Radiochemical method development

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Abstract

We have developed methods for chemical characterization of the environment under a multi-task project that 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, 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). The new ICP-MS methods have greater sensitivity and efficiency and could replace many radiometric techniques. We are using flow injection analysis to integrate and automate the separation methods with the ICP-MS methodology. The objective of automating methods is 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 US Department of Energy's analytical methods compendium) and acceptable for use in regulatory situations.

1. Introduction

Our nation faces a daunting challenge to clean up and protect our environment; before launching any cleanup, one must characterize the type, concentration, and extent of the contamination. During cleanup 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 and methods are essential in the execution of these efforts. R&D efforts to improve capabilities can translate

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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 information quality (e.g., chemical speciation). Radiochemical analysis is of particular concern to the US Department of Energy, which expends over $300 million annually on this activity. Unlike organic and inorganic analytes, which are widely found as contaminants, comparatively little effort has been expended on improvements of radiochemical analyses. Desirable characteristics of any new methods for characterization of the Department's radiochemical contamination are the following: faster, to reduce turnaround times; cheaper, to reduce the burden on taxpayers; performs better, to achieve desired data quality objectives; minimizes generation of secondary mixed waste, through reduction of scale and elimination of steps; moves toward real-time analysis; speeds site characterization.

We have developed improved methods for separation of environmental levels of technetium-99, 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. Another section discusses the additional research being conducted to improve other aspects of environmental radiochemical analysis.

2. Rapid determination of technetium-99 in soil and water

Technetium-99 ($t_{1/2} = 2.1 \times 10^5$ yr) is a pure beta emitter that is formed as a fission product from ^{235}U and ^{239}Pu. Technetium-99 is as abundantly produced as ^{137}Cs and ^{90}Sr. The main sources of ^{99}Tc released to the environment are the processing of nuclear fuel and the testing of nuclear weapons. Minor contributions come from radiopharmaceuticals and leachates from radioactive waste sites.

In an oxidizing environment, the ^{99}Tc exists predominantly in the heptavalent state as the pertechnetate ion, TcO_4^-, which is soluble in water. Because this solubility tends to make the ion conservative in surface waters and mobile in aquifers, an increasing number of measurements are made each year to monitor technetium in the environment near radioactive waste sites and nuclear processing facilities.

Current analytical methods are time consuming and generate a significant amount of mixed waste. The present standard methods require so much time partly because of their multiple steps, including extraction, precipitation, ion exchange, and electrodeposition. The wastes that are generated often contain corrosives, organics, and radioactive tracers, which can result in disposal problems.

We have developed and validated a rapid, accurate procedure to collect and assay ^{99}Tc in aqueous samples [1]. All materials used in the procedure are commercially available. An optional preliminary concentration step is followed by a measurement step, in which two sequential anion exchange membranes are used to extract the ^{99}Tc selectively. Both membranes are then counted directly in a beta counter, and the total

original concentration is calculated. Recovery of technetium via the membranes is usually on the order of 99%, but certain interferences, especially nitrate, may reduce recovery to as low as 30%. The preferred way to minimize this interference is to avoid the addition of nitrate to collected water samples. The primary advantages of the method are a short turnaround time (2.7 h) per sample and an average analysis time of 30 min (eight aqueous samples over a 240 min period).

2.1. Procedure

2.1.1. Setup step
A prewetted sandwich consisting of an anion membrane disk, a Whatman No. 41 paper disk, and an anion membrane disk (all 47 mm) is fixed into the filter holder, and the apparatus is tested for leaks with deionized water. The paper disk is inserted between the two ion exchange disks to prevent cross-contamination.

2.1.2. Recovery and measurement step
A standard volume (100 ml) of sample water or prepared soil extract is passed through the sequential membrane system at a rate of 2 ml/min. The membranes are dried in a drying oven at 50–60 °C for 15 min and then are counted directly in a beta counting system.

2.1.3. Concentration step (optional)
When necessary, technetium is concentrated from water samples by the following method. For every liter of sample, 100 mg of AG-MP1 anion resin is added to scavenge the pertechnetate ion. The water sample is stirred for 15 min. The resin is then filtered and washed into a small glass column (0.5 × 15 cm). This extraction is repeated twice more, and the resin portions are combined on the column. The technetium is eluted from the column with $KMnO_4$ solution (0.1 M) until the entire resin column is saturated with the characteristic purple of the permanganate ion. A 10% (volume) excess of permanganate is then added. The column is rinsed with deionized water to remove the excess permanganate. To the eluant, solid $NaHSO_3$ is added until the solution is no longer purple. The solution is diluted to 100 ml with deio,ized water and then passed through an ion exchange membrane setup for the technetium assay.

