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Improved Radioanalytical Methods

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Abstract

Methods for the chemical characterization of the environment are being developed under a multitask project for the Analytical Services Division (EM-263) within the U.S. Department of Energy (DOE) Office of Environmental Management. This project focuses on improvement of radioanalytical methods with an emphasis on faster and cheaper routine methods. We have developed improved methods, for separation of environmental levels of technetium-99 and strontium-89/90, radium, and actinides from soil and water; and for separation of actinides from soil and water matrix interferences. Among the novel separation techniques being used are element- and class-specific resins and membranes. (The 3M Corporation is commercializing Empore™ membranes under a cooperative research and development agreement [CRADA] initiated under this project). We have also developed methods for simultaneous detection of multiple isotopes using inductively coupled plasma-mass spectrometry (ICP-MS). The ICP-MS method requires less rigorous chemical separations than traditional radiochemical analyses because of its mass-selective mode of detection. Actinides and their progeny have been isolated and concentrated from a variety of natural water matrices by using automated batch separation incorporating selective resins prior to ICP-MS analyses. In addition, improvements in detection limits, sample volume, and time of analysis were obtained by using other sample introduction techniques, such as ultrasonic nebulization and electrothermal vaporization. Integration and automation of the separation methods with the ICP-MS methodology by using flow injection analysis is underway, with an objective of automating methods to achieve more reproducible results, reduce labor costs, cut analysis time, and minimize secondary waste generation through miniaturization of the process. The final product of all activities will be methods that are available (published in the literature and in DOE's compendium of analytical methods) and acceptable for use in regulatory situations. Concerted efforts are being made to facilitate implementation of the methods at DOE sites to realize the improvements offered. The technical results of the individual tasks and the results of the integration efforts are presented.

Key Words: Inductively coupled plasma-mass spectrometry, radioanalytical, membrane technology, actinide separations

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Introduction

Over the past decade, the U.S. Department of Energy (DOE) has come under intense public scrutiny and pressure to comply with current environmental regulations and to rectify environmental contamination created by past operations. We face a daunting challenge to clean up and protect our environment; however, before launching any cleanup, one must characterize the type, concentration, and extent of the contamination. During this cleanup process, one must monitor the progress; and after cleanup, one must often monitor the site to ensure that the cleanup was successful. Chemical characterization and monitoring techniques are essential in the execution of these efforts. Research-and-development efforts to improve capabilities can translate into **major** savings and improvement in environmental cleanup by reducing the unit cost of measurements (e.g., fewer steps in an analysis), reducing the time required to provide the information to the user (e.g., field analysis), or improving the quality of information (e.g., chemical speciation). Radiochemical analysis is of particular concern to the DOE, which already expends over \$300 million annually on this activity; and these costs are forecast to increase. Unlike organic and inorganic analytes, which are widely found as contaminants, comparatively little effort has been expended on improvements in radiochemical analyses.

Desirable characteristics of any new methods for characterization of the DOE radiochemical contamination include the following:

- Faster, to reduce turnaround times
- Cheaper, to reduce the burden on taxpayers
- Better performance, to achieve desired data quality objectives
- Minimized generation of secondary mixed waste, through reduction of scale and elimination of steps
- Movement toward real-time analysis
- Speeding of site characterization

We have developed improved methods for separation of environmental levels of technetium-99,¹ radium, and actinides from soil and water; separation of actinides from soil and water matrix interferences; and isolation of strontium. We are also developing methods for simultaneous detection of multiple isotopes (including nonradionuclides) by using a new instrumental technique, inductively coupled plasma-mass spectrometry (ICP-MS). These accomplishments are discussed in the following sections.

Radiochemical Analyses Using Empore™ Technology

Numerous techniques, such as coprecipitation, ion exchange, solvent extraction, and extraction chromatography, have been described for the determination of radionuclides in environmental samples. Generally, these classical techniques are hazardous, costly, and lengthy. Moreover, these methods tend to generate huge quantities of secondary waste.

