E. Merck		Frankfurter Str 250	64271 Darmstadt, Germany
1	Carol Gallatin	EBASCO environmental		143 Union Boulevard, Suite	Lakewood, CO 80228
1	Dr. René Galli	Umwelttechnik AG	CH-8048	Vulkanstrasse 110	Zurich, Switzerland
1	Bob Galloway	Sandia National Lab		Dept. 6622, P. O. Box 5800	Albuquerque, NM 87185
1	Richard B. Gammadge	Oak Ridge National	P. O. Box 2008	Bethel Valley Rd.	Oak Ridge, TN 37831-6384
1	Dr. Bob Garber	1609 Chandler Road			Knoxville, TN 37922
1	Stephen Garvin	Building Research	Kelvin Road	Scottish Laboratory	East Kilbride, Glasgow,
1	Dr. James E. Gaskin	Environment Canada	351 St. Joseph Blvd.	7th Floor PVM	Hull, Quebec, Canada K1A
1	Wayne Gaves	Ordela Inc.		1009 Alvin Weinberg Drive	Oak Ridge, TN 37830
1	Daniel Geisbacher	Slovak Inspection for the		84222 Bratislava	Slovak Republic,
1	David George	P. O. Box 25007 DFC-D3120			Denver, CO 80225
1	Dr. Ralf George	E&E Umwelt Beratung,	Postfach 7	Chemnitzer Straße 13	09222 Gröna, Germany
1	Dale Gergely	Apex Environmental Inc.		675A Emory Valley Road	Oak Ridge, TN 37830
1	Bob Gerlach	Lockheed		980 Kelly Johnson Drive	Las Vegas, NV 89119
1	Clare Gerlach	Lockheed		980 Kelly Johnson Drive	Las Vegas, NV 89119
1	Lucinia Ghigliotti	Environmental Quality Board		P. O. Box 11488	Santurce, Puerto Rico 009
1	Joe Giaquinto	Martin Marietta Energy	Building 2026, MS 6043	P. O. Box 2008	Oak Ridge, TN 37831-6043
1	H. K. Bud Gibson	Analytical Technologies Inc.		426 Heatherbrook Drive	Jefferson City, TN 37760
1	Luther V. Gibson, Jr.	Martin Marietta Energy	P. O. Box 2003	Building K-1600 MS 7313	Oak Ridge, TN 37831-7313
1	Remo Gigante	Nytest Environmental, Inc.		60 Seaview Blvd.	Port Washington, NY 11050
1	Richard Giglio	Compu Chem Laboratory	3308 Chapel Hill/Nelson	P. O. Box 12652	Research Triangle Park, NC
1	Vic Gill	WEMCO Fernald	P.O. Box 398704		Cincinnati, OH 45239-8704
1	Dr. Ján Girman	Geologický Ústav Dionýza	817 04 Bratislava	Mlynská dolina 1	Slovakia,
1	Nick Glassey	MS 82-2		P. O. Box 398704	Cincinnati, OH 45239
1	William B. Gloersen	USNRC Region II	101 Marietta Street NW	Suite 2900	Atlanta, GA 30323
1	Rolf Gloor	Institut Bachema AG	Sonneggstrasse 63	Analytische Laboratorien	8033 Zurich, Switzerland
1	Robert S. Glowacky	Aqua Tech Environmental	P.O. Box 76	State Route 1000	Melmore, OH 44845
1	Michael G. Goergen	Fire & Environ. Consult. Lab,		1451 East Lansing Drive,	East Lansing, MI 48823
1	Paula M. Goggin	A. T. Kearney, Inc.	P.O. Box 1438	225 Reinekers Lane	Alexandria, VA 22313
1	Dr. Gary L. Goken	3M		3M Center Building	St. Paul, MN 55144-1000
1	Norbert Golchert	Argonne Nat Lab, Bldg. 200,		9700 South Cass Ave.	Argonne, IL 60439
1	Alex Goldberg	USEPA		2890 Woodbridge Avenue	Edison, NJ 08837
1	Charles Good	Portsmouth Gaseous		P. O. Box 628	Piketon, OH 45661
1	Paula Goode	USEPA/NAREL		1504 Avenue A	Montgomery, AL 36115-2401
1	Ms. E. C. Goodson	US DOE E & L P D	P O Box A		Aiken, SC 29802
1	Paul Grahovac	Westinghouse Idaho Nuclear	P. O. Box 4000	MS 3301	Idaho Falls, ID 83415
1	Steve Grant	ETC		284 Raritan Center Pkwy.	Edison, NJ 08818
1	Mike Gray	Supleco Inc.	Supleco Park	Vice President of Marketing	Bellefonte, PA 16823-0048
1	Branislav Grbović	Borovac C.E.	11040 Belgrade	Bilećka 28a	Yugoslavia,

<u>No. of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	David W. Green	Argonne National Laboratory		9700 South Cass Ave	Argonne, IL 60439-4837
1	Dr. Wayne H. Griest	Oak Ridge National Lab	P.O. Box 2008	Bldg 4500-S	Oak Ridge, TN 37831-6120
1	Jeffrey C. Griffin	Westinghouse SRC	Building 773A	P. O. Box 616	Aiken, SC 29802
1	John Griggs	USEPA/NAREL		1504 Avenue A	Montgomery, AL 36115-2601
1	Ms. Zoe Grosser	Perkin Elmer		50 Danberry Rd	Wilton, CT 06897-0219
1	J. Gulens	AECL Research		Chalk River Laboratories	Chalk River, Canada K0J
1	Robert E. Gunther	Analytical Resources Inc.		333 Ninth Avenue North	Seattle, WA 98109-5187
1	Dr. Pálmai György	Budapesti Műszaki Egyetem	1521 Budapest	Kémiai Technológia Tanszék	Budaköki út 8, Hungary
1	Bill Haas	AMES Laboratory	ISU	110 Spedding Hall	Ames, IA 50011
1	Dr Martin Haas	West Valley Nuclear	P. O. Box 191	MS Z26	West Valley, NY 14171
1	Dr. Roswitha T. Haas	Oak Ridge National		1060 Commerce Park	Oak Ridge, TN 37830
1	Dr. Fred Haebeler	U. S. Protection Agency		401 M St, SW (RD-680)	Washington, DC 20460
1	Dr. Mary Jane Hahngenson	Morrison Knudsen	1500 West 3rd Street	MK-Ferguson Plaza	Cleveland, OH 44113-1406
1	Richard Haimann	CH2M Hill	2510 Red Hill Avenue	P. O. Box 15960	Santa Ana, CA 92705-0960
1	Dr Howard L Hall	Lawrence Livermore	P O Box 808	L-233	Livermore, CA 94551
1	Jack R. Hall	IT Corporation		9000 Executive Park Drive,	Knoxville, TN 37923
1	Steve Hall	USEPA/Region IV Environ.		College Station Rd.	Athens, GA 30613
1	Ahmed A. Halouma	Martin Marietta Energy		P. O. Box 2003	Oak Ridge, TN 37831-7606
1	Rich F. Hamon	AECL Research		Whiteshell Laboratories	Pinawa, Manitoba,, Canada
1	Kenneth L. Hanna	Division of Environmental		1410 North Hilton	Boise, ID 83706-1290
1	Bermis Hannah	Division of Radiation Control	State Office Building	State Dept. of Public Health	Montgomery, AL 36130-1701
1	Sorin Hant	Research Institute for	2000 Dloiesri	3r Republica 2914	Romania,
1	Sara Harmon	Oak Ridge National	P. O. Box 2008	Bethel Valley Rd.	Oak Ridge, TN 37831-6384
1	Nancy Harold	Martin Marietta Energy	2003 K1004A	Blair Rd K-25 MS 7446	Oak Ridge, TN 37830-7446
1	William L. Harper	Martin Marietta Energy		P. O. Box 2009, MS 8189	Oak Ridge, TN 37831
1	Ed Hart	WINCO	P. O. Box 4000	MS 51 17	Idaho Falls, ID 83402
1	June C. Hart	Westinghouse SRC	Building 703-2A	P. O. Box 616	Aiken, SC 29802
1	Jim T. Harvey	Eichrom Industries Inc.		8205 S. Cass Avenue, Suite	Darien, IL 60559
1	Keith Hausknecht	Artesian Laboratory		630 Churchmens Road	Newark, DE 19702
1	Dr. Ruth Hawley-Fedder	Lawrence Livermore Nat	P. O. Box 808	L-310	Livermore, CA 94550
1	Howard Hawthorne, Ph.D.	Reynolds Electrical &		P. O. Box 98521	Las Vegas, NV 89193-8521
1	RoseAnn Haynes	DEQ		1712 SW 11th	Portland, OR 97221
1	Fred Heackev	MMES-HAZWRAP	Trico. Office Fac.	831 Tricounty Blvd.	Oliver Springs, TN 37840
1	Jim Heffner	Westinghouse - Savannah	P. O. Box 616	Savannah River Laboratory	Aiken, SC 29808
1	Ed Heithmar	USEPA, EMSL - Las Vegas	P. O. Box 93478	944 E. Harmon	Las Vegas, NV 89193-3478
1	H. A. Helms	Westinghouse SRC	MS Building 704-28S, Room	P. O. Box 616	Aiken, SC 29802
1	Thomas Helms	ASG Incorporated		800 Oak Ridge Turnpike	Oak Ridge, TN 37830