2.1.4. Calculations
The efficiency of the tandem membrane setup was calculated as

$$E = 1 - B/A,$$

where E is the collection efficiency of each membrane, A is the number of beta counts per minute on the first membrane, and B is the number of beta counts per minute on the second membrane. The calculation assumes an equilibrium process and that the membranes are uniform in their functionality. The concentration (A_0) of analyte is calculated as

$$A_0 = A/(E \times \text{volume} \times \text{counter efficiency}),$$

Table 1
Comparison of methods for technetium-99 analysis

Method name	Single sample time (h)	Average sample time (h)	Labor (h per sample)	Secondary waste
[99]Tc assay [2]	3	0.75	0.20	20 ml mixed
HASL-300 [3]	24	1.4	0.25	500 ml mixed
Holm Method [4]	216	26.4	3	97 ml mixed
This Method	2.7	0.50	0.20	Membranes

where A and E are as defined previously, and counter efficiency is measured as counts per minute divided by disintegrations per minute (cpm/dpm).

Table 1 compares our method for analysis of ^{99}Tc with other methods.

3. 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 ($t_{1/2} = 1600$ 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 sulphate 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 to other established procedures. In addition, the electrodeposition techniques decrease the sample size and reduce the turnaround time of the analysis to approximately 24 h, including counting time.

We have developed an improved method for the determination of low levels of [226]Ra and [224]Ra in environmental samples by alpha spectrometry [5]. 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 disc from a solution of ammonium oxalate and hydrochloric acid. Electrodeposition conditions are optimal when 400 µg of platinum is added, ammonium oxalate and hydrochloric acid are used as the electrolyte solution, and 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 sample analysis time is 24 h, 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. Matrix effects were studied for salts of barium, magnesium, iron, and calcium.

Future work will focus on preconcentration processes to analyze samples with very low levels of contaminants (e.g., surface water) and on the determination of ^{228}Ra by using beta spectroscopy with the same electrodeposition disc that was used for the ^{226}Ra determination.

4. Determination of actinides in soil

Techniques like ion exchange, liquid–liquid extraction, and precipitation have been described for the separation and preconcentration of the actinides. However, these traditional methods are time consuming and generate large quantities of mixed wastes. Newer extraction chromatographic materials like TruSpec and TevaSpec resins and an ion exchange material (Diphonix) are highly suitable for the concentration and separation of the actinide elements from soil matrices. These materials are highly selective and are the basis for efficient analytical procedures that generate significantly less waste than the more traditional procedures. The goal of our work [6, 7] was to develop improved separation methodologies to reduce the manpower and waste costs associated with laboratory analyses of actinides in soils. The analytical scheme was designed to satisfy the requirements of both radiometric and non-radiometric detection methods. ICP-MS requires only a group separation of the transuranics, whereas alpha spectrometry requires the sequential isolation of the actinides. In addition, the separation schemes were designed to allow analysis of actinides in soils, either acid leached or totally dissolved through fusion.

4.1. Acid digestion procedure

TruSpec SPS is used to perform group separations of the actinides, and TevaSpec is used to isolate the trivalent actinides from the lanthanide elements. Thorium and plutonium are individually isolated on a prepacked Bio-Rad AG 1-X8 anion column. Soil samples are dried, homogenized, ashed, repetitively leached with 6 M HCl followed by 8 M HNO$_3$, and taken up in 2 M HNO$_3$–0.5 M Al(NO$_3$)$_3$ after evaporative elimination of the HCl. Ascorbic acid is used to reduce trivalent iron, which interferes with the uptake of americium by TruSpec. The trivalent actinides, including americium, and the lanthanides are eluted from a TruSpec column with 4 M HCl. Plutonium and thorium are removed with 0.1 M tetrahydrofuran-2,3,4,5 tetracarboxylic acid (THFTCA). Finally, uranium is eluted with the addition of 0.1 M ammonium bioxalate. The trivalent actinides are separated from the lanthanides by using TevaSpec resin.

The THFTCA fraction containing the plutonium and thorium can be directly analyzed by ICP-MS. However, plutonium and thorium must be separated prior to alpha spectrometry on an equilibrated, prepacked Bio-Rad AG 1-X8 anion exchange column.

The ammonium bioxalate fraction from the TruSpec column containing the uranium and residual thorium is dissolved in 8 M HNO_3 and passed through an anion exchange column that retains the thorium. The column effluent containing purified uranium can be directly analyzed by ICP-MS. However, for alpha spectrometry the solution is treated with aqua regia and then with concentrated HNO_3 prior to electrodeposition.