Empore™ technology has proven to be highly effective for sample preparation in the analysis of organic compounds, wastewaters, and other aqueous samples. In collaboration with the 3M Corporation (St. Paul, Minnesota), we are expanding this technology to the determination of selected radionuclides. We have developed analytical methods for ^{99}Tc and $^{89/90}\text{Sr}$ that are based on Empore™ solid-phase extraction disks and are applicable to the analysis of aqueous samples (i. e., surface water, groundwater, and drinking water).

Strontium or technetium is easily isolated by pulling a sample aliquot through an appropriate Empore™ Rad Disk with vacuum. The disk is subsequently assayed for beta activity. Radiometric interferences are minimal. The method is efficient, safe, reliable, and potentially field-deployable. Sample preparation and counting source preparation steps may be condensed into a single step, thereby reducing labor costs and eliminating many potential sources of laboratory error. Moreover, many of the hazardous chemicals associated with traditional procedures are eliminated. Samples are easily batched, and a 1-L sample may be prepared with as little as 20 min of effort; a significant improvement over traditional procedures, as illustrated in Table 1. Results from the analyses of performance evaluation samples and laboratory-spiked samples exhibit good accuracy and precision with no indication of bias, as shown in Table 2.

Rapid Determination of Radium Isotopes by Alpha-Spectrometry

Because radium and its daughters are radioactive and occur naturally in environmental matrices like drinking water, the determination of long-lived alpha emitters like ^{226}Ra ($t_{1/2} = 1,600$ yr) is very important from the standpoint of geochemical studies and human health. The most frequently used procedure for determining radium is the radon emanation procedure (HASL-300, Ra-03). This technique involves collection and measurement of ^{222}Rn , a daughter of ^{226}Ra . Large sample volumes, a multiweek waiting period for the ingrowth of the radon, and the absence of internal quality control detract from the utility of this method. Other methods in use involve coprecipitation with barium sulfate, followed by counting with a gamma-ray spectrometer; application of thermal ionization mass spectrometry; and electrodeposition, followed by alpha-spectroscopy. The electrodeposition methods are direct, highly sensitive, and highly specific in comparison with other established procedures. In addition, the electrodeposition techniques decrease the sample size and reduce the turnaround time of the analysis to approximately 24 hr, including counting time.

Table 1. Comparison of Methods for Technetium-99 Analysis

Method Name	Single Sample Time (hr)	Average Sample Time (hr)	Labor Time (hr per sample)	Secondary Waste
⁹⁹ Tc assay ^a	3	0.75	0.20	20 mL, mixed
HASL-300 ^b	24	1.4	0.25	500 mL, mixed
Holm method ^c	216	26.4	3	97 mL, mixed
This method	2.7	0.50	0.20	Membranes

^a R. Williams, Martin Marietta Utility Services, Inc., Paducah, KY, personal communication.

^b *Environmental Measurements Laboratory Procedures Manual, HASL-300, 27th ed., Vol. 1; Technetium-99 in Water and Vegetation, Tc-01; revised edition, 1992.*

^c E. Holm, "Determination of Tc-99 in Environmental Samples," *Nuclear Instruments: Methods in Physics Research, 223, 204-207, 1984.*

Table 2. Measurements by Empore™ Rad Disks

Natural Samples				
Sample	Volume (mL)	Activity (pCi/L) (Measured)	Activity (pCi/L) (Spiked)	Accuracy (%)
Well water ^a + ⁸⁹ Sr	400	376 ± 7	387 ± 7	97
Tap water ^a + ⁸⁹ Sr	1,000	396 ± 8	387 ± 7	102
Mississippi Riv ^b + ⁹⁰ Sr	500	9.9 ± 0.4	10.7 ± 0.5	93
Well water ^a + ⁹⁹ Tc	8000	336 ± 16	347 ± 12	97
Deionized water ^a + ⁹⁹ Tc	1000	532 ± 31	550 ± 31	97
Mono Lake water ^c + ⁹⁹ Tc	1000	723 ± 21	723 ± 17	100
Performance Evaluation Samples				
Sample	Volume (mL)	⁹⁰ Sr Activity (pCi/L) (Measured)	⁹⁰ Sr Activity (pCi/L) (Reported)	Accuracy (%)
EMSL/LV water ^d	400	13.5 ± 0.5	15 ± 5	90
	400	11.4 ± 0.8	15 ± 5	76
EML water ^e	25	1,872 ± 32	1,854 ± 88	101
	25	1,924 ± 32	1,854 ± 88	104