1	Bob Henry	Fisons Instruments Inc.		P. O. Box 20460	Boulder, CO 80308-3460
1	John Hicks	Anal. Resources Inc.		333 9th Avenue N	Seattle, WA 98109-5187
1	Scott Higgenbottom	DOE - SR Field Office		Bldg 704S	Aiken, SC 29802
1	Kathy Hillig	BASF Corp.		1609 Biddle Avenue	Wyandotte, MI 48192
1	George Hilton	Public Health Laboratory		1610 NE 150 th Street	Seattle, WA 98155
1	E. Ray Hinton, Ph.D.	Martin Marietta Energy		P. O. Box 2009	Oak Ridge, TN 37831-8189
1	James S. Ho	USEPA		26 W. Martin Luther King	Cincinnati, OH 45268
1	Bob Hochel	Westinghouse - Savannah	P. O. Box 616	Savannah River Laboratory	Aiken, SC 29808
1	Steven L. Hoeffner, Ph.D.	RUST	100 Technology Drive	Clemson Technical Center	Anderson, SC 29625
1	David F. Hoffman	Martin Marietta Energy	K-25 Site	P. O. Box 2003	Oak Ridge, TN 37831-7458
1	Ken Hofstetter	Savannah River - P. O. Box		Savannah River Laboratory	Aiken, SC 29808

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>				
1	Mary N. Hoganson	Halliburton NUS	900 Trail Ridge Road	Savannah River Center	Aiken, SC 29803-5297	
1	Fred Hohorst	Winco	P. O. Box 4000		Idaho Falls , ID 83415	
1	J. P. Hojnicky	Monarch Analytical		349 Tomahawk Drive	Maumee, OH 43537-1696	
1	Kari Holder	Westinghouse Idaho Nuclear	P. O. Box 4000, Mail Stop	1355 Fremont	Idaho Falls, ID 83415	
1	Susan Holdroyd	AEA Technology	Didcot	424.4 Harwell	Oxfordshire, OX11 ORA UK	
1	George R. Holeman	P. O. Box 1661			New Haven, CT 06507-1661	
1	Susan Holladay	8155 Davis Ferry Road			London, TN 37774	
1	Mark H. Hollenback	Geotech, Inc.	P.O. Box 14000		Grand Junction, CO 81502	
1	Michael T. Hornsher	University of Findlay		1000 N Main St	Findlay, OH 45840	
1	Steven Hoppe	Advanced Analytical		2414 West 12th Street, Suite	Tempe, AZ 85281	
1	M. Hotchandani	ORNL		P. O. Box 2008	Oak Ridge, TN 37831	
1	Steven Howard	E-304	P. O. Box 3000	EG&G Mound Applied	Miamisburg, OH	
1	Lyman H. Howe III	TVA Environmental		1101 Market Street	Chattanooga, TN	
1	David P. Howekamp	Dir., Air and Toxics Division	75 Hawthorne Street	EPA Region 9	San Francisco, CA 94105	
1	Garry R. Howes	Zeneca Bio Products	Belasis Avenue	P. O.Box 2	Billingham, Cleveland TS23	
1	Pavel Hucko	Water Research Institute		Nbr. arm. gen L. Svobodu 5	812 49 Bratislava, Slovakia	
1	Barbara Huettenhain	Bechtel	P. O. Box 193965	50 Beale Street	San Francisco, CA	
1	Doris Huff	Argonne National Laboratory		Bldg. 200, 9700 S. Cass	Argonne, IL 60439	
1	Cleo R. Hughes	Nuclear Fuel Services Inc.		1205 Banner Hill Road	Erwin, TN 37650	
1	Joseph Hughes	BDM Federal, Inc.		20300 Century Boulevard	Germantown, MD 20874	
1	Ben Hunter	Westinghouse Idaho Nucl.		P. O. Box 4000, MS 5202	Idaho Falls, ID 83403	
1	Dave Hunter	Env. Chemistry & Toxicology	46 N. Medical Drive	Bureau of Environment	Salt Lake City, UT 84113	
6	Duane Hunter	EG&G Rocky Flats, General	P. O. Box 464		Golden, CO 80402-0464	
1	Gordon S. Hunter	Gilson Medical Electronics	P. O. Box 27	300 West Beltline Highway	Middleton, WI 53562	
1	Mark W. Huntley	Westinghouse Idaho Nuclear		P. O. Box 4000	Idaho Falls, ID 83402	
1	Dr. Chris D. Hutchinson	Ministry of Defense, Atomic		Aldermaston	Reading, Reading, UK	
1	Ralph Ilgner	Oak Ridge National	Building 4500 S	P. O. Box 2008, MS 6120	Oak Ridge, TN 37831-6120	
1	Dr. Kenneth G W Inn	NIST, Ionizing Radiation		Bldg 245, Rm C229	Gaithersburg, MD 20899	
1	Brenda Irvine	FERMCO	P. O. Box 538704	Mail Stop 65-2	Cincinnati, OH 45253-8704	
1	Pr. Zinifer R Ismagilov	Acamedy of Sciences of		Prospekt Akademika	Novosibirsk, 630090	
1	Kurt Jackson	Dept. of Health Services	P. O. Box 942732	601 N. 7th Street	Sacramento, CA 94234-7320	
1	Larry P. Jackson, Ph.D.	Environmental Quality		26 Keenan Drive	Peterborough, NH 03458	
1	R. F. Jakubik	BDM Federal Inc.		20300 Century Blvd., Suite	Germantown, MD 20874	
1	John Jankousky	SM Stoller		5700 Flatiron Parkway	Boulder, CO 80301	
1	Mr. Lynn N. Jaussi	Lockheed Analytical		975 Kelly Johnson St	Las Vegas, NV 89119	
1	Carol Jautzen	Westinghouse Savannah	Building 773A	Savannah River Techn.	Aiken, SC 29808	
1	Richard A. Javick	FMC Corp.		P. O. Box 8	Princeton, NJ 08543	
1	Beloeil Jean-Yves	DPEN/CE/CA		Centre d'Etudes de VaPoluc	21 IS/Tille, France	
1	Dr. Roger Jenkins	ORNL Bldg 4500-S,		P. O. Box 2008	Oak Ridge, TN 37831-6120	
1	Zvonka Jeran	Nuclear Chemistry		61001 Ljubljana Jamova 39	Slovenia,	
1	Dr. Jan John	Technical University of		Brehová 7	115 19 Prague 1, Czech	
1	Craig Johnson	ECOTEK Lab. Services Inc.		3342 International Park	Atlanta, GA 30316	
1	Harris Johnson	Analytics Inc.		1380 Seaboard Industrial	Atlanta, GA 30318	
1	Michael J. Johnson	DOE-EML		376 Hudson St	New York, NY 10014	
2	Monique Johnson	DOE/NVO		P. O. Box 98518	Las Vegas, NV 89193	
1	Val Johnson	Technical Measurements		2888 Bluff Street No. 147	Boulder, CO 80301	
1	Val Johnson	Technical Measurements		2888 Bluff Street No. 147	Boulder, CO 80301	
1	C. Martin Johnson, Jr	SAIC	P. O. Box 2501	301 Laboratory Road	Oak Ridge, TN 37831	

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Tom Johnston	Neptune and Company		1505 15th Street Suite B	Los Alamos , NM 87544
1	Greene A. Jones	Director, Environmental	841 Chestnut Building	EPA Region 3	Philadelphia, PA 9107
1	Tammy Jones	USEPA EMSL - Las Vegas	P. O. Box 93478	944 E. Harmon	Las Vegas, NV 89193-3478
1	Sheila Jordan	Waste Policy Institute		555 Quince Orchard Road,	Gaithersburg, MD
1	Dr. Bhanu Joshi	Vegas Analytical Lab		3894 Schiff Drive	Las Vegas, NV 89103
1	Marina C. Jovanovich	Environmental Scientist	P. O. Box 808, L-453	Lawrence Livermore	Livermore, CA 94551
1	Art Jurgensen	Westinghouse - Savannah	P. O. Box 616	Savannah River Laboratory	Aiken, SC 29808
1	Larry Kaelin	Senior Field Chemist	2890 Woodbridge Avenue	c/o Weston/Reac	Edison, NJ 08837
1	Murali Kalavapudi	Energetic Inc.		7164 Columbia Gateway	Columbia, MD 21046
1	Dr. Sándor Kántor	Technical University of	H-1521 Budapest	Chemical Technology	Műgyetem rkp 1-3,
1	Paul Kaplan	Sandia National Lab	P. O. Box 5800	MS 1326	Albuquerque, NM
2	Stuart Kaplan	470 L'enfant Plaza East,			Washington, DC 20024
1	Dan Kapsch	E G & G Mound	P O Box 3000		Miamisburg, OH
1	Mr. Joel Kamofski	2130 Bonar Street			Berkeley, CA 94702
1	Bill Kavanagh	U.S. AEHA			APG, MD 21010-5422
1	Nenad Kecojević	Termovent Production Eng.		Rada Neimara 4	Beograd, Yugoslavia
1	John Keller	Oak Ridge National		P. O. Box 2008	Oak Ridge , TN 37831-6128
1	Dr. Kevin P. Kelly	Laboratory Automation Inc.		555 Vandiver Drive	Columbia, MO 65202
1	Elizabeth Kelly	A-1m MS F600	LANL		Los Alamos, NM 87545
