

PURIFICATION AND SEPARATION OF U, PU AND AM IN SOIL SAMPLES BY EXTRACTION CHROMATOGRAPHY FOR ALPHA-SPECTROMETRY ANALYSES

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ABSTRACT

The measurement of radioactivity concentrations in soil is an important tool for the monitoring of the environment. For this purpose, within our laboratory has been implemented a radiochemical procedure for the determination of alpha-emitting isotopes of uranium, plutonium and americium in soil samples. The main steps of the procedure include leaching and dissolution of the sample, separation by extraction chromatography, source preparation and alpha-spectrometry. The analysis of environmental samples for low levels of U, Pu, Am and other actinide elements is often hampered by sample-dependent problems involving the composition and/or mineralogy of specific samples. While relatively small samples (1-2 g of soil) are required to reach the extremely low detection limits occasionally mandated for environmental monitoring, ^{232}U , ^{242}Pu and ^{243}Am were added to the sample for chemical yield monitoring and to correct the results and to improve precision. Actinides are separated and purified by extraction chromatography with UTEVA and TRU resin, co-precipitated with cerium fluoride, filtered, and counted by alpha-particle spectrometry. The separation yields for the analyses were determined following each separation step and the global separation yields were determined for the entire analytical process. Results show a chemical yield of 90% for uranium, 30% for plutonium and 70% for americium. Also, the activity values obtained for these samples were comparable with the reference material values.

Keywords: actinide, extraction chromatography, soil

Introduction

A great number of analytical methods have been developed and applied for the determination of plutonium, uranium and americium isotopes in environmental and nuclear samples using alpha spectrometry.

The method implemented in our laboratory is based on chemical separation of actinides using UTEVA and TRU resin and their quantification by alpha spectrometry. A procedure is presented to provide sequential determination of actinides. The method begins with digestion and dissolution of the sample. Tracers and/or carrier can be added to the sample for the purpose of chemical yield monitoring. U isotopes are separate from Pu and Am by using U-TEVA resin followed by TRU resin to Pu from Am.

After chemical separation actinides are co-precipitated using cerium fluoride, filtered and counted by alpha-particle spectrometry.

Several problems are frequently encountered in the determination of actinide elements in solid environmental samples such as: to find an efficient sample preparation and dissolution procedure that can carry out the chemical separation maintaining high recovery yield of target elements and to obtain final samples in appropriate chemical and physical forms for the analytical instruments to be used.

In order to avoid the interferences caused by the organic matter present in the soil samples in the following steps of the separation process of the actinides is it highly recommended to eliminate it by dry-ashing the samples at various temperatures.

To promote the release of radionuclides from solid environmental matrices such as geological materials the samples are leached and decompose with mineral acids. Plutonium in these samples can be leached with acids such as HNO₃, hydrochloric acid and hydrogen peroxide. Most of the U in the terrestrial environment is contained in silicate minerals, which are often resistant to leaching with mineral acids other than hydrofluoric acid (HF). Determination of U in terrestrial samples, therefore, requires an application of total sample decomposition in most cases.

Experimental

Reagents

All the reagents were analytical grade and the water was deionized. The ²³²U, ²⁴²Pu, ²⁴³Am tracers were prepared in nitric acid with a specific activity of approximately 0.711, 0.543 and 0.762 Bq/g. For the extraction chromatography we used TRU and UTEVA resin (particle size 50-100µm, internal diameter: 6mm, wet volume 5ml), purchased from Eichrom Technologies, Inc.

Quality control

Soils and sediments reference materials were used to test the procedure. We used NIST SRM 4357 (Ocean Sediment). The massic activities of the isotopes are presented in **Table 1**.

Table 1 Massic activities in SRM 4357 (Ocean Sediment)

Nuclide	²³⁸ Pu	²³⁹ Pu+ ²⁴⁰ Pu	²³⁴ U	²³⁵ U	²³⁸ U	²⁴¹ Am
Certified massic activity (mBq·g ⁻¹)	2.32 ±0.06	10.4 ±0.2	-	-	-	-
Uncertified massic activity (mBq·g ⁻¹)	-	-	12	0.6	12	10

Sample preparation

After ashing, grinding and mixing, approximately 1 g of SRM 4357 Ocean sediment was weighted and transferred to a Teflon baker. ²³²U, ²⁴²Am and ²³⁹Pu tracers were added (**Figure 1**).

The sample with the tracers were dissolved in a mixture of concentrated acid nitric, perchloric acid and fluorhidric acid (1:3:1) and heated till dried. 10 ml of concentrated nitric acid was added to the sample, heated and 10 ml hydrogen peroxide was added slowly to avoid effervescent boiling. This procedure was repeated until a clear residue was obtained.