^a Argonne National Laboratory, Argonne, Illinois.

^b Mississippi River near Le Claire, Iowa.

^c Mono Lake, California.

^d U.S. Environmental Protection Agency Program administered by Environmental Monitoring on Systems Laboratory - Las Vegas.

^e U.S. Department of Energy Program administered by Environmental Measurements Laboratory, NY, NY.

We have developed an improved method to determine low levels of ^{226}Ra and ^{224}Ra in environmental samples by using alpha-spectrometry.² A cation exchange column is used to separate the analyte from other constituents in the sample (1-50 mL). Optimal separation of the radium isotopes from the matrix is achieved on a cation exchange column when 100 mL of 1.5 M HCl is used for washing and 45 mL of 6 M HCl is used to elute the sample. After preconcentration and separation, the radium is electrodeposited onto a stainless steel disk from a solution of ammonium oxalate and hydrochloric acid. Conditions for electrodeposition are optimal when 400 μg of platinum are added, when ammonium oxalate and hydrochloric acid are used as the electrolyte solution, and when an electrodeposition current of 600 mA is used. Radium-224 is used as a yield tracer, through standard addition, to allow assessment of the quality of an individual analysis. Elapsed time for sample analysis is 24 hr, including both analysis and counting times.

Linear responses are greater than two orders of magnitude. Detection limits of the procedure, taken as three times the standard deviation of several reagent blank analyses, are $(1.8 \pm 0.3) \times 10^{-4}$ 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% when samples of drinking water, well water, and dissolved bones were analyzed. Precision was calculated to be less than 5% for the determination of ^{226}Ra , with a 95% confidence level. Matrix effects were studied for salts of barium, magnesium, iron, and calcium. The method has been submitted to and published by the DOE methods compendium³ as method RP450.

Determination of Actinides in Soil

The goal of this work was to develop improved separation methods to reduce the manpower and waste disposal cost associated with laboratory analysis of the actinides in soil. The analytical scheme was designed to satisfy the requirements of both radiometric and nonradiometric methods. The ICP-MS procedure required only a group of separations of the transuranics,⁴ while alpha-spectrometry required sequential isolation of the actinides. Additionally, the separation scheme was designed for analyzing actinides in soil, whether the soils had been acid leached or totally dissolved through fusion. Newer extraction chromatographic materials like TruSpec and TevaSpec resins and an ion-exchange material (Diphonix) were proved to be highly suitable for the concentration and separation of the actinide elements from soil matrices.⁵ These materials were highly selective and were the basis for efficient analytical procedures that generate significantly less waste than the more traditional procedures.

The extraction chromatographic resins used in the described procedure offered several distinct advantages over most ion-exchange, coprecipitation, and liquid-liquid extraction procedures. Extraction chromatography allowed for the specificity of solvent extraction with the convenience of column chromatography. Both the acid concentration and the volumes used in these systems were significantly lower than those required for traditional methods, thereby resulting in significant waste reductions; however, these lower acid volumes and concentrations made it difficult to maintain large samples in solution. As a result, Diphonix™ resin was used to preconcentrate the actinides from larger soil samples that had been totally dissolved by the sodium hydroxide procedure.⁵ Diphonix offers distinct advantages. Diphonix is highly selective for the actinides in very acidic solutions, even in the presence of complexing agents such as sulfates, phosphates, and fluorides. Additionally, because Diphonix remains effective in the presence of HF, the silica, which occurs in considerable quantities in soil, could be handled more effectively. It was kept in solution, rather than volatilized, as in more traditional methods, an important consideration in waste minimization.