1	Sandra L. Kenefick	Dept. of Health Serv. Admin.	322 Newton Research	University of Alberta	Edmonton, Canada T6G 2G6
1	Chris Kent	INEL		P. O. Box 4000	Idaho Falls, ID 83403
1	Paul Kester	Tekmar	P. O. Box 429576		Cincinnati, OH 45242-9576
1	Mohmeb M. Khalil	Westinghouse SRC	Building 735-15A	P. O. Box 616	Aiken, SC 29802
1	Chris Kinard	EG&G Mound Applied	P. O. Box 3000		Miamisburg, OH
1	W. Frank Kinard	Department of Chemistry		College of Charleston	Charleston, SC 29424
1	James King	DynCorp Viar		300 North Lee Street	Alexandria, VA 22314
1	Dr Robert Kinnison	Reynolds Electrical &		P. O. Box 98521	Las Vegas, NV 89193-8521
1	Dan Kirkpatrick	University Hygienic Lab	University of Iowa	102 Oakdale Campus H101	Iowa City, IA 52242-5002
1	Leon N. Klatt	ORNL	P. O. Box 2008		Oak Ridge, TN 37831-6306
1	Larry Klingler	EG&G Mound		P. O. Box 3000	Miamisburg, OH 45343
1	C. S. Klusek	DOE Environmental		376 Hudson Street	New York, NY 10014-3621
1	B. George Kniazewycz	BNFL Inc.	1501 N. Broadway Suite 250	P. O. Box 30306	Walnut Creek, CA 94598
1	David A. Knott	Martin Marietta Energy	P. O. Box 2003		Oak Ridge, TN 37831-7606
1	Craig Knowles	Radiological Health Bureau	6 Hazen Drive	Div. of Public Health	Concord, NH 03301-6527
1	Dr. Michael Koch	Head of Dept.	P. O. Box 210243	Hansstraße 20 D-80686	D-80672 München, Germany
1	Eric N. Koglin	U.S. EPA	P. O. Box 93478	Envir. Monitoring Sys. Lab	Las Vegas, NV 89193-3478
1	David S. Kohl	B&W Nuclear Environ.	P. O. Box 11165	Lynchburg Technology	Lynchburg, VA 24506-1165
1	Dr. Petr Kohout	KAP spol s.r.o.		Skokanská 80	169 00 Praha 6, Czech
1	Prof. Dr. Johann Korkisch	Institute of Analytical	Währingerstrasse 38	University of Vienna	A-1090 Vienna, Austria
1	J. Louis Kovach	NUCON		P. O. Box 29151	Columbus, OH 43279
1	Steven H. Kramer	Rocky Mountain Analytical		4955 Yarrow Street	Arvada, CO 80002
1	Tom Krause	Benchmark Corporation		4501 Indian School Road NE	Albuquerque, NM 87110
1	John Krueger	Los Alamos National	MS J595	EM-7 Waste Management	Los Alamos, NM 87545
1	Dr. Danuta Kudelska	Institute of Environmental	1-6 92 Warsaw	Kalektorska 4	Poland,
1	Jon D. Kuhns	ACS Savannah River		524 Greenwich Drive	Aiken, SC 29803
1	Shri Kulkarni	Manager, QA Department,	P. O. Box 1294	Research Triangle Institute	Research Triangle Park, NC
1	David F. Kwesell			4315 Stonehaven Drive	Colorado Springs, CO 80906
1	Sylvia S. Labie	Quality Assurance Section	2600 Blair Stone Road	Laboratory Complex Suite	Tallahassee, FL 32399-2400

<u>No. of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Dr. John J. LaBrecque	IUIC M-581		P. O. Box 020010	Miami, FL 33102
1	Dr. Radu Laciutusee	Research Institute for Soil	B-dul Marash 61	71331 Bucharest 32	Romania,
1	Virgil C. Lacy	Fernald Env. Management		P. O. Box 538704, MS 35	Cincinnati, OH 45252-874
1	Patricia C. Ladezanin	Westinghouse SRC	Building 772F	P. O. Box 1616	Aiken, SC 29802
1	Guy A. Laing	Lockheed		980 Kelly Johnson Drive	Las Vegas, NV 89119
1	Don Lancaster		P. O. Box 911	1220 Valley Forge Rd, Unit 4	Valley Forge, PA 19482
1	Kenneth T. Lang	U.S. Department of Energy,		Trevion II, Hanford	Washington, DC 20585-0002
1	Matt Lardy	IT Corporation		P. O. Box 2800	Richland, WA 99352
1	Michele Laria	International Atomic Energy	P. O. Box 100	Wagramer Strasse 5	A-1400 Vienna, Austria
1	Kari Larjava	VIT Chemical Technology	FIN-02044	P. O. Box 1403	VTT, Finland
1	Joan LaRock	LaRock Associates, Inc.		801 Pennsylvania Avenue,	Washington, DC 20004
1	Mike Larson	Enseco		2544 Industrial Boulevard	West Sacramento, CA
1	David Lasher	Berringer Labs, Inc.		15000 West 6th Avenue,	Golden, CO 80401
1	Mary A. Lasky	Environmental Chemist	P. O. Box 670	QSEA	Dunbar, WV 25064
1	Vern Laurie	US EPA (8201)		401 M Street SW	Washington, DC 20460
1	John M. Lavoie	P. O. Box 3000		Mound Plant	Miamisburg, OH 45342
1	Fred E. Lawson	Duke Power	13339 Hagers Ferry road	MG0342	Huntersville, NC
1	Kathy Lawson	Battelle Columbus		505 King Avenue	Columbus, OH 43201-2653
1	George A. Lawton	Program Analyst	Building 53, Box 25227	EPA Office of Enforcement	Denver, CO 80225
1	Sarah Layton	7135 Minstrel Way		Suite 303	Columbia, MD 21045
1	Craig Leaseure	LANL	P. O. Box 1663		Los Alamos, NM 87545
1	Greg LeBlanc	Chem Corp		P. O. Box 200	Matthews, NC 28106
1	Anne W. Lee	AnalytiKEM		28 Springdale Road	Cherry Hill, NJ 08003
1	Bill Lee	MACTEC	Building 201	9800 S. Cass Avenue	Argonne, IL 60439
1	Dr. Yun Ko Lee	Reynolds Elect. & Eng. Co.,		P. O. Box 98521	Las Vegas, NV 89193-8521
1	Kun Jai Lee, Ph.D.	Korea Advanced Inst. of Sci.	Yusung-Gu	373-1 Kusung-Dong	Taejeon 305-701, Korea
1	Steve Leffler, Ph.D.	Nuclear Remediation		P. O. Box 85608	San Diego, CA 92186-9784
2	Margaret Legel, MBL	Argonne National Laboratory		9800 S. Cass Avenue	Argonne, IL 60439
1	Dr. Chris Leibmann	LANL		EM-9/MS: K484	Los Alamos, NM 87545
1	William H. Lemons	Core Laboratories		8210 Mosley Road	Houston, TX 77075
1	Alexandra T. Leo	Sandia National Laboratories		Environmental Protection	Livermore, CA 94551-0969
1	Megan Lerchen	Washington Dept of Ecology	P. O. Box 47600		Olympia, WA 98504-7600
1	Moshood O. Leshi	Ecology and Environment		4801 Woodway, 280 West	Houston, TX 77056
1	Barry Lesnik	USEPA OSW-Methods		401 M St., S.W., OS-331	Washington, DC 20460
1	Ronald Leuenberger	Princeton University,	P. O. Box 451		Princeton, NJ 08543
1	Brian Levine	Knolls Atomic Power Lab		P. O. Box 1072	Schenectady, NY 12301
1	Dr. Ronald F. Lewis	US EPA		26 W. Martin Luther King	Cincinnati, OH, 45268
1	Leroy C. Lewis	Westinghouse Idaho Nuclear	P. O. Box 4000		Idaho Falls, ID 83403-5210
1	Albert A. Liabastre, Ph.D.	U.S. Army EHA Fort		2489 King Arthur Circle,	Atlanta, GA 30345
1	Gordon Lien	SRS		704-28S	Aiken, SC 29802
1	Dan Lillian	DOE/LMD Trevion II		12800 Middlebrook Rd	Germantown, MD 20874
1	John P. Lilly	Nuclear Fuel Services Inc.		2211 N. Greenwood Drive	Johnson City, TN 37604
1	T. H. Lin	APHIS/USDA	6505 Belcrest Road	Federal Building-1 Room 533	Hyattsville, MD 20782
1	Peter Lindahl	ANL - E		9700 South Cass Ave	Argonne, IL 60439-4831
1	Greg Linder	USEPA ERL-C		200 Southwest 35th Street	Corvallis, OR 97333
1	John R. Lloyd	Lockheed		975 Kelly Johnson Drive	Las Vegas, NV 89119
1	Vicki Lloyd	EPA/ORP/NAREL		1504 Avenue A	Montgomery, AL 36115-264
1	Dr. Viorica Lopez-Avila	Midwest Research Institute		625-B Clyde Avenue	Mountain View, CA 94043

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Irwin N. Lourie	Department of		555 North Lake	Conshohocken, PA 19428