The sample was dissolved in 20 ml 3M HNO₃ and filter on a 45µm membrane filter to avoid UTEVA resin clogging. After dissolving the sample, 4 ml of ferrous sulfamate was added to the filtrate to reduce Pu(IV) to Pu(III). A drop of ammonium thiocyanate indicates the presence of Fe(III). Fe(III) could interfere in the chromatographic procedure so it was reduced to valence state II by adding ascorbic acid till the red colour vanished.

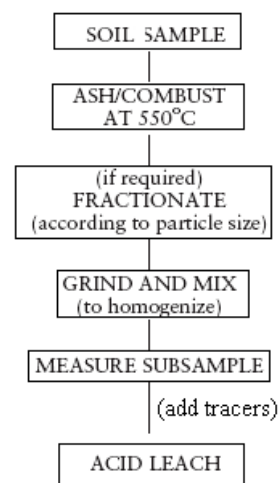


Figure 1

Flow-chart of sample preparation procedure

Separation procedure

TRU resin shows high retention for trivalent and tetravalent species of actinides. On the other hand, these tetravalent and hexavalent species have high value for the coefficient of distribution for UTEVA resin. However, by decreasing pH, the affinity for tetravalent and hexavalent actinides decreases, too.

UTEVA resin. The uranium separation and purification was performed by UTEVA resin. UTEVA resin consists of diamyl-amylphosphonate (DAAP). TRU resin shows high retention for trivalent and tetravalent species of actinides. An amount of 0.7 g of resin, suspended in water was transferred in a plastic column and brought to a 3M nitric acid media by adding app. 10 ml 3M HNO₃. Since UTEVA resin retains only uranium and tetravalent actinides, the effluent is collected for the Pu and Am separation while Uranium is stripped by adding 15 ml of 1M HCl.

TRU resin. TRU resin consist of an extractant system composed of octyphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP) which is then sorbed in an inert polymeric substrate.

TRU column was activated by adding 2M HNO₃ (5 ml). The effluent from UTEVA resin is passes through TRU resin. Both Am and Pu are retained by the resin. The beaker was rinsed by 2M HNO₃ (5 ml) and the rinse was eluted in the column. 5ml 2M HNO₃- 0.1M NaNO₂ is added to the column to improve Pu(IV) to Pu(III) reduction. 0.5M HNO₃ was added to the column and allowed to drain. The collected elute was discarded as waste. 9M HCl (3 ml) was added to the column to convert it to chloride system. After converting to chloride system, Am was eluted into a clean baker by adding 20 ml of 4M HCl, the elute was evaporated to dryness and 0.5ml concentrated HCl and 10ml water was added to have an appropriate media for co-precipitation. The column was rinsed with app. 25 ml of 4M HCl – 0.1M HF and elute was discharged as waste. Pu was eluted by adding 10 ml 0.1M NH₄HC₂O₄.

Figure 2 shows a simplified flow chart of the separation procedure.

