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RADIOCHEMISTRY METHODS IN DOE METHODS FOR EVALUATING
ENVIRONMENTAL AND WASTE MANAGEMENT SAMPLES

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Radiochemistry Methods in DOE Methods For Evaluating Environmental And Waste Management Samples

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Abstract

Current standard sources of radiochemistry methods are often inappropriate for use in evaluating U. S. Department of Energy environmental and waste management (DOE/EM) samples. Examples of current sources include EPA, ASTM, *Standard Methods for the Examination of Water and Wastewater* and HASL-300. Applicability of these methods is limited to specific matrices (usually water), radiation levels (usually environmental levels), and analytes (limited number). Radiochemistry methods in *DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods)* attempt to fill the applicability gap that exists between standard methods and those needed for DOE/EM activities. The Radiochemistry chapter in *DOE Methods* includes an "analysis and reporting" guidance section as well as radiochemistry methods. A basis for identifying the DOE/EM radiochemistry needs is discussed. Within this needs framework, the applicability of standard methods and targeted new methods is identified. Sources of new methods (consolidated methods from DOE laboratories and submissions from individuals) and the methods review process will be discussed. The processes involved in generating consolidated methods and editing individually submitted methods will be compared.

DOE Methods is a living document and continues to expand by adding various kinds of methods. Radiochemistry methods are highlighted in this paper. *DOE Methods* is intended to be a resource for methods applicable to DOE/EM problems. Although it is intended to support DOE, the guidance and methods are not necessarily exclusive to DOE. The document is available at no cost through the Laboratory Management Division of DOE, Office of Technology Development.

Introduction

The United States Department of Energy (DOE) is responsible for environmental restoration and waste management (EM) at its various sites (1). Samples taken to support EM activities encompass a large variety of matrices, ranging from non-radioactive well water samples, to soil columns contaminated with leaking tank waste, to highly radioactive tank waste (2). Analysis of these samples is often required to be conducted according to practices accepted by various federal, state, and local agencies (3). These agencies often require that analyses be conducted according to standard methods to ensure data comparability and consistency. Available standard methods (4-8), however, do not always meet the various EM project needs. The document, *DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Methods)*, is designed to fill that gap (9).

Radiochemistry Support for DOE/EM Activities

The purpose of *DOE Methods* is three-fold. It is intended to bridge the gap between standard methods and methods needed or applicable to EM activities. It also provides new technology for field use and accelerates regulatory acceptance of these methods (9***others??**). Many of these new technologies result in analytical waste reduction and faster analysis times. Finally, the document eliminates unnecessary methods development costs by making applicable methods accessible to all facilities in a timely manner.

In 1993, DOE/EM sampling and analysis method needs were estimated (10). The radiochemistry needs were defined at that time, but have been updated and are shown in Table 1, Radiochemistry Methods Needs List. The list includes Field and Laboratory analysis categories as well as sub-categories of specific matrices (soil, aqueous, high level radioactivity, and organic). Various screening techniques are identified as well as isotope specific analyses. The identified needs are based largely on experience with EM activities at the Hanford site, waste classification guidelines given in 10CFR61, and input from scientists at other sites. (The letter "X" in Table 1 is used to show a method is needed; specific method identifications are given in place of the "X" where applicable.)

Several sources of standard methods were reviewed for applicability to DOE/EM needs (4-8). These standard methods tend to be limited to the analysis of a few isotopes and water and soil matrices. Drinking water is well represented and soil is less well represented. These methods are also generally designed for low-level rather than high-level radioactive samples.

After a review of currently available methods, several needs stand out. In the sample preparation category, application of microwave digestion for radionuclides and sample preparation for volatile isotopes such as ^{129}I are needed. In almost all categories, methods that produce less mixed hazardous waste are needed.

Guidance

The Radiochemistry section in *DOE Methods* includes a guidance chapter and analytical methods. The guidance chapter discusses very general considerations specific to radiochemical laboratories. It includes a definition section that is used to define specific terms as they relate to radiochemistry analyses. This includes, for example, the definition of decision level count rate and minimum detectable activity. General considerations are also discussed regarding instrument calibration. Data reporting guidelines are also provided.