1	Irwin N. Lourie	PA-DER		1739 Williams Way	Morristown, PA 19403
1	Yarylo Lu	Department of Chemistry		Carleton University	Ottawa, Ontario, Canada
1	KGW Lun	NIST		Bldg. 245, Room C229	Gaithersburg, MD 20899
1	John Lytle	RUST GEOTECH		P. O. Box 14000	Grand Junction, CO 81596
	Susan MacLean	Lawrence Livermore		P. O. Box 808, L-383	Livermore, CA 94551
1	Ray Maddalone	TRW		One Space Park 01/2030	Redondo Beach, CA 90278
1	Jim Maezer	9700 S. Cass Avenue	Argonne National Lab	Building 205	Argonne, IL 60439
1	Dr. Giolietta Magnoni	Via Atanagi 43	61043 Cagli (PS)		Italy,
1	Richard J. Maguire	Itytronics, Inc.	P.O. Box 590	224 Calvary Street	Waltham, MA 02254-0590
1	Roger N. Mahannah	Westinghouse Savannah		Rm 157, 772-F	Aiken, SC 29808
	Peter Makinson	British Nuclear Fuels		Springfield Words	Salwick, Preston, UK PR4
1	Andras Mako	Acadmey of Sciences	Faculty Keszthely Soil Sci.	PATE University of	H-8360 Keszthely, Deak F.
1	Steven Malcolm	Mason & Hanger	P. O. Box 30020	Pantex Plant	Amarillo, TX 79177
2	Thomas M. Malloy	Office of Technology		P. O. Box 3767	Butte, MT 59702
1	Shipho Mamba	Dept. of Chemistry		University of Alberta	Edmonton, Canada T6G 2G2
2	Peggy Mann	PRC Environmental		1921 Rohlwing Road Suite D	Rolling Meadows, IL 60008
1	Lisa Manning	Environmental Laboratories		5350 Campbells Run Road	Pittsburgh, PA 15025
1	Chung-Rei Mao	US Army Corps of Engineers		12565 West Center Road	Omaha, NE 68144
1	George Marinenko	SAIC		555 Quince Orchard Road	Gaithersburg, MD
1	Dr. Claudio Mariotti	Water Resources Dept.		61047 S. Lorenzo in Campo	Pesaro, Italy
1	Guy Marlette	USDOE Rad & Environ Sci		785 DOE Place	Idaho Falls, ID 83401-1562
1	John H. Marlow	West Valley Nuclear	P.O. Box 191		West Valley, NY 14171-0191
1	Bruce Marron	Benchmark Corporation		4501 Indian Scholl Rd NE	Albuquerque, NM 87110
1	Dr. Paul Marsden	Sci Applications International		10260 Campus Point Drive	San Diego, CA 92121
1	S. Fredric Marsh	Los Alamos National		Mail Stop E501	Los Alamos, NM 87545
1	John P. Martinson	Authorization systems, Inc		1801 Rockville Pike No. 216	Rockville, MD 20852-1633
1	Mike Maskarinec	Oak Ridge National		P. O. Box 2008	Oak Ridge, TN 37831-6120
1	Lisa Matis	Hallibarton NLS		900 Trail Ridge Road	Aiken, SC 29803
1	Keith Scanlan Matlock	Vitreous State Lab		Catholic University of	Washington, DC 20069
1	Lynn S. Matthews	Thru-Put Systems Inc.		P. O. Box 617290	Orlando, FL 32861-7290
1	Tim Matthews	Thru-Put Systems		450 East South Street, Suite	Orlando, FL 32801
1	Molinari Mauro	PRAOIL	Muanofopi	Str 2-F7	Italy,
1	Ms. Billy Mauss	Washington Dept. of Ecology		1315 West 4th Avenue	Kennewick, WA 99336-5032
1	Robert Maxfield	GTEL		Meadowbrook Industrial Park	Milford, NH 03055
1	Sherrod Maxwell	Westinghouse Savannah		P. O. Box 616	Aiken, SC 29808
1	Mike May	University of South Carolina		171 University Parkway	Aiken, SC 29801
1	Steven L. McBride	SAIC		655 Metro Place South	Columbus, OH 43017
1	Craig R. McCaffrey	OHMICRON		375 Pheasant Run	Newtown, PA 18940
1	Russell McCallister	USEPA	401 "M" Street SW	Mail Code 5204G	Washington, DC 20460
1	Sandy McCarty	PACE, Inc.		5930 McIntyre Street	Golden, CO 80403
1	Teena McCillan	Navy Public Works Center		Code 930, Building 2-140	Norfolk, VA 23511
1	Luke McCormick	12565 W/ Cemter Rpad			Omaha, NE 68144-3864
1	David E. McCurdy	Yankee Atomic Electric Co.		580 Main Street	Bolton, MA 01740
1	Clay D. McCurley	Bechtel	P. O. Box 193965	50 Beale Street	San Francisco, CA
1	Gary McGibbon	KNL Laboratory Services	P. O. Box 1833		Tampa, FL 33601
1	Roger McGinnis	Roy F. Weston Inc.		700 5th Avenue Suite 5700	Seattle, WA 98104
1	James A. McHugh, Ph.D.	Hilbert Associates Inc.		640 Maple Avenue	Saratoga Springs, NY 12866

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Terry McKibbin	Enseco IRMAL		4955 Yarrow Street	Arvada, CO 80002
1	Mike McNerlin	American Interplex Corp.		8600 Kanis Road	Little Rock, AR 72211
1	Robert Meck, Ph.D.	Office of Regulatory		U. S. Nuclear Regulatory	Washington, DC 20555
1	April M. Meeks	Building 2026 MS 6043	P. O. Box 2008	ORNL	Oak Ridge, TN 37831
1	Allen Meier	U. S. Geological Survey	P. O. Box 25046	MS 973	Denver, CO 80225
2	Terry J. Mendoza	Lawrence Livermore		P. O. Box 808, L-231	Livermore, CA 94550
1	Sharon Mertens	Radian Company		P. O. Box 201088	Austin, TX 78720
1	J. Marie Meszaros	MMES, Y-12	P. O. Box 2009	MS 8189, Bldg 9995	Oak Ridge, TN 37831
1	Barbara M. Metzger	2890 Woodbridge Avenue		Raritan Depot Building 10	Edison, NJ 08837-3679
1	Robert Metzger	Radiation Safety Engineering		3245 N. Washington Street	Chandler, AZ 85225-1121
1	Jill Meuser	GJPO		P. O. Box 14000	Grand Junction, CO 81506
1	Ken Mayer	Jacobs Engineering		7295 Highway 945	St. Charles, MO 63304
1	Kevin Mayer	ORNL	P. O. Box 2008	Building 7710, MS 6379	Oak Ridge, TN 37831
1	Paul Meyer	Langan Environmental		River Drive, Center 1	Elmwood Park, NJ 07407
1	Julianne J. Miller	Raytheon Services Nevada		1551 Hillshire Drive	Las Vegas, NV 891134
1	Rodney T. Miller	PACE Incorporated		1710 Douglas Drive North	Minneapolis, MN 55422
1	T. R. Miller	ORNL	P. O. Box 2008	1000 Bethel Valley Rd, Bldg	Oak Ridge, TN 37831-6142
1	Paul Mills	SAIC		10260 Compents Pt. Drive,	San Diego, CA 92121
1	Bruce Mincher	EG&G Idaho, Inc.	P.O. Box 1625	TRA, Building 649	Idaho Falls, ID 83415-7111
1	Julie L. Miranda	MMES - ORNL MS 6142	P. O. Box 2008		Oak Ridge, TN 37831-6142
1	Jim Mitchell	U. S. EPA		77 West Jackson Boulevard	Chicago, IL 60604-3590
1	Farideh Moghadami	SAIC		555 Quience Orchard Road,	Gaithersburg, MD
1	Dr. Geol. Mauro Molinari	Eni Chem	Milanofiori Strade 2 Plazzo	Praoil	20094 Assago, (Milano) Italy
1	Dr. Dean Momohara	Analytical Resources Inc.		333 Ninth Avenue N	Seattle, WA 98109
1	Mathew Monagle	LANL		K484	Los Alamos, NM 87545
1	Jeffrey Mones	Navy Public Works Center		Code 930, Building 2-140	Norfolk, VA 23511
1	Ronnie Moody	1845 Wickersham Drive			Knoxville, TX 37922
1	Chester D. Moon	Manufacturing Technology		3326 East Second Street	Muscle Shoals, AL
1	Bob Mooney	Section Head Nuclear Safety	1511 Third Avenue Suite No.	Department of Health	Seattle, WA 98101
1	Richard Moraski		P. O. Box 462071		Aurora, CO 80046-2071
1	Rick Morehead	Restek Corporation		110 Benner Circle	Bellefonte, PA 16823-8812
1	Rebecca Morris	Martin Marietta Energy		Y-12 Plant, Bldg. 9995, MS	Oak Ridge, TN 37831
1	Dr Roy W Morrow	ORNL Gaseous Diffusion	P. O. Box 2003	Martin Marietta K-25 MS	Oak Ridge, TN 37831-7440
