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RAPID, QUANTITATIVE ANALYSIS OF AMERICIUM,
CURIUM AND PLUTONIUM ISOTOPES IN HANFORD
SAMPLES USING EXTRACTION CHROMATOGRAPHY AND
PRECIPITATION PLATING

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April 1994

Presented at the
3rd International Conference on
Methods & Applications of
Radioanalytical Chemistry
April 10-16, 1994
Kailua-Kona, Hawaii

Prepared for
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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Title

RAPID, QUANTITATIVE ANALYSIS OF AMERICIUM, CURIUM AND PLUTONIUM ISOTOPES IN HANFORD SAMPLES USING EXTRACTION CHROMATOGRAPHY AND PRECIPITATION PLATING, J. H. Kaye, R. S. Strebin, and R. D. Orr*, Chemical Sciences Department, Pacific Northwest Laboratory, Richland, WA 99352

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Abstract

Recently developed methods for the rapid, quantitative analysis of americium (Am), curium (Cm), and plutonium (Pu) isotopes in Hanford soil, sludge, and waste-tank samples are described. After dissolution, dilutions are made as necessary based on alpha-energy analysis of a small aliquot of the original solution. Isotopic tracers are then added and Am-Cm and Pu are separated by extraction chromatography, coprecipitated with neodymium fluoride, and counted. Examples of alpha spectra are given, and results obtained for Hanford sludge samples are presented.

Introduction

The Analytical Chemistry Laboratory at the Pacific Northwest Laboratory is frequently requested to measure Am and Pu isotopes in a wide variety of sample matrices, including soils, sludges, and cores taken from the 149 single-shell and 28 double-shell tanks where defense wastes resulting from the processing of nuclear fuel are being stored. In order to reduce analysis cost and turnaround time, an improved method was desired that would more easily and rapidly separate and concentrate those elements that were present in low concentration from the major chemical constituents in these matrices, while continuing to provide good separation from interferences. It was also desired that the method generate much less mixed waste (waste that is both hazardous and radioactive). A procedure meeting these requirements will be described, which involves use of TRU-Spec™ extraction chromatography material (Eichrom Industries, Inc., Darien, IL) for the separation of Am and Pu. The pioneering work on development of this material was performed by E. Philip Horwitz et al. at Argonne National Laboratory¹. After separation, the fluorides are precipitated, filtered, and counted by alpha spectrometry, using methods similar to those published by Sill² and Hindman^{3,4}.

Experimental

This method is applicable to the analysis of ^{241}Am , ^{244}Cm , ^{238}Pu , and $^{239+240}\text{Pu}$ in a variety of matrices. The actinides were brought into solution by standard methods, which included leaching with hot nitric and/or hydrochloric acids or, in the case of waste-tank samples, fusion with potassium hydroxide and potassium nitrate or sodium peroxide followed by acid dissolution. The levels of alpha activity in Hanford samples vary over many orders of magnitude, and unless prior knowledge of the sample is available, an initial screening analysis is usually necessary to determine what sample size is needed. For the case of Am-Cm and Pu analysis, a coprecipitation with neodymium fluoride, followed by alpha energy analysis, allowed approximate $^{239+240}\text{Pu}$ and $^{238}\text{Pu} + ^{241}\text{Am}$ activities to be determined. Aliquots were then made as necessary, the appropriate amounts of isotopic tracers were added, and the Am-Cm and Pu fractions were separated and measured by alpha-energy analysis.

Screening Method for Estimation of Alpha Activities

In the following procedure, the actinides thorium (Th), neptunium (Np), plutonium, americium and curium, and optionally, uranium (U), were precipitated together as fluorides, for counting by alpha-energy analysis. Alpha emitters that had similar energies, such as ^{238}Pu and ^{241}Am , could not be distinguished.

Equipment Needed - Metrical filters, 25 mm dia, 0.1 μm pore size (Gelman M5PU025); polypropylene separators, 25 mm dia (Gelman 61756); filter holder, 50-mL polysulfone filter funnel (Gelman 4204) with stainless-steel support screen (Gelman 79791).

Reagents Needed - ^{236}Pu , ^{230}Th , or other actinide tracer (optional, for yield estimation); conc HF (48%); conc HCl (12M); 3M HCl; (optional - TiCl_3 , 20%; safranine O, 0.1%, for uranium determination); Nd or Ce carrier, 0.5 mg/mL. All reagents were analytical grade.

Precipitation Plating Procedure

To an aliquot of sample solution in a small beaker, 20 to 100 dpm of ^{236}Pu or other isotopic tracer was added for yield estimation. The solution was diluted to 10 mL with 3M HCl, held at near boiling for 5 min, and transferred to a plastic centrifuge tube. The beaker was rinsed with 3M HCl, and this was added to the centrifuge tube.