Table 3 compares the concentrations of leachable Th, U, and Pu isotopes that were determined by α -spectrometry and ICP-MS.^{5,6} These results are not compared with certified values because leachate activity is not necessarily equivalent to total activity. Also note that radiometric determinations of ^{234}U were obtained from unspiked leachate aliquots because ^{233}U interferes with the determination of ^{234}U .

Table 3. Comparison of Leachable Actinide Activity in Soils as Determined by ICP-MS and α -Spectrometry

Sample	Mass (g)	^{230}Th (Bq kg ⁻¹) ^a		^{239}Pu (Bq kg ⁻¹) ^a		^{234}U (Bq kg ⁻¹) ^a		^{238}U (Bq kg ⁻¹) ^a	
		ICP-MS	α -Spec.	ICP-MS	α -Spec. ^b	ICP-MS	α -Spec	ICP-MS	α -Spec
SRM 4350B	2.02	18±2	18.1±0.7	< 4 ^d	0.7±0.1	16±1	18±1	13±1	14.2±0.9
	1.9	17±2 ^e	19.6±0.7	< 3	0.7±0.1	16±1	19±1	13±1	14.8±0.8
SRM 4353	2.05	26±2	32±1	6±1	6.8±0.4	20±3	20±1	18±3	20±1
	1.84	30±2 ^e	27±1	7.2±0.4	7.2±0.4	19±1	22±1	18±2	22±1
SRM 4354	1.43	12±1	11.8±0.7	5±1	4.0±0.4	14±1	13.6±0.6	14±2	13.1±0.6
	1.49	11±2 ^e	13.3±0.7	3.9±0.6	3.3±0.4	14±1	14.4±0.8	14±1	14.2±0.8
QAP 37	3.397	10.6±0.7	10.7±0.6	7±1	6.1±0.3	12.1±0.7	13.8±0.4	11.0±0.9	12.9±0.4
QAP 38	2.89	33±5	34.4±0.7	8±2	9.6±0.6	15.8±0.9	17.9±0.8	16±1	17.0±0.8
QAP 39	3.08	9±1	9.3±0.6	2.0±0.4	1.1±0.1	8.5±0.6	9.4±0.5	8.1±0.8	9.4±0.5

^a Mean and standard deviation of the determination, where the standard deviation is derived from propagation of experimental uncertainty (ICP-MS) or counting statistics (α -spectrometry [α -Spec]).

^b Results for $^{239}\text{Pu} + ^{240}\text{Pu}$.

^c Results for $^{233}\text{U} + ^{234}\text{U}$.

^d Limit of detection, defined as 3 times the uncertainty in the blank equivalent concentration.

^e Duplicate results obtained by preparation and analysis of a second leachate aliquot.

Measurement of Long-Lived Actinides by Inductively Coupled Plasma-Mass Spectrometry

Inductively coupled plasma-mass spectrometry is relatively new in the radiochemical field and has been shown to be a very rapid technique for the determination of long-lived radionuclides. Quadruple ICP-MS has been used to determine ^{99}Tc , ^{129}I , and actinide isotopes in environmental samples; however, many investigators have employed ICP-MS solely for the detection of a single radioisotope or radioactive element. This approach fails to take advantage of the capability of the mass spectrometer for rapid sequential analysis.

The determination of long-lived actinides in soil by ICP-MS has been accomplished as described previously.^{5,6} We selected soil samples for this study because of the difficulties inherent in their preparation for analysis. We employed ultrasonic nebulization to enhance the sensitivity of the instrument and used extraction chromatography to eliminate the sample matrix, concentrate the analyte, and separate uranium from the other actinides (to minimize spectral interferences) prior to instrumental analysis. Instrument detection limits for actinides range from 50 mBq/L (^{239}Pu) to 0.002 mBq/L (^{235}U). Alpha-spectrometric determinations of ^{230}Th and ^{239}Pu and the $^{234}\text{U}/^{238}\text{U}$ activity ratio in soil leachates compare well with results from ICP-MS determinations.