1	Stan Morton	DOE Radio. & Environ. Sci.		850 Energy Drive	Idaho Falls, ID 83401-1562
2	Carol Moser	Lawrence Livermore		P. O. Box 808, L546	Livermore, CA 94551
1	T. R. Mueller	ORNL	P. O. Box 2008	1000 Bethel Valley Rd Bldg	Oak Ridge, TN 37831-6142
1	Robert Munter	Soil Testing Laboratory	University of Minnesota	1903 Hendon Avenue	St. Paul, MN 55108
1	Richard J. Murphy	Enseco IRMAL		4955 Yarrow Street	Arvada, CO 80002
1	Robert O. Murphy	Los Alamos National		CST-7, MS E516	Los Alamos, NM 87545
1	Allan Murray	ANSTO	1601 Massachusetts Avenue	Embassy of Australia	Washington, DC 20036
1	John S. Murray	Barringer Labs		15000 W. 6th Avenue	Golden, CO 80401
1	Curtis V. Nakaishi	U. S. Dept. of Energy,	P. O. Box 880	3610 Collins Ferry Road	Morgantown, WV
1	Dr. M. B. Neace	Mercer University		Stetson School of Business	Macon, GA 31207
1	Don Nelson	Argonne National Laboratory		Building 200, F125	Argonne, IL 60439
1	Roger A. Nelson	Jacobs Engineering Group		2155 Louisiana NE Suite	Albuquerque, NM 87110
1	Ahmad Nevissi	University of Washington		WH-10	Seattle, WA 98195
1	Son Nguyen	P. O. Box 808		L-457	Livermore, CA 94551
1	John Nicklas	WINCO, MS-5117	P. O. Box 4000		Idaho Falls, ID 83403

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Paul Nigrey	Dept. 6642		Sandia National Laboratory	Albuquerque, NM
1	Jeab Nivatvongs	Ch2M Hill		625 Herndon Parkway	Herndon, VA 22070
1	Linda Nonno	A-1m MS F600	LANL		Los Alamos, NM 87545
1	David L. Norwood	Nat. Air and Rad. Env.		540 South Morris Avenue	Montgomery, AL 36115-2601
1	Peter G. Novick	Dyncorp. Viar		300 N. Lee Street	Alexandria, VA 22314
1	Dr. Carter Nulton	Roy F. Weston, Inc.		208 Welsh Pool Rd.	Lionville, PA 19353
1	Tom O'Connell	Radiation Control Program	305 South Street, 7th Floor	Dept. of Health	Jamaica Plain, MA 02130
1	Charles O'Dell	U. S. Department of Energy		EM-361, Trevion II	Washington, DC 20585
1	Kent Oakes	Engineering Science		1700 Broadway Suite 900	Denver, CO 80290
1	Frank J. Oakley	Fisher Scientific	P. O. Box 4829	2775 Pacific Drive	Norcross, GA 30091
1	Mike Oberthur	Dept. of Health Lab.	P. O. Box 1964	1330 West Michigan St.	Indianapolis, IN 46206
1	Jose A. Olivares	LANL	P. O. Box 1663	MS J514	Los Alamos, NM 87545
1	Kent Orlandini	Building 203	9700 S. Cass Avenue	Argonne National Laboratory	Argonne, IL 60439
2	Dr. Edward B. Overton	Institute for Environmental	Louisiana State University	Room 42 Atkinson Hall	Baton Rouge, LA 70803
1	Kirk Owens	SAIC		20300 Century Boulevard	Germantown, MD 20874
1	Jeffrey Paar	MMES	Building K1007	P. O. Box 2003	Oak Ridge, TN 37831-7056
1	S. Pacheco	Tetrattech Inc.		348 W. Hospitality Lane	San Bernardino, CA 92408
1	R. Terry Pack	Martin Marietta Energy	MS 6043	P. O. Box 2008, Bldg 2026	Oak Ridge, TN 37831-6043
1	Terry Pack	Martin Marietta Energy	Building 4500S, MS 6146	P. O. Box 2008	Oak Ridge, TN 37831-6146
1	Michael A. Paessun	Enseco	4101 Shuffel Drive, NW	Wedsworth/ALERT	North Canton, OH 44720
1	Art Palmer, C. H.P.	U. S. Ecology		5333 Westheimer, Suite 1000	Houston, TX 77056
1	Hemant S. Pandya	DOE-EML		376 Hudson St	New York, NY 10014-3621
3	G. Joe Pardue	MMES	P. O. Box 2003	K-25, Highway 38, Bldg	Oak Ridge, TN 37831-7169
1	Jim Parks	Civil Engineering E-201		University of Texas	El Paso, TX 79968
1	Jerry Parr	Quanterra Inc.		4955 Yarrow	Arvada, CO 80002
1	Jack Parrott	U. S. NRC		Mail Stop 5E4	Washington, DC 20555
1	Bahman Parsa	DEQ/BRIAS	CN411-380 Scotch Road	Div. of Env. Safety, Health	Trenton, NJ 08625-0411
1	Charles Passo	Packard Marketing		800 Research Parkway	Meriden, CT 06450
1	Ulrich Peball	Proterra Umwelttechnik	Gerasdorfer Straße 151	Ges. m. b. H	A-1211 Wien, Postfach 200
1	C. J. Pecover	The Department of Transport		2 Marsham Street	London, England SW1P 3EB
1	Ian L. Pegg, Ph.D.	Catholic University of		Vitreous State Laboratory	Washington, DC 20064
1	Maxine B. Pennington	Allied-Signal Aerospace Co.,	P. O. Box 419159	2000 East 95th Street	Kansas City, MO
1	Nathan A. Pera	Environmental Testing &		2924 Walnut Grove Road	Memphis, TN 38111
1	Kusum Perera	CA Dept of Health Serv San		2151 Berkeley Way	Berkeley, CA 94704
1	Deborah K. Perez	MMES		P. O. Box 628	Piketon, OH 45661
1	Willard W. Perry	Midwest Research Institute		32108 Canyon Crest Court	Westlake Village, CA 91361
1	M. A. Peters, Ph.D.	EG&G Rocky Flats, Rocky	P. O. Box 464	R & PP Labs, Manager	Golden, CO 80402-0464
1	Karen Peterson	Washington State	P. O. Box 47827		Olympia, WA 98504-7827
1	Stephen F. Peterson, Ph.D.	SRS		P. O. Box 616	Aiken, SC 29802
1	Charles Phillips	EG&G Mound Applied		P. O. Box 3000	Miamisburg, OH
1	Steve Pia	USEPA, EMSL - Las Vegas	P. O. Box 93478	944 E. Harmon	Las Vegas, NV 89193-3478
1	Jeff Pike	Westinghouse Savannah		P. O. Box 616, MS 703-H	Aiken, SC 29802
1	Emily Pimental	PRC Environmental		120 Howard Street Suite 700	San Francisco, CA 94105
1	Stanislaw Piorek	Metorex		860 Town Center Drive	Langhorne, PA 19047
1	L. R. Pittwell	67 Blenheim Road		Caversham	Reading, RG 47 RP United
1	Jim Ploscyca	IEA Inc.		P. O. Box 12846	Research Triangle Park, NC
1	Dr. Russell H. Plumb	Lockheed	980 Kelly Johnson Drive	Environmental Sci. & Tech.	Las Vegas, NV 89119
1	Piotr S. Poborski	Polski Klub Ekologiczny	40-832 Katowice	ul. Kossutha 6	Poland,

<u>No. of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Dr. Piotr Pobotski	ul Kossutho 6		40-832 Katouice	Poland,
1	Timothy A. Policke	Westinghouse SRC		Building 704-1T, TXN	Aiken, SC 29808
1	Tara M. Popik	BP Research		4440 Warrensville Center	Cleveland, OH 44128-28
1	Dr. James Poppiti	DOE/RESL		656 Quince Orchard Road	Gaithersburg, MD 20878
1	Donivan Porterfield	Los Alamos National	MS K484		Los Alamos, NM 87545
1	Don Potter	Hewlett Packard	2850 Centerville Road	Analytical Marketing Center	Wilmington, DE 19808
1	Kathleen M. Power	Woodward-Clyde	4582 South Ulster Street	Stanford Place 3, Suite 1200	Denver, CO 80237
1	Dr. Laurie J. Prell	Martin Marietta Energy	P. O. Box 2009	MS 8081	Oak Ridge, TN 37830
1	Ruth A. Presley	Lawrence Livermore Nat.		P. O. Box 808, L-629	Livermore, CA 94550
1	Jim Preston	Barringer Laboratories Inc		15000 W. 6th Ave, Suite 300	Golden, CO 80401
1	Steven L. Pruskin			8882E Town Country	Ellicott City, MD 21043
1	Wally Quaider	US DOE - Fernald	P. O. Box 398705		Cincinnati, OH 45239-8705
1	Dave Quinn	Viking Instrument		P. O. Box 7000-712	Redondo Beach, CA 90277
1	Chuck Ramsey			P. O. Box 280385	Lakewood, CO 80228
1	Dr. Umesh Rao	Rexene Corporation, R&D		P. O. Box 3986	Odessa, TX 79760