If U was to be determined, 1 drop of 0.1% safranine O and 1 to 3 drops of 20% TiCl_3 were added, with stirring. (Note: If the addition of TiCl_3 does not produce a strong, permanent violet color, Fe is probably present. A few more drops of TiCl_3 must be added to produce a permanent violet color, or the reduction and subsequent precipitation of U will be incomplete².)

To the centrifuge tube, 50 μg Nd or Ce carrier was added, with stirring. (Note: This step may not be necessary if the sample contains lanthanides. One gram of typical soil contains about 75 μg of the light lanthanides².) Five milliliters of conc HF were then added, with stirring, and the resulting fluoride precipitate was allowed to stand for at least 30 min. (Note: If TiCl_3 was added, the violet color should change to light green, and any slight initial turbidity due to Ti^{+4} should clear up.²) A polypropylene separator was placed on a stainless-steel support screen mounted on a vacuum filtration flask, then a metricel 25-mm 0.1 μ filter was mounted, followed by a polysulfone filter funnel (optional). The filter was rinsed with 2 mL of ethanol, then with 2 to 4 mL of distilled water. The sample was mixed vigorously for 30 sec on a vortex mixer and filtered. The centrifuge tube was rinsed twice with 4 mL of distilled water, and the rinsings were filtered. The filter containing the fluoride precipitate was then removed, dried under a heat lamp, mounted onto a stainless-steel disk with the aid of a small piece of double-stick ScotchTM tape and counted on a surface-barrier detector.

Separation Procedure for Am-Cm and Pu

Equipment Needed

Eichrom TRU-Spec™ pre-packed column (Eichrom Industries, Inc., Darien, IL).
Other equipment as for screening method above.

Reagents Needed

^{242}Pu or ^{236}Pu and ^{243}Am or ^{244}Cm tracers; Fe carrier, 10 mg/mL as $\text{Fe}(\text{NO}_3)_3$; conc HNO_3 , 16M; 2M HNO_3 ; 2 M HNO_3 saturated with ascorbic acid (make up fresh before use); 0.025M HNO_3 ; 0.1M ammonium bioxalate (1.2 g ammonium oxalate plus 0.9 g oxalic acid dissolved in 100 mL of distilled water); NaNO_2 , solid; conc HF (48%); 9M HCl; 4M HCl; 0.1M hydroquinone in 4M HCl (1.1 g hydroquinone diluted to 100 mL with 4M HCl.)

Separation Procedure

The original solution was aliquoted or concentrated as necessary, based upon the screening results, such that a suitable aliquot contained approximately 20 to 50 dpm of the analytes to be determined. Pu and Am (or Cm) tracers were then added. If the sample contained Fe, such as a soil leachate, an $\text{Fe}(\text{OH})_3$ precipitation was done to concentrate the sample. This precipitate was dissolved in a minimum amount of concentrated HNO_3 and made up to 5-mL volume in 2M HNO_3 . Samples not containing Fe were evaporated to a small volume and brought up with 2M HNO_3 to 5-mL volume. If the sample did not already contain at least 10 mg of Fe, as determined from the sample preparation history, that amount of Fe^{+3} carrier was added.

Saturated ascorbic acid (in 2M HNO_3) was added in 1 to 3 mL increments until further addition no longer caused the solution to momentarily turn blue. This reduces Fe to the +2 valence and prevents it from loading onto the TRU-Spec™ column.

A TRU-Spec™ disposable column was pre-treated with 5 to 10 mL of 2M HNO₃. The sample was added to the column, and the column was washed with 2 to 5 mL of 2M HNO₃. The flow rate was approximately 0.3 mL per min.

Five hundred milligrams of NaNO₂ were dissolved in 5 mL of distilled water. One hundred microliters of the dilute NaNO₂ solution were added to 5 mL of 2M HNO₃, and this was added to the column to adjust the Pu valence from +3 to +4. The column was then washed with 20 mL of 2M HNO₃. All column eluents to this point were discarded.

If it was desired to elute the actinides as a group, 15 mL of 0.025M HNO₃ were added, followed by 15 mL of 0.1M ammonium bioxalate. These eluants were combined, evaporated, wet-ashed, and dissolved in 3M HCl. The fluorides were precipitated and counted as described earlier.

If it was desired to separate the Am-Cm and Pu individually, the Am-Cm fraction was eluted from the column with 2 mL of 9M HCl, followed by 13 mL of 4M HCl. The Pu fraction was then eluted with 15 mL of 4M HCl in 0.1M hydroquinone; the eluants were evaporated to dryness, wet-ashed, and dissolved in 3M HCl.

To the Pu eluant, 50 µg of Nd or Ce carrier was added, and the fluorides were filtered and plated as described earlier. If the eluant solution for the Am-Cm fraction contained less than 50 µg of lanthanides, as determined from the sample type and amount of dilution, then 50 µg of Nd or Ce carrier was added before fluoride precipitation and alpha-energy analysis. If this solution contained 50 µg of lanthanides or more, no extra carrier was added, so that degradation of alpha resolution was minimized.