Hydrogen adducts of the major naturally occurring actinide isotopes ^{232}Th and ^{238}U interfere with the ICP-MS determination of ^{233}U and ^{239}Pu . When the instrument sensitivity for U and Th was optimized, $^{232}\text{ThH}^+/^{232}\text{Th}^+$ was found to be $(3.9 \pm 0.2) \times 10^{-5}$ with pneumatic nebulization; with ultrasonic nebulization, the ratio was $(2.10 \pm 0.07) \times 10^{-5}$. Under the same conditions, $^{238}\text{UH}^+/^{238}\text{U}^+$ was found to be $(3.2 \pm 0.2) \times 10^{-5}$ and $(1.8 \pm 0.1) \times 10^{-5}$ respectively, for pneumatic and ultrasonic nebulization. Conditions that reduced hydrogen number density or increased plasma temperature (or both) decreased the hydride/atomic ratio.

Additionally, thorium, uranium, and uranium progeny (e.g., ^{226}Ra) were isolated from a variety of natural water matrices by using automated batch separation incorporating selective resins. Minimal treatment of the sample was required in advance of the chemical separation procedure (i.e., samples were acidified; enriched isotopes were added and equilibrated; and, in certain cases, samples were filtered to remove biomass and other particulate matter). Major elemental constituents were removed by the chemical separation. The isolated actinides and their detectable progeny were then determined by using isotope dilution combined with ultrasonic nebulization. Preconcentration factors of approximately 15 were achievable, thereby allowing determination of the isotopes of interest at concentrations below 1 pg/L.

A system based on flow injection analysis (FIA) for the on-line determination of uranium in environmental samples has been characterized and tested.⁷ The simple FIA manifold uses off-the-shelf components to precisely manipulate the carrier, sample, eluent, and washing streams through a column separation module. The separation module preconcentrates the sample by a factor of 30 and removes the potentially interfering environmental matrix. TRUTM resin, a commercially available resin for extraction chromatography, is packed into a glass separation column (5 × 50 mm) in the limited dispersion (D = 2.8) FIA system. Detection is performed by using ICP-MS. The determination of ²³⁸U in groundwater samples was used as an example. The total analysis time for each 5.0-mL aqueous sample is 6 min. The detection limit for ²³⁸U is 0.30 ng/L. By using certified groundwater samples, a precision of 1.1% (n = 4) and an accuracy of ±1.8% for ²³⁸U at 62.6 ng/L were observed. We have also designed another FIA ICP-MS system that minimizes the influence of polyatomic ions (e.g., ²³⁸UH⁺) on the determination of minor actinides (e.g., ²³⁹Pu⁺) by ICP-MS. Compared with the classical radioanalytical batch method using TRUTM, the FIA method uses half as much resin per column, shortens the analysis time by at least 10-fold, and permits extended reuse of the column resin.

Ongoing Activities

Development of techniques and methods must be followed by validation of the methodology. We are conducting a validation of the procedure for the measurement of strontium-89 and strontium-90 in water. The validation analyses are being conducted by six commercial radioanalytical laboratories. Results will yield information on the precision and accuracy of the method, as well as an evaluation of the written draft procedure.

Implementation at DOE Sites

The methods described herein represent substantial improvements over currently employed methods — notably in the overall cost. The significant barriers to implementation are (1) communication of the availability of the methods and (2) inertia. We have communicated (and continue to communicate) our research progress through the peer-reviewed literature (see references section of this paper), through presentations at technical conferences, and through submissions to the DOE methods compendium.³ Overcoming the inertia to maintain the status quo on the part of both laboratories and those who prepare contract work scopes may require management incentives. Costs for setup and for training are a minor consideration.

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