Improved Analytical Methods for Human and Environmental Monitoring of Americium-241 at Los Alamos Utilizing Extraction Chromatography and Alpha Spectroscopy

Steve Goldstein, Catherine Hensley, Claudine Armenta, and Richard Peters
Inorganic Trace Analysis, Group CST-9, MS K484
Los Alamos National Laboratory
Los Alamos, NM 87545

Introduction

Recently, there has been an increasing demand for simpler, faster, less expensive, and environmentally safer analytical procedures for measurement of radionuclides in environmental and biological samples. Although radioanalytical facilities and funding have remained fixed, sample throughput has increased in analytical laboratories due to a number of factors. There has been a growing emphasis on environmental surveillance to evaluate the effects of current nuclear operations on human health in worker and general populations, while efforts to remediate sites contaminated by former nuclear activities have also increased. Developments in solid-phase extraction chromatography have simplified the separation of radionuclides from complex matrices in preparation for alpha spectroscopy relative to traditional methods (Horwitz et al., 1990; 1991; 1992; 1993) and can potentially improve sample throughput and data quality in environmental radioanalytical laboratories.

Here we present results of methods developed/adapted for separation and analysis of ^{241}Am in air, water, and urine samples with less than 1 gram of inorganic residue utilizing extraction chromatography and alpha spectroscopy. Prior methods required the use of a complex multistage procedure for separation of Am from these matrices (e.g. Knab, 1979, Noyce et al., 1990), whereas the newer simplified methods require only a single 2 mL extraction chromatographic separation utilizing a supported bifunctional organophosphorus extractant (Horwitz et al., 1990; 1993) for isolation of Am/REE from other components of the sample. Analytical characteristics of the new extraction chromatography methods are described, these results are compared with existing techniques, and the limitations and implications of the newer methods for analyses of ^{241}Am are discussed.

Experimental

Water: Basic features of the analytical method for water samples are illustrated in Figure 1. Water samples are collected in the field and acidified with nitric acid to a pH of <2 to prevent adsorption of radionuclides onto the container. Samples are filtered in the laboratory through 0.45 micron filters to remove suspended solids, and a 500 mL aliquot is used for analysis of Am and Pu isotopes. Samples are further acidified with nitric acid, ^{243}Am tracer is added to quantify chemical recovery through the procedure, and samples are evaporated to dryness on a hotplate. The residue is treated successively with concentrated nitric acid and hydrogen peroxide to dissolve organic components, hydrofluoric acid to dissolve silicates, and hydrochloric acid to dissolve iron oxides. If a Pu analysis is required, then the Pu in the sample is then separated using anion exchange separations, and the Am fraction from this column is taken to dryness. The sample

is dissolved in 20 mL 3M nitric acid, [152]Eu tracer is added to monitor separation chemistry, and a saturated sodium nitrite solution is added to reduce Pu to the IV oxidation state. The centrifuged sample is added to a 2 mL TRU-SPEC column, the major components are washed with 3M and 1M nitric acid, Pu is washed with 10M hydrochloric acid, and Am and the REE are collected with 4M hydrochloric acid. Samples are prepared for alpha spectroscopy following standard lanthanide fluoride precipitation methods (Knab, 1980; Hindman, 1986), using 50 µg Nd carrier to precipitate Am onto 25 mm Millipore filters (0.05 µm).

Air Filters: Procedures for dissolution of air filters are illustrated in Figure 1. Cellulose/microsorban air filters are digested in platinum crucibles by dry ashing in a muffle furnace at 500°C for 4 hours. The inorganic residue is then dissolved using nitric and hydrofluoric acids to destroy the silicate matrix, hydrogen peroxide and perchloric acid to further dissolve organic materials, and boric acid to remove insoluble fluorides. [243]Am tracer is then added to the sample to quantify tracer recovery, and samples are equilibrated with nitric acid. Separation procedures for air filters are identical to those described above for water samples.

Urine: Procedures for urine samples are outlined in Figure 1. 24 hour equivalent samples are collected and the volume, specific gravity, and temperature of the sample are measured. An 800 mL sample is aliquoted into a Teflon bottle and [243]Am is added to quantify chemical recovery. The sample and tracer are equilibrated by heating at 120°C for at least 1 hour, and the Am is coprecipitated with calcium phosphate and collected by decanting and centrifugation. The sample is redissolved in 25 mL 2M nitric acid and saturated sodium nitrite solution is added to convert Pu to the IV oxidation state. The filtered sample is added to a 3 mL TRU-SPEC column, the major components are washed with 2M and 1M nitric acid, Pu is washed with 10M hydrochloric acid, and Am and the REE are collected with 4M hydrochloric acid. Samples are prepared for alpha spectroscopy following standard electrodeposition methods (Talvitie, 1971) onto 5/8" stainless steel planchets.