Alpha Counting Procedure

The metrical filters were counted on passivated implanted planar silicon (PIPS) detectors 450 mm² in active area. The standard source-to-detector distance was approximately 3 mm. Four Canberra Model 7404 Quad Alpha Spectrometers (16 detectors) were interfaced through Canberra Model 589 Analog

Multiplexers, a Canberra Model 8701 analog-to-digital converter (ADC), and a Canberra Model 556 Acquisition Interface Module (AIM). The AIM was linked via Ethernet to a Canberra, VAX-based counting system. Data reduction was performed with use of Canberra alpha-spectroscopy application software.

Results

This procedure has been applied to the analysis of soils, sludge, waste tanks, and Bikini Atoll coral sand. Typically, a number of samples of the same type are analyzed as a batch. The results for a typical sample batch are presented in Table I for $^{239+240}\text{Pu}$ and ^{238}Pu and in Table II for ^{241}Am . The sample set in this instance consisted of two sludge samples run in triplicate, a duplicate matrix spike (leachate from sludge sample spiked with known amounts of ^{239}Pu and ^{241}Am), and two blanks. Examples of alpha spectra for Hanford samples are presented in Figures 1-3.

Discussion

The uncertainty values given in Tables I and II were calculated by spreadsheet methods and include the propagated counting, pipetting, and weighing uncertainties. The accuracy of the method was verified by spiking aliquots of Sludge 1 leachate with known amounts of ^{239}Pu and ^{241}Am . As determined from the average matrix spike calculated results, the Pu and Am values were biased high by 4 % and 1 %, respectively. The activities in the blanks, normalized to the quantity of sample analyzed, were negligible.

To one of the soil samples, a large amount of ^{243}Am tracer was added to determine how much Am ended up in the Pu fraction. About 0.05 % of the Am was found, indicating that at least this much Am was not eluted from the TRU-Spec™ column with HCl.

Figure 1 is an alpha spectrum of Pu for a Hanford soil sample, prepared by precipitation plating. Figure 2 is a spectrum of Pu for another Hanford soil sample, where Pu was electrodeposited. As can be seen by comparing the $^{239+240}\text{Pu}$ peak with that of Figure 1, the resolution obtainable by

electrodeposition and fluoride precipitation methods are fairly comparable. Figure 3 is an Am spectrum for a sludge sample.

Conclusions

The versatility of TRU-Spec™ extraction chromatography material for the separation of Am and Pu combined with fluoride precipitation and alpha-energy analysis is demonstrated to be reliable and cost-effective for analyzing Hanford samples in a variety of matrices. The amount of waste generated has been reduced by approximately a factor of four, and the acid concentrations in the waste are lower. The time required for analyzing a batch of 8 to 12 samples, after sample preparation, has been reduced from 3 days to 1 day.

Acknowledgements

Pacific Northwest Laboratory is operated for the U. S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

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Table I. Plutonium Analysis Results for Sludge Samples

Sample ID	Pu-239+240		Pu-238		Calculated Bias
	uCi/g	+/- 1 sigma*	uCi/g	+/- 1 sigma*	
Sludge 1	2.05	0.055	0.338	0.015	
Sludge 1	2.11	0.056	0.356	0.016	
Sludge 1	2.42	0.082	0.406	0.024	
Sludge 2	5.57	0.018	0.857	0.049	
Sludge 2	5.54	0.185	0.955	0.055	
Sludge 2	5.55	0.188	0.955	0.057	
Blank 1	<0.004		<0.001		
Blank 2	<0.002		<0.003		
Matrix Spike	17.80	0.491	0.448	0.026	+6 %
Matrix Spike	17.30	0.495	0.439	0.027	+2 %

*The error is based on the propagated counting, pipetting, and weighing errors.

Table II. Americium Analysis Results for Sludge Samples

Sample ID	Am-241 uCi/g	+/- 1 sigma*	Calculated Bias
Sludge 1	1.91	0.038	
Sludge 1	1.85	0.046	
Sludge 1	1.82	0.036	
Sludge 2	4.37	0.085	
Sludge 2	3.83	0.076	
Sludge 2	4.30	0.085	
Blank 1	<0.002		
Blank 2	<0.002		
Matrix Spike	14.30	0.271	+4 %
Matrix Spike	13.50	0.255	-2 %

*The error is based on the propagated counting, pipetting, and weighing errors.

Figure Captions

Figure 1. Alpha Spectrum for Plutonium, Hanford Soil 1, by Fluoride Precipitation

Figure 2. Alpha Spectrum for Plutonium, Hanford Soil 2, by Electrodeposition.

Figure 3. Alpha Spectrum for Americium, Hanford Sludge, by Fluoride Precipitation

Figure 1. Alpha Spectrum for Plutonium, Hanford Soil 1
by Fluoride Precipitation

Figure 2. Alpha Spectrum for Plutonium, Hanford Soil 2
by Electrodeposition

Figure 3. Alpha Spectrum for Americium, Hanford Sludge
by Fluoride Precipitation

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