4.2. Fusion dissolution procedure

Soil samples are dried, homogenized, ashed, fused with flake NaOH, taken up in deionized water, and reduced. The resulting $Fe(OH)_3$, which coprecipitates the actinides, is separated by centrifugation. The $Fe(OH)_3$ is dissolved in HCl, and silica is removed by centrifugation after formation of a colloid with polyethylene glycol. Actinides are separated on a Diphonix (60–100 mesh) column as a group by using 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). The HEDPA solution is decomposed prior to elemental separations with a double-oxidation procedure. Elemental separations are performed as described under section 4.1.

The extraction chromatographic resins used in the described procedures offer several distinct advantages over most ion exchange, coprecipitation, and liquid–liquid extraction procedures. Extraction chromatography allows for specific solvent extraction with the convenience of column chromatography. Both the acid concentrations and volumes used in these systems are significantly lower than those required for traditional methods, thereby significantly reducing waste volumes. However, these lower acid volumes and concentrations make it difficult to maintain large sample sizes, or soils digested with HF, in solution. As a result, Diphonix resin is used to preconcentrate the actinides from larger soil samples that have been totally dissolved by sodium hydroxide fusion.

Results [7] obtained through ICP-MS and alpha spectrometry agree quite well. For analytes present as contaminants ($^{239/240}$Pu, ^{241}Am), the laboratory results for standard reference materials were in good agreement with the accepted values [6]. However, for the acid digestion procedure, the results for matrix constituents (^{238}U, ^{234}U, ^{232}Th) were quite low, because the silicate matrix was not decomposed. The NaOH fusion technique allows for accurate analysis of both matrix constituents and contaminants.

5. 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. Quadrupole 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 single radioisotopes or radioactive elements. This approach fails to take advantage of the mass spectrometer's capability for rapid sequential analysis.

We have accomplished the determination of long-lived actinides in soil by ICP-MS [7, 8]. 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}U/^{238}U activity ratio in soil leachates compare well with results from ICP-MS determinations.

We also studied hydrogen adducts of the major naturally occurring actinide isotopes, ^{232}Th and ^{238}U, by using ICP-MS and found that these adducts interfere with the determinations of ^{233}U and ^{239}Pu. When the instrument sensitivity for U and Th was optimized, ^{232}ThH$^+$/^{232}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}UH$^+$/^{238}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 and/or increased plasma temperature decreased the hydride/atomic ratio.

6. Ongoing activities

To build on the accomplishments discussed above, additional research is being conducted to improve other aspects of environmental radiochemical analysis. We are developing new separations for strontium and cesium, developing new scintillation detectors for alpha and beta emitters, and continuing investigations into applications of ICP-MS to radiochemical analysis. Method integration is key to improvement of efficiency. We are devoting significant effort to the application of flow injection analysis techniques to this problem, with an ultimate objective of a continuous-flow dissolution-separation-measurement system. We believe that this fully integrated radiochemical analysis system is an achievable objective. Initial results indicate that we can achieve significant savings with comparable or even with improved figures of merit when we automate manual methods.

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 routine radioanalytical laboratories. Results will yield information on the precision and accuracy of the method as well as an evaluation of the written draft procedure.

Acknowledgements

References

[1] J.G. King, K.A. Orlandini and M.D. Erickson, The rapid separation and measurement of technetium-99, Radiochim. Acta, submitted.

[2] R. Williams, Martin Marietta Utility Services, Inc., Paducah, KY, personal communication.

[3] Environmental Measurements Laboratory Procedures Manual, HASL-300, 27th edn., Vol. 1; Technetium-99 in Water and Vegetation Tc-01; revised edition, 1992.

[4] E. Holm, Determination of Tc-99 in environmental samples, Nuclear Instruments: Methods in Physics Research, Vol. 223, 1984, pp. 204–207.

[5] J.S. Alvarado, K.A. Orlandini and M.D. Erickson, Rapid determination of radium isotopes by alpha-spectrometry, J. Radioanal. Nucl. Chem., in press.

[6] L.L. Smith, J.S. Yaeger, J.S. Crain, E.P. Horwitz, H. Diamond and R. Chiarizia, Improved methods for determination of actinide elements in soil, J. Radioanal. Nucl. Chem., in press.

[7] J.S. Crain, L.L. Smith, J.S. Yaeger and J.S. Alvarado, Determination of long-lived actinides in soil leachates by ICP-MS, J. Radioanal. Nucl. Chem., in press.

[8] J.S. Crain and J.S. Alvarado, Hydride interferences upon the determination of minor actinide isotopes by inductively coupled plasma-mass spectrometry, J. Anal. Atomic Spectrometry, 9 (1994) 1223–1227.