Results and Discussion

Analytical characteristics for each matrix analyzed are summarized in Table 1. Based on experimental samples traced with Pu, U, and Th, separation factors for the procedure are greater than 250-1000 for these elements. Energy resolution decreases with deposited solids (i.e. lanthanides), with full width half maximum increasing from 40-50 KeV for <100 µg solids to 70 KeV for samples with 100-200 µg lanthanides. Process blanks for the procedures are typically < 0.003 pCi/sample. Typical tracer recoveries are 60-80%, with average recoveries during 1994-1995 of 64% for water samples (n=234), 71% for air filter samples (n=136), and 75% for urine samples (n=122). Samples with greater than 0.5 g inorganic residue may have slightly lower tracer recoveries due to somewhat lesser retention by the extraction chromatography resin with increasing Fe (Horwitz et al., 1993). Minimum detectable amounts (Currie, 1968) based on an average tracer recovery of 70%, a counting period of 80,000 seconds, a typical counting efficiency of 20-30%, and a typical background of 2.5 counts are ~0.02 pCi/sample. Accuracy is evaluated from in-house type standard prepared by adding known amounts of [241]Am onto blank matrices, and by analyses of certified reference materials produced by NIST and DOE-EML.

Typical accuracy is 101% for water samples (n=16), 102% for air filter samples (n=14), and 95% for urine samples (n=17) with ^{241}Am ranging from 0.1 to 100 pCi/sample.

Results are compared with prior procedures in Table 2. The prior separation procedure required two columns, a cation exchange column for isolation of the Am and REE, followed by isolation of Am using a methanol/nitric acid anion exchange column (Knab, 1979). Tracer recoveries for the air filter and water samples increased from ~54% for the prior method to ~70% for the new extraction chromatography separations. A measure of the method reliability and robustness is the analytical dispersion or standard deviation in tracer recovery, which has improved by a factor of 2 relative to the prior method. Based on the higher tracer recoveries, detection limits have also improved by ~20%. Accuracy has also improved substantially for water and air filter samples, with biases decreasing from ~10-15% to approximately 1-2%, a change attributable in part to the new procedure. Analytical throughput for the chemical separations has increased by a factor of six, decreasing column chemistry duration from 3 to 0.5 days for the procedures. Depending on the matrix, this has improved the procedural throughput by a factor of ~two from 7 to 4 days. Environmental concerns associated with acid and organic waste generation and disposal have also decreased dramatically, and safety issues with disposal of hazardous mixtures (e.g. methanol/nitric acid) have been avoided.

Although this method has been successfully implemented and designed for matrices with relatively small amounts of inorganic residue (typically < 0.5g), it can be easily scaled to slightly larger silicate samples (e.g. 1-2 g soil samples) by utilizing a larger TRU-SPEC column and reducing the amount of Nd tracer added during coprecipitation. However, application to large (10g) silicate samples will require either a step for preconcentration of actinides, significantly larger TRU-SPEC column sizes, or utilization of other extraction chromatography materials (e.g. REE spec) which have greater affinities for Am and the REE. In addition, a reliable and safe separation method for Am and the REE will be required, since average soil REE concentrations are 100-200 µg/g and energy resolution decreases above 100-200 µg deposited solids. The application of extraction chromatography separation methods and microwave digestion techniques for 10 g samples (Smith et al., 1995) should improve throughput for larger silicate samples to the extent found in this study. However, for larger soil samples (100g) obtained in environmental characterization and restoration studies where detection limit and accuracy requirements are less stringent (1 pCi/g), a faster and more suitable alternative is to directly measure ^{241}Am by gamma spectroscopy.

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Tables:

Table 1. Analytical characteristics of the extraction chromatography method.

	Water	Air Filter	Urine
Separation Factors (Pu, Th, and U)	>250-1000	>250-1000	>250-1000
Full Width Half Maximum (KeV)	40-50	50-70	50-70
Process Blanks (pCi/sample)	<0.003	<0.003	<0.003
Tracer Recovery +/- 1σ (%)	64 +/- 10	71 +/- 11	75 +/- 16
MDA (pCi/sample)	0.026	0.023	0.016
Accuracy +/- 1σ_m (%)	101 +/- 4	102 +/- 2	95 +/- 2

Table 2. Comparison of extraction chromatography and prior separation method for environmental matrices.

	Water Extraction	Water Prior	Air Filter Extraction	Air Filter Prior
Tracer Recovery +/- 1σ (%)	64 +/- 10	57 +/- 20	71 +/- 11	52 +/- 24
MDA (pCi/sample)	0.026	0.029	0.023	0.032
Accuracy +/- 1σ_m (%)	101 +/- 4	89 +/- 2	102 +/- 2	85 +/- 2
Time required (days)	0.5	3	0.5	3
Hazardous waste	no	yes	no	yes

Figure 1.