1	K. G. Rao	Eastern Laboratory Svc.		571 North George Street	York, PA 17404
1	Tim Raub	Analytical Labs of Skelly &		2521 N. Front Street	Harrisburg, PA 7110
1	Donald R. Rayno	IEA, Inc		120 Southcenter Ct., Suite	Morrisville, NC 27560
1	Leah Reed			300 N. Lee Street	Alexandria, VA 22314
1	Jacky Reginster	Spaque		Avenue Destenay 7	
1	Bob Reinowski	NJ Dept. Env. Prot & Energy		380 Scotch Rd	Trenton, NJ 08625
1	Stephen E. Remaley	USEPA		75 Hawthorne Street, P-3-2	San Francisco, CA
1	Stella Renato	DIPTM	Viale Taramelli 12	Chimica Generale	27100 Pavia, Italy
1	Lisa Wong Rerup	R&D Chemist	1988 Triumph Street	ASL	Vancouver BC, Canada V5V
1	Dennis Revell	USEPA/Region IV Environ		College Station Rd.	Athens, GA 30613
1	Russell F. Rhoades	Director, Envir. Services	1445 Ross Avenue, 12th	First Interstate Bank Tower	Dallas, TX 75202-2733
1	Rick Rice	HazCon		4636 E. Marginal Way S	Seattle, WA 98134
1	Andrea Richmond	ORNL	Room X10-D228	P. O. Box 2008 4500 N, MS	Oak Ridge, TN 37831-6178
1	Susan Rizk	SAIC	800 Oak Ridge Turnpike	P. O. Box 2501	Oak Ridge, TN 37831
1	Ross K. Robeson	Lockheed	975 Kelly Johnson Drive	Analytical Laboratory	Las Vegas, NV 89119
1	Al Robinson	NISI		3100 George Washington	Richland, WA 99352
1	Larry Robinson	ORNL	Building 4500 South	P. O. Box 2008	Oak Ridge, TN 37831-6128
1	Kenneth A. Rodes	General Engineering	P. O. Box 30712	2040 Savage Road	Charleston, SC 29417
1	Lymari Rodriguez Rosado	Calle 16, S-1 River View			Bayamon, PR 00961
1	Raimund Roehl	CA Public Health		2151 Berkeley Way	Berkeley, CA 94704
1	Debbie Rosaco-Reece			300 N. Lee Street	Alexandria, VA 22314
1	Debbie Rosano-Reece	DynCorp. VIAR	555 Quince Orchard Road,	c/o Waste Policy Institute	Gaithersburg, MD
1	Ann Rosecrance	Core Laboratories		5295 Hollister Road	Houston, TX 77042
1	Ann Roseurance	Core Laboratories		10205 Westheimer	Houston, TX 77042
1	Mark Ross	COMPUCHEM	P.O. Box 12652	3308 Chapel Hill/Nelson	Res Tri Park, NC 27709
1	Roxie R. Ross	International Tech. Anal.		2800 Geo. Wash. Way	Richland, WA 99352
1	Jim Roth	Alpha Analytical Laboratory		8 Walkup Drive	Westboro, MA 01581
1	Lou Roudebush	ENCOTEC		3985 Research Park Drive	Ann Arbor, MI 48108
1	Anita Rounds	Westinghouse	P. O. Box 2068	Naval Reactors Facility	Idaho Falls, ID 83401
1	Mitch Rubenstein	205 W. Galena			Milwaukee, WI 53212
1	Thomas L. Rucker, Ph.D.	SAIC	301 Laboratory Road	P. O. Box 2501	Oak Ridge, TN 37831
1	Marister Ruiz	Florida Power & Light		6001 A Village Boulevard	West Palm Beach, FL 33411
1	Jacqueline A. Ruller	DURATEK		8955 Guilford Road, Suite	Columbia, MD 21046

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Dale Rushnek	3194 Worthington Avenue			Fort Collins, CO 80526
1	Price Russ	LLL		P. O. Box 808 Mail Stop	Livermore, CA 94550
1	Evelyn M. Ryan	Lawrence Livermore	P. O. Box 808	L-546	Livermore, CA 94551
1	Shelly J. Sailer	EG&G Idaho Inc.	P. O. Box 1625	Idaho National Engineering	Idaho Falls, ID 83415-4107
1	Tomás Sákra	Faculty of Chemical	nám Cx legii 565	Department of Environment	532 10 Bardubice, Czech
1	Dr. Batur Salamon	GEO-PRO Consulting	H-1173 Budapest	Barátka u. 68/B	Hungary,
1	Debbie Salem	WSRC		P. O. Box 161, Building	Aiken, SC 29802
1	Ernest A. Sanchez	TMA/Emberline	P. O. Box 387	7021 Pan American Hwy.	Albuquerque, NM
1	David A. Sanders	3M Industrial and Consumer		3M Center Building	St. Paul, MN 55144-1000
1	William H. Sanders III	Director, Environmental	77 Jackson Boulevard	EPA Region 5	Chicago, IL 60604-3507
1	Javier Santillax	HQ AFCEE/ERC		8001 Inner Circle Drive	Brooks AFB, TX 78235
1	Richard Sassoon	SAIC		555 Quince Orchard Road,	Gaithersburg, MD
1	Marcella Saynuk	Mitre Corporation		7525 Anderson Road W739	McLean, VA 22102
1	Ed Scalsky	Westinghouse Idaho Nuclear	P. O. Box 4000		Idaho Falls, ID 83403
1	Michael Schaffer	Radiation Policy	6801 Telegraph Road	Defense Nuclear Agency	Alexandria, Va 22310
1	Robert L. Schenley	Martin Marietta Energy	Building 2026	P. O. Box 2008	Oak Ridge, TN 37831-6043
1	Maureen Schilb	Westinghouse Savannah		Building 320-M	Aiken, SC 29803
1	George E. Schmauch	Air Prod. & Chem. Inc.		7201 Hamilton Blvd.	Allentown, PA 18195
1	Sue Schneider	West Valley Nuclear	P. O. Box 191	10282 Rock Springs Road	West Valley, NY 14741
1	Susan N. Schriver	Weston International		1 Weston Way	West Chester, PA 19380
1	Carla Schultz	Radian Corp.		2455 Horsepen Road	Herndon, VA 22071
1	Roy Schumacher	EG&G Mound		P. O. Box 3000	Miamsburg, OH 45343-3000
1	Dr Donald F. Schutz	Teledyne Isotopes		5 Van Buren Ave	Westwood, NJ 07675
1	Frank B. Schweitzer	MITRE, Attn: AFCEE/ESR		Building 624W	Brooks AFB, TX 78235-5000
1	Dennis Scordia	FLUID Metering Inc.	P. O. Box 179		Oyster Bay, NY 11771
1	Nancy Seabolt	IT Corp.		5815 Middlebrook Pike	Knoxville, TN 37921
1	Dr. Ferdinand Sebesta	Faculty of Nuclear Science	Brehova 7	Technical University of	115 19 Prague 1,
1	Awia L. R. Sekaly	Department of Chemistry		Carleton University	Ottawa, Ontario, Canada
1	Charles Sellers	USEPA OSW-Methods		401 M St., S.W.	Washington, DC 20460
1	Wade Selph	GAMMA-METRICS		5788 Pacific Center Blvd.	San Diego, CA 92121
1	Dr. Frank A. Settle, Jr.	Department of Chemistry		Virginia Military Institute	Lexington, VA 24450
1	Emanuele Sevá	Snam		P. O. Box 12060	20120 Milano, Italy
1	Gregory L. Shala	Martin Marietta Energy	Building C-743 T-9	P. O. Box 1410	Paducah, KY 42001
1	Shawn Shanmugan, Ph.D	Oak Ridge Associated	P. O. Box 117		Oak Ridge, TN
1	Cathy E. Sharp	Oak Ridge Analytical		1345 Oak Ridge Turnpike,	Oak Ridge, TN 37830
1	Kris Shifty	WINCO	P.O. Box 4000	MS 5117	Idaho Falls, ID 83403
1	Kim Shirley	US DOE		785 DOE Place, MS 83401	Idaho Falls, ID 83401
1	Bob Siegrist	Oak Ridge National	P. O. Box 2008	Bethel Valley Rd.	Oak Ridge, TN 37831-6384
1	Dr. David Sill	E G & G, MS 7111	P. O. Box 1625		Idaho Falls, ID 83415
1	Anne Silva	Lawrence Livermore		7000 E. Avenue, L546	Livermore, CA 94550
1	Robert Silva	Lawrence Livermore Nat	P. O. Box 808	L-232	Livermore, CA 94550
1	Ronald T. Simonton	U. S. DOE Pinellas Area		P. O. Box 2900	Largo, FL 34649
1	Ranjit D. Singh Ph.D.	AECL Research	Chalk River Ontario	Chalk River Laboratories	Ontario, Canada K0J 1J0
1	Raj Singhvi	USEPA, Environmental		Woodbridge Avenue	Edison, NJ 08837
1	Dick Siscanaw	USEPA/Region I New		60 Westview St.	Lexington, MA 02173
1	Ted Skingel	TALEM, Inc.		306 West Broadway Avenue	Fort Worth, TX 76104
1	Randall P. Slagle	Nuclear Fuel Services		1205 Banner Hill Rd	Erwin, TN 37650