Concepts from other parts of the *DOE Methods* document are intended to be integrated with the radiochemistry chapter. These include general guidance on quality assurance (QA) and quality control (QC), safety and waste handling, and the sampling and analysis plan. Use of the performance-based approach to application of methods and deviation from standard methods for sample analysis is encouraged (Appendix B of *DOE Methods*).

Methods

The number of radiochemistry methods has grown from 1 to 17 over the past 18 months. The methods are summarized Table 2.

Table 2. Radiochemistry Methods in *DOE Methods* (April 1994)

Method Number	Title	Summary
Field Screening Methods		
RS100	In-Situ 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.
Sample Prep Methods		

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.
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-94 and Niobium-93m 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 recovery of ^{95}Nb .
RP500	Purification of Strontium in Water Before Strontium-89/Strontium-90 Measurement	Strontium is purified by use of an Eichrom Sr-Spec® column. Chemical yield is traced radiochemically or gravimetrically. Several initial volume reduction and follow-on counting options are presented.
RP501	Determination of Total Radioactive Strontium in High-Level Samples using Extraction Chromatography	Strontium is purified by use of an Eichrom Sr-Spec® column. Chemical yield is determined with ^{85}Sr tracer. Counting is performed with gas proportional counters or by LSC. Purification options are presented if high amounts of ^{137}Cs or Pu are expected.
RP510	Determination of Strontium-90 in Dissolved Environmental Samples using Chelex-100	Strontium is purified in an aqueous sample by carbonate precipitation followed by an iron-hydroxide scavenge. After ^{90}Y in-growth, the Y fraction is purified using a Chelex-100 column. Yttrium is eluted and mounted as the oxalate for subsequent gas-flow proportional counting. Yield is determined by ^{85}Sr and stable Y.
RP520	Determination of Strontium-90 in Soil, Water, and Filter Samples	Complete sample dissolution is accomplished by fusion. Strontium is precipitated as the sulfate. After suitable ^{90}Y in-growth, Y is purified by a series of hydroxide and oxalate precipitations. Yttrium oxalate is counted on a gas-flow proportional counter. Yield is determined by ^{85}Sr and stable Y.
RP530	Determination of Selenium-79 in Aqueous Samples	Selenium is isolated using ion exchange and precipitation techniques. The activity of ^{79}Se is determined by liquid scintillation counting relative to a ^{14}C calibration. Yield is determined by the chemical recovery of stable Se.

RP550	Technetium-99 Analysis using Extraction Chromatography	Pertechnetate is purified on a TEVA•Spec® column. The resin may be mixed with LSC cocktail and counted by LSC or the Tc may be eluted and measured by ICP/MS.
RP580	Water Distillation from Soil and Aqueous Matrices using a Lachat Micro-Dist™ System for Tritium Determination	Water from soil and aqueous matrices is distilled using a Lachat 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. Samples are added directly to LSC cocktail and counted.
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.
Instrumentation Methods		
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 principles of liquid scintillation counters are discussed, including steps to construct a quench curve (efficiency calibration)
Surface Analysis		
RA010	Method for Utilization of Alpha Track Detectors 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 Electret Ionization Chambers 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 a measure of alpha activity using an appropriate calibration factor.

Some of the radiochemistry methods unique to *DOE Methods* that apply to DOE/EM activities include borehole logging (RS100), activated Ni determination (RP300), ^{79}Se determination (RP530), and gross alpha emission from indoor surfaces (RA010 and RA020). Other methods utilize new technologies that result in faster turn-around time and much smaller waste streams when compared to standard methods. These include ^{90}Sr determination (RP500 and RP501) and ^{99}Tc analysis (RP550). In other cases, the methods represent alternatives in analytical approaches to analysis problems. All methods included in *DOE Methods* have been used on real EM samples.

Method Incorporation Process

Criteria for including methods in *DOE Methods* are three-fold: 1) the method must meet EM needs; 2) the method is not essentially a standard method; and 3) the method is formatted to the document specifications. Methods are received from several sources. Methods developed from Laboratory Management Division (LMD) funding constitute a significant source. Methods from individual contributors are sought based upon applicability of their work. Another source is method consolidation from procedures in the *DOE Procedures Database*.