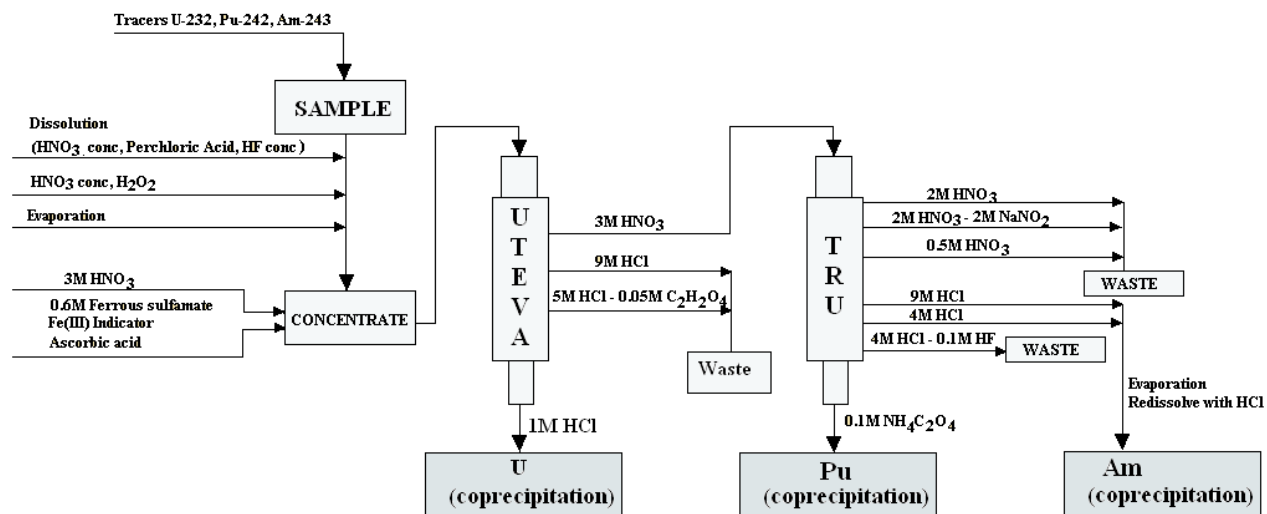


Figure 2 Flow-chart of sequential separation procedure for actinide

Co-precipitation with cerium fluoride

Source preparation for alpha particle counting was performed by co-precipitation with cerium fluoride. Am, U and Pu co-precipitated if 0.1 ml Ce(NO₃)₃ 0.004M and 1 ml HF was added. For Uranium co-precipitation, 0.5 ml 10% TiCl₃ was also needed. After minimum 30 minutes, the solution was filtered on a 0.1 μm; filter was dried on a IR lamp and mount on a stainless steel planchet.

Alpha spectrometry

Measurement of actinides was carried out by using a passivated implanted planar silicon (PIPS) detector with a typical resolution of 24 keV. The efficiency of the detector was determined for source preparation by co-precipitation and found to be 21%.

Results and discussion

To optimize the chemical yield and to minimize any error, which can affect the activity measurement, we were induced to investigate and validate the best chromatographic technique able to separate $^{234,235,238}\text{U}$, ^{241}Am and $^{239+240}\text{Pu}$.

We analyzed two samples of SRM 4357 (Ocean sediment) from NIST. Since actinides are analyzed sequentially by using the whole sample, there is no need to divide the sample into many small subsamples, one for each analysis is required. When analyzing the entire sample eliminates the problem of sample in homogeneity that may exist among aliquots of subsamples.

Figure 2 shows an example of the plutonium spectra for the SRM 4357 ocean sediment samples. The ^{242}Pu tracer recovery was 41.3% and the Full Width Half Maximum (FWHM) was 44.1keV showing a good alpha-peak resolution. **Figure 3** shows an example of the americium spectra. The ^{243}Am tracer recovery was 67.1% and the FWHM was 48.4 keV. Figure 4 shows an example of the uranium spectra. The ^{232}U tracer recovery was 89% and the FWHM was 64.2 keV showing a good alpha-peak resolution.