1	Gary T. Smiley	Energy, Mines and		c/o 555 Booth Street	Ottawa, Ontario, Canada

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Dr. James S. Smith	Trillium Inc.		74 Grace's Drive	Coatesville, PA 19320
1	Graham M. Smith	Intera Information	Henley-on-Thames	Chiltern House 45 Station	Oxfordshire, RG9 1AT,
1	Jane Smith	Dept. of Health Laboratory	P. O. Box 1964	1330 West Michigan Street	Indianapolis, IN 46206
1	Lesa L. Smith	Building 203	9700 S. Cass Avenue	Argonne National Lab	Argonne, IL 60439
1	Mike Smith	FERMCO	P. O. Box 398704	Mail Stop 65	Cincinnati, OH 45239-8704
1	Roy-Keith Smith	Analytical Services, Inc.		110 Technology Parkway	Norcross, GA 30092
1	Stacy M. Smith	ORNL		P. O. Box 2008	Oak Ridge, TN 37831-2008
1	Timothy W. Smith	Reynolds Elect & Eng. Co.		P. O. Box 98521	Las Vegas, NV 89193-8521
1	Wilkins R. Smith	Energetics		7164 Gateway Drive	Columbia, MD 21046
1	Tim Snider (JN2)	505 King Avenue		Battelle Columbus	Columbus, OH 43201-2693
12	Michael L. Snyder	ISOTRAK	2636 S. Clearbrook Drive	Amersham Corporation	Arlington Heights, IL 60005
1	David E. Soltris	AT Kearney Inc.	225 Reinekers Lane		Alexandria, VA 22314
1	G. Edward Soméus	Product Control Ltd.	H 1046 Budapest	Branch Office 7	Mikszath 81, Hungary
1	Joe Soroka	Roy F. Weston		Suite 407, 1090 King George	Edison, NJ 08837
1	Theresa M. Spalletta	Versar Laboratories		6850 Versar Center	Springfield, VA 22151
1	Ron Spencer	Westinghouse SRC	704-28-5	Def. Waste Processing	Aiken, SC 29811
1	William Spencer	Savannah River	P. O. Box 616		Aiken, SC 29808
1	Wayne J. Spetnagel	Martin Marietta PORTS	P. O. Box 628, MS-2212		Piketon, OH 45661
1	Pat Spink	Windochem Software		383 Falcato Drive	Milpitas, CA 95035
1	William Stagg	B&W Nuclear Env. Services		P. O.Box 11165	Lynchburg, VA 24506-1165
1	Sonia Stahr	Martin Marietta Energy	P. O. Box 1410		Paducah, KY 42001
1	Jerry L. Stakebake	EG&G Rocky Flats		P. O. Box 464	Golden, CO 80402-0464
1	Robert F. Stalzer, Ph.D.	Lab/Man Consulting Group	P. O. Box 257	A2LA	Montchanin, DE 19710
1	Daniel L. Standiford	Westinghouse Electric	101 W. Greene Street	P. O. Box 2078	Carlsbad, NM 88221
1	Eric Steindl	Restek Corp		110 Banner Circle	Bellefonte, PA 16823
1	R. Stephens	California EPA		2151 Berkeley Way	Berkeley, CA
1	Gloria Stevens	Oakridge		P. O. Box 2567	Grand Junction, CO 81503
1	Joe Stewart	Oak Ridge National	P. O. 2008	Bethel Valley Rd.	Oak Ridge, TN 37831-6384
1	Alma Stiffin	NBL		9800 S. Cass Avenue	Argonne, IL 60439
1	Russ Stimmel	Radiochemistry Supervisor	975 Kelly Johnson Drive	Lockheed Corporation	Las Vegas, NV 89119
1	Bozika Stojanovic	IAYS	11000 Beograd	Institut Za Arhitekturu	Bul revolucije 73, Yugoslavia
1	Jim Stokley	Oak Ridge National	P. O. Box 2008	MS 6128	Oak Ridge, TN 37831-6128
1	Mike Story	355 River Oaks Parkway			San Jose, CA 95134
1	Mr. Page Stoutland	Rocky Flats Plant	Building T130A	P. O. Box 4013, Building	Golden, CO 80401
1	Daryl Strandberg	TMI Analytical Services		2600 Three Leaves Drive	Mt. Pleasant, MI 48858
1	Larry Strattan	USEPA/NEIC	P. O. Box 25227	Bldg. 53, Denver Federal	Denver, CO 80225
1	Mr. Paul Strickler	Environmental Express		443 Long Point Road	Mt. Pleasant, SC 29464
1	Joyce Stubblefield	U S DOE Super collider		2550 Beckleymeade MS	Dallas, TX 75237
1	Rita Stubblefield	Environmental Restoration		P. O. Box A	Aiken, SC 29802
1	Kelly Stuhr	Radiation Safety Engineering		3245 N. Washington Street	Chandler, AZ 85225-1121
1	Brian D. Sujata	Rockwell International	P. O. Box 7922	6633 Canoga Avenue	Canoga Park, CA
1	Bud Summers	AccuLabs Research		4663 Table Mountain Drive	Golden, CO 80403-1650
1	Casper Sun	Brookhaven National		Building 703-M	Upton, NY 11961
1	Chris Sutton	FERMCO	P. O. Box 398704	MS-35	Cincinnati, OH 45239-8704
1	Dr. Chris Sutton	Halliburton NUS		8330 Westglen Drive	Houston, TX 77063-6392
1	M. J. Swain	Westinghouse SRC	Building 704S	P. O. Box 616	Aiken, SC 29802
1	Dan L. Swannack	EDS		2012 South 314th Street Suite	Federal Way, WA 98003
1	R. Paul Swift	ICF Kaiser Engineers		7411 Beach Drive E	Port Orchard, WA 98366

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Leonard S. Sygitowicz	Reynolds Electrical &	P. O. Box 98521		Las Vegas, NV 89193-8521
1	Reld Tait	DOW Chemical Co. USA		Building 1261	Midland, MI 48667
1	Ms. Dorian A. Takach	Lockheed - ESAT		Four Courter Place	Fairfield, NJ 07004
1	Carol Talbert	Roy F. Weston Inc.		208 Welsh Pool Road	Lionville, PA 19341-1333
1	Jonathan L. Talbott, Ph.D.	Halliburton NUS Corporation		5350 Campbells Run Road	Pittsburgh, PA 15205
1	Dr. John E. Taphom III	Martin Marietta Energy	P. O. Box 628, MS-2147		Piketon, OH 45661
1	Gordon Tate	26 Punchbowl Drive			Haifax NS, Canada B3P
1	Bill Taylor	Graseby NUTECH-RTL		4022 Stirrup Creek Drive,	Durham, NC 27701-9000
1	James R. Taylor	U. S. Dept. of Energy	EM-55	Office of Technology Dev.	Washington, DC 20585
1	Karen Taylor	Lockheed		135 Rairtan Center Parkway	Edison, NJ 08818
1	Roy Taylor	Whiteshell Nuclear		Analytical Science	Pinawa, Manitoba, Canada
1	Norma Teasley	Martin Marietta Energy	MS 6043	P. O. Box 2008, Bldg 2026	Oak Ridge, TN 37831-6043
1	Bill Templeton	TMA/EBERLINE		601 Scarboro Road	Oak Ridge, TN 37830
1	Rob Terry	Radiation Control Div.	P. O. Box 17123	Dept. of Health	Denver, CO 80217
1	Prof. Dr. Konstantin Terytze	Umweltbundesamt		Mauerstraße 51	10117 Berlin, Germany
1	Ken Thames	US DOE E & L P D	P O Box A		Aiken, SC 29802
1	Dr. Myint Thein	ORNL, P. O. Box 2008		Bldg 4500, MS 6105	Oak Ridge, TN 37831-6105
1	Dianne S. Therry	Roy F. Weston, Inc.		208 Welsh Pool Road	Lionville, PA 19341-1313
1	Ron Thiel	EG&G Rocky Flats	P.O. Box 464	Building 881	Golden, CO 80402-0464
1	Tom Thomas	Lockheed Idaho		P. O. Box 1625	Idaho Falls, ID 83415-3423
1	Shelton J. Thompson	Nuclear Fuel Services		205 Banner Hill Rd	Erwin, TN 37650
1	Lawrence Ticknor	A-1, MS F600	LANL		Los Alamos, NM 87545
1	Norma Tidwell	Environmental Chem.	1571 Perry Street, P. O. Box	Bureau of Public Health Lab.	Columbus, OH 43213
1	Andrew R. Tintle	Laboratory Complex, Suite		2600 Blair Stone Road	Tallahassee, FL 32399-2400
1	Dragana Todorovic	Institute of Nuclear Sciences	P. O. Box 522	11001 Belgrade	Yugoslavia,
1	Yves Tondevr	Triangle Labs. Inc.		6320 Quadrangle Drive	Chapel Hill, NC 27514
1	Thomas C. Tonkins	Geotechnical Instruments	Leamington Spa	Sovereign House Queens	Warwickshire, CV31 3JR
1	Tony Toste	S.W. Missouri State			Springfield, MO 65804-0089
24	Linda Treadwell	Oak Ridge National	Building 1060 MSIN 6480	Commerce Court	Oak Ridge, TN 37830