The method-consolidation process is intended to produce a method that encompasses all nuances of similar analytical techniques used at the various DOE sites. The *DOE Procedures Database* is scanned for appropriate procedures. The "appropriateness" of a procedure may be determined by analyte and/or matrix and/or other factors. The procedures are then faxed or copied to the consolidator. The procedures are read, and notes are taken regarding the basic chemistry involved, applicable matrices, detection limits, bias, waste generated, special equipment/facility needs, time involved for the chemical analysis, comparability to standard methods, and similarity to other procedures as they are read. Based on the described parameters, specific procedures are categorized. Similar procedures that meet the criteria for *DOE Methods* are then consolidated. Consolidation generally begins by selecting one well-written procedure. Options are added to that procedure as extraction products of the other similar procedures. The consolidated method is then sent to the original procedure authors for concurrence and/or editorial comments. Quality control data are also petitioned if the chemistry is not significantly altered. If the method is significantly altered and/or contributing laboratories are unable to submit their QC data as support for the method, then the method is sent to National Air and Radiation Environmental Laboratory (NAREL) for validation studies.

The method consolidation process is ongoing. Only currently available procedures in the *DOE Procedures Database* are accessible to the consolidator. Key lab managers are encouraged to provide new methods and method updates as they become available to the *DOE Procedures Database*. The published methods in *DOE Methods* can be expanded to include new options and new method-performance data. Therefore, the use and applicability of existing methods can be expanded.

After consolidation is complete, the method incorporation and review process is virtually identical to that of the individually contributed methods. The first stage is to produce a *draft* method for incorporation in *DOE Methods*. The method is reformatted as appropriate to meet document requirements. It then undergoes editing by the technical and document editors. A proof copy is sent to the original author(s) for concurrence. Method performance data and a peer review for a *draft* method are not required.

For a method to shed its *draft* status, several steps must be completed. The method is submitted for external peer review. The method review team is composed of volunteers representing a wide

variety of disciplines within radiochemistry. Reviewers are from sites including (but not limited to) Los Alamos National Laboratory, Oak Ridge National Laboratory, Idaho National Engineering Laboratory, Westinghouse Savannah River Plant, Westinghouse Hanford, IT Corporation, and Barringer Laboratory. Reviewers have approximately 3 weeks to review each method. Received reviewer comments are then returned to the author for resolution. Each comment must be resolved to the satisfaction of the author and technical editor. Finally, the method must have incorporated a complete method-performance section. This entails an evaluation of precision, bias, and limit of detection for at least one applicable matrix. Once these criteria are satisfied, the method will be distributed as *verified*.

Credit is given to authors for methods published in *DOE Methods*. Method author(s) and the sponsoring laboratory are credited on each method if it is submitted as an individual contribution. Consolidated methods are credited using references to the standard operating procedures. The method consolidator is identified as well as all contributing procedures, authors of procedures, and originating facility.

Future Growth of Radiochemistry Methods in *DOE Methods*

The radiochemistry section of *DOE Methods* continues to grow with emphasis on meeting the needs identified in Table 1. Input to the guidance chapter and individual methods (draft and verified) is encouraged. Users are also encouraged to provide pertinent information, such as additional interferences and/or limitations as well as expanded matrix applicability and performance data. Comments and information will be forwarded to the chapter editor for resolution and incorporation.

Several new methods are likely to be added to the October 1994 issue. Four of these are

- RP280 Lead-210 in Water Using Extraction Chromatography
- RP800 Sequential Separation of Am and Pu By Extraction Chromatography
- RS110 Actinide Screen
- RS551 Technetium-99 Analysis Using Filter Membrane Extraction

Additional methods applicable to the intent of *DOE Methods* may be submitted at any time for potential inclusion in the document. *DOE Methods* is becoming a standard method reference for radiochemistry. With the addition of more radiochemistry methods, its applicability and usefulness to DOE/EM activities is expanding.

Conclusion

DOE Methods is a useful source for radiochemistry methods. It is intended to supplement other standard radiochemistry methods. It is rapidly expanding and is responsive to users' comments/input. Regulatory acceptance is being sought. Our goal is to make *DOE Methods* help meet the needs of DOE/EM programs.

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