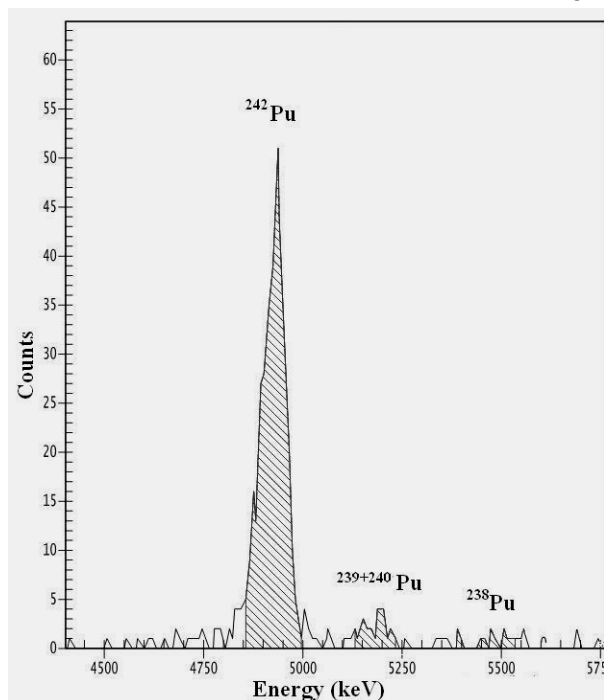


Figure 3 Alpha-spectra showing Pu isotopes in SRM 4357 Ocean Sediment

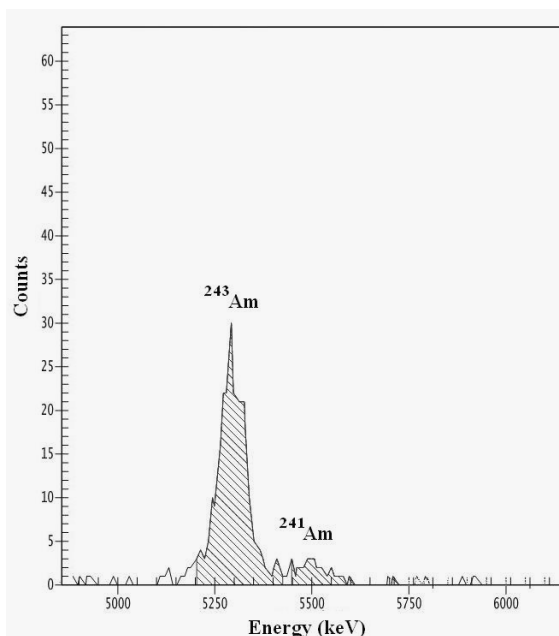


Figure 4 Alpha-spectra showing Am isotopes in SRM 4357 Ocean

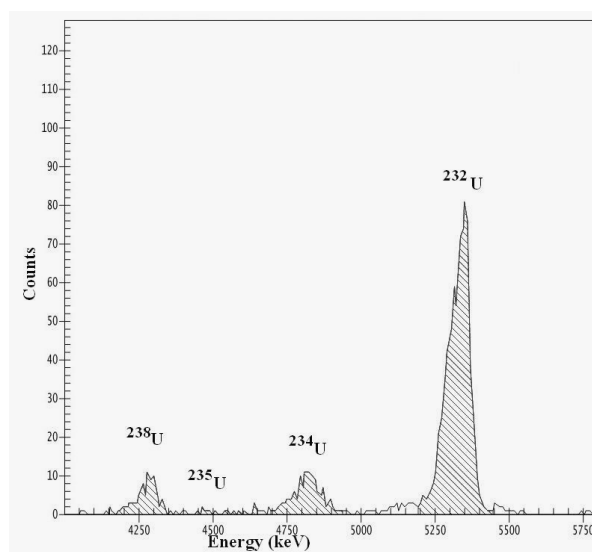


Figure 5 Alpha-spectra showing U isotopes in SRM 4357 Ocean

Recovery yields of U, Pu and Am isotopes are given in **Table 2**. The recovery yield for each tracer was found to be constant.

Table 2 Recovery yields of U, Pu and Am

Tracer	% S01	% S02
²³² U	89±5	85±5
²⁴³ Am	67.1±4	70.7±4
²⁴² Pu	31.2±2	41.3±2

The lower the MDA the better is the quality of the analysis because very low levels of contamination can be detected. This is particularly important for plutonium isotopes, and in general, for highly radiotoxic elements, for which small amounts of radioactivity lead to high internal dose values, from the radiation protection point of view. The minimum detectable activities for U, Pu and Am isotopes are presented in **Table 3**. The MDA obtained is much lower than the measured values.

Table 3 Minimum detectable activity (MDA) for the investigated U, Pu and Am isotopes

Nuclide	²³⁸ Pu	²³⁹⁺²⁴⁰ Pu	²³⁴ U	²³⁵ U	²³⁸ U	²⁴¹ Am
MDA, mBq/g	0.54	0.38	0.19	0.45	0.32	1.05

Table 4 shows that the measured values for Pu isotopes were within the certified reference values. Although values provided by NIST for U and Am isotopes were uncertified they provided results from their laboratory intercomparisons. Therefore, the results for U and Am isotopes were within the values provided by NIST, excepting ²³⁴U. Results were reported in mBq/g.

Table 4 Analysis results SRM 4357(Ocean sediment)

Nuclide	Reference, mBq/g	Measured S01, mBq/g	Measured S02, mBq/g
²³⁸ Pu	2.29±0.05	1.8 ± 1.3	1.1±0.9
²³⁹⁺²⁴⁰ Pu	10.4 ±0.2	8.8 ±1.6	8.8±1.3
²³⁴ U*	12	22.3 ± 1.6	22.1±1.6
²³⁵ U*	0.6	1.1 ± 0.5	1.05±0.5
²³⁸ U*	12	12.9 ±1.2	12.8±1.2
²⁴¹ Am*	10	15 ±2.5	16 ± 1.6

* uncertified massic activities

Conclusion

We studied and adopted in our laboratory a good method to determine U, PU and Am isotopes in environmental samples, with a rather constant chemical yield and resolved peaks. The U, Am and Pu spectrum showed good resolution. However, such resolution is highly dependent on the total elimination of the organic matter and total dissolution of the sample.

Alpha-energy measurements allowed us to find the minimum detectable activity (MDA) and the values are much lower than the activities of the sample Tracers recoveries were constant for each isotopes which indicate the efficiency and selectiveness of the method.

The results obtained in this work lead us to improve the purification and the separation of U, Pu and Am isotopes with the perspective to optimize a routine procedure and offer a more rapid and effective surveillance tool.

Development of rapid and efficient sample preparation method for actinide elements in environmental matrices should be followed by further studies.

References

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