1	Scott Tucker	Chemical Nuclear Lab.		100 Technology Drive	Anderson, SC 29625-9462
1	Ralph R. Turner	Oak Ridge National	P. O. Box 2008	Bethel Valley Rd.	Oak Ridge, TN 37831-6384
1	Jack Tuschall	Ecotek LSI		3342 International Park	Atlanta, GA 30316
1	Andy Valkenburg	Energy Laboratories		1107 South Broadway	Billings, MT 59102
1	Douglas J. Van Cleef	Analytical Technologies, Inc.		225 Commerce Drive	Fort Collins, CO 80524
1	Willem T. van der Zee	European Patent Office	Patentlaan 2	Directorate 1.2.59 Mechanics	NL - 2288 EE, Rijswijk The
1	S. J. Van Hook	Martin Marietta Energy	P. O. Box 2009	MS-8081	Oak Ridge, TN 37831-8081
1	Pierre Van Iseghem	SCK • CEN		Boeretang 200	B-2400 Mol, Belgium
1	Dr. Diane E. Vance	P. O. Box 2009		Building 9769	Oak Ridge, TN 37831-8081
1	Kenneth N. Vara	B&W Nuclear Env. Services,	P. O. Box 11165	Lynchburg Technology	Lynchburgh, VA 24506-1165
1	Brinley Varchol	Westinghouse Env.		P. O. Box 398704	Cincinnati, OH 45239-8704
1	Theodore Varouxis	Associated Design and		814 N Henry St	Alexandria, VA 22314
1	Luis E. Velazquez	U. S. DOE		P. O. Box 2001	Oak Ridge, TN 37830
1	Dr. Vasili I. Velichkin	Russian Academy of	Staromonetny per. 35	IGEM	Moscow 109017, Russia
1	Elaine Vikara	US EPA		2890 Woodbridge Avenue	Edison, NJ 08837
1	Dr. Harold A. Vincent	US EPA EM SL	P. O. Box 93478		Las Vegas, NV 89193-3478
1	Ollie A. Vita	Martin Marietta Energy	P.O. Box 628	MS 2228	Piketon, OH 45661
1	Dr. O. V. Voitsekhovitch	Ukrainian	Nauka 37		Kiev, Ukraine 252028
1	Prof. Mirjana Vojinovic	Trg Dositeja Obradovi'ca 6		21000 Novi Sad	Yugoslavia,

<u>No of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	Jonathan Wade	E G & G Rocky Flats	P. O. Box 464	Building 881 Waste Projects	Golden, CO 80402
1	Donald K. Wadsworth	M H Chew & Associates, Inc		1424 Concannon Blvd	Livermore, CA 94550
1	Dr. David M. Walker	Manager, Atlanta Operations	192 Covered Bridge Road	EG&G Nuclear Instruments	Smyrna, GA 30082
1	John Wallace	P. O. Box 1620		S-Cubed	San Diego, CA 92038
1	Any Wallo	Air, Water, Radiation	1000 Independence Avenue	U.S. Department of Energy	Washington, DC 20585
1	Brian C. Walsh	Westinghouse - Bettis	P. O. Box 79		West Mifflin, PA 15122
2	Sandy Wander	SAIC		2109 Air Park Road SE	Albuquerque, NM 87106
1	Paul W. Wang	Ames Laboratory		106 Spedding Hall	Ames, IA 50011-3020
1	Yin Wang	McGill University,	21111 Lakeshore Road, Ste.	P. O. Box 142	Montreal, Canada H9X 3V9
1	John A. Warner	MG Industries		2460 Blvd. of the Generals	Valley Forge, PA 19482
1	Stephen W. Warren	U. S. Department of Energy	Environmental Restoration	Office of Northwestern Area	Washington, DC 20585-0002
1	Larry C. Waters	Anal. Chem. Div. ORNL	P. O. Box 2008		Oak Ridge, TN 37831-6120
1	Cliff Watkins	ER & WM Sample Mgt OFC	EG&G Idaho Inc.	P. O. Box 1625	Idaho Falls, ID 83415-3406
1	Laura Watlington	WINCO		P. O. Box 1625, MS 5117	Idaho Falls, ID 83415-5117
1	Randy Waugh	Martin Marietta Utility Svcs.		P. O. Box 628	Piketon, OH 45661
1	Jack N. Weaver	NC State University	P.O. Box 7909		Raleigh, NC 27695
1	Nelson Wechter	Rohm and Haas DVI		5000 Richmond Street	Philadelphia, PA 19137
1	Richard G. Weibe	E G & G WASC, Inc		2550 Beckleymeade Ave	Dallas, TX 75237-3997
1	Ruth F. Weiner, Ph.D.	Environmental Evaluation		7007 Wyoming Boulevard	Albuquerque, NM 87109
1	Larissa Welch	P. O. Box 2003			Oak Ridge, TN 37831-7440
1	Joanne Wendelberger	A-1m MS F600	LANL		Los Alamos, NM 87545
2	Mary F. Wendt	PRC Environmental		1921 D Rohlwing Road	Rolling Meadows, IL 60008
1	Nancy W. Wentworth	U.S.EPA QA Mgmt Staff,	RD-680	401 M Street, S.W.	Washington, DC 20460
1	Dr. D. Westwood	Drinking Water Inspectorate	43 Marsham Street	Dept. of Env. A322 Romney	London, SW1P3PY UK
1	Alicia Whitehall	Harding Associates	707 17th Street	2400 Arco Tower	Denver, CO 80202
1	Elizabeth A. Wiley	Los Alamos Technical		8633 Gage Boulevard	Kennewick, WA 99336
1	Charles W. Wilkerson	LANL CLS-1	P. O. Box 1663	MS G740	Los Alamos, NM 87545
1	Terry Williams	Alabama Dept. of Public	P. O. Box 303107	Radiation Control	Montgomery, AL 36130-3017
1	Donald M. Wilson	EPA, National Institutes of		Building 13, Room 2W64	Bethesda, MD 20892
1	Steve Wilson	U. S. Geological Survey	P. O. Box 25046	MS 973	Denver, CO 80225
1	Michael G. Winslow	Environmental Sci &	P.O. Box 1703		Gainesville, FL 32602-1703
1	Amy Wong	Los Alamos National Lab		MS G740	Los Alamos, NM 87545
1	Carolyn T. Wong	Radiation Lab, San. &		2151 Berkley Way	Berkley, CA 94704
1	Dr. Bruce A. Woods	EPA Region 10		1200 6th Ave ES-095	Seattle, WA 98101
1	Ray Worden	RUSKA Laboratories, Inc.	P.O. Box 630009	3601 Dunvale	Houston, TX 77063
1	Kelly Wright	EG&G, Idaho, Inc	P. O. Box 1625	MS4110	Idaho Falls, ID 83415-4110
1	Kelvin L. Wright	Waste Policy Institute		555 Quince Orchard Road	Gaithersburg, MD
1	Dr. Anthony L. Wright	Martin Marietta Energy		P. O. Box 2009	Oak Ridge, TN 37831-8088
1	Robert K. Wyeth	RECRA Environmental Inc.		10 Hazelwood Drive	Amherst, NY 14228-2298
1	Steve Wyrick	SAIC		555 Quince Orchard Road,	Gaithersburg, MD
2	Tian Xie	Method Development	3342 International Park Drive	EcsTek LSI	Atlanta, GA 30316
1	Nabil Yacoub	California State Haz Mat Lab		2151 Berkley Way	Berkley, CA 94704
1	Judith S. Yaeger	Argonne	CMT/203	9700 South Cass Avenue	Argonne, IL 60439-4843
1	Karrie Yancey	Photovac International Inc		25-b Jeffryn Blvd W	Deer Park, NY 11729
1	Frances Yang	NYS Dept. Env.		270 Michigan Avenue	Buffalo, NY 14203
1	Lowell Yemin	EBASCO Division of	89th Floor	2 World Trade Center	New York, New York 10046
1	Mary C. Yerwolf	EG&G Idaho Inc. /INEL		P. O. Box 1625	Idaho Falls, ID 83421-4107
1	Dr. Shao-Pin Yo	Eureka Lab. Inc		6790 Florin Perkins Road	Sacramento, CA 95828

<u>No. of Copies</u>	<u>Name</u>	<u>ORGANIZATION</u>			
1	John Young	Westinghouse SRC		S R T C Building 773-A	Aiken, SC 29808
1	Robert C. Young	Westinghouse SRC	Building 773-42A	P. O. Box 616	Aiken, SC 29802
1	Jack P. Young, Ph.D.	Martin Marietta Energy		P. O. Box 2008	Oak Ridge, TN 37831-6142
1	Ching Ping Yu	ETC		284 Raritan Center Pkwy.	Edison, NJ 08818-7808
1	Jeffrey Zelikson	Director, Hazardous Waste	75 Hawthorne Street	EPA Region 9	San Francisco, CA 94105
1	Sun Zhenjun	Laiyang Agricultural College	Shandong Province	Laiyang City 265200	China,
1	Olga M. Zhukova	Chief of Bureau	110 Skaryma Avenue	Republican Center of	220645 Minsk, Belarus
1	Paul Zietz	Jacobs Engineering Group		2155 Louisiana NE, Suite	Albuquerque, NM 87110