

Rapid analysis of americium and plutonium in environmental samples by alpha-spectrometry

H Salar Amoli* & J Barker

School of Pharmacy and Chemistry, University of Kingston,
Surrey, KT1, 2EE, UK

Email: h.salar-amoli@kingston.ac.uk

Received 23 April 2007; revised 17 August 2007

A new method to assay americium and plutonium in soil samples is reported here. Using the method, it is possible to have a uniform and thin layer of the sample on alpha-spectrometer disc by electroplating. Prior to electrodeposition, the sample is separated by short column chromatography. A current of 900 mA and a plating time of 90 min in the pH range 2–2.5 have been found to be the best conditions for the deposition of americium. Optimum conditions for separation and electrodeposition of plutonium from soil samples have also been obtained. The modified procedures have been successfully applied for the simultaneous determination of Am and Pu.

IPC Code: Int.Cl.⁸ G01N21/00

Americium and plutonium elements of actinides are the most dangerous among nuclides with respect to radioecology and radiation safety. Soil containing these elements produces an increasing radiological hazard for several decades after the original deposition. Plutonium is the most widespread element among transuranic elements represented by four isotopes (²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu and ²⁴¹Pu). The beta-emitting ²⁴¹Pu ($T_{1/2} = 14.3$ years) is also of specific interest. Following the Chernobyl accident in Belarus, it has been shown¹ that the activity of the alpha-emitting isotopes ²⁴¹Am ($T_{1/2} = 432$ years) increases due to the beta-decay of ²⁴¹Pu. It means that the concentration of americium increases in all components of the environment where plutonium is accumulated². So, monitoring of these nuclides in soil samples is quite important. Many methods are reported for measuring the contents of americium and plutonium in soils and sediments^{3–6}.

Sample preparation is required to remove interferences prior to assay. There have been significant advances in the last 5–10 years for radiochemical separations using small chromatography

columns^{7,8}. These improvements in column extraction chromatography have advanced our knowledge in analytical technology and environmental analysis^{9,10}. Though these analyses often involve different sample types and analyte levels, all have certain commonalities¹¹.

The proposed new method recovers actinides from large soil samples in a small volume of nitric acid that can be easily loaded onto small column extraction chromatography for rapid separation and analysis. This method provides total sample dissolution, high recovery of actinides and excellent purification of americium and plutonium for measurement by alpha-particle spectrometry. However, the method has been applied for the electrodeposition of Am and Pu in environmental sample containing trace amounts of nuclides. The present studies allow soil analysis of actinides in various residential soil samples.

Experimental

The alpha-spectrometric system (CABBRA model 7401) with 300 mm² silicon surface detector was used. Electrodeposition device was made, as described in our earlier papers^{12,13}. Standard solution of ²⁴¹Am was the product of North America Scientific Inc. Each working solution of americium was prepared by dilution of stock solution in 1 M HNO₃. A standard solution of ²³⁹Pu was obtained from National Institute of Standards and Technology (USA), and diluted to appropriate concentration using 3 M nitric acid.

Ashed (550°C) soil sample (2 g) was weighed into a PTFE beaker, 20 mL of 16 M HNO₃ were added to it and the mixture allowed to reflux for 3 h on a hotplate. After cooling, the sample was filtered through a PTFE millipore syringe filter and spiked with a known amount of americium and/or plutonium.

The solution was then passed through a chromatography column (Dowex ® 1×8, 80 mm by 7 mm diameter) and washed with 50 mL of 8 M HNO₃. Plutonium is retained in the column while americium passes through without being adsorbed. Then, plutonium was eluted with 50 mL of freshly made 0.1 M NH₄I in 12 M HCl.

Table 1 — Electrodeposition yields of ^{241}Am and ^{239}Pu as a function of current (Deposition time=90 min, Am=2 Bqg $^{-1}$, Pu=0.5 Bqg $^{-1}$)

Current (mA)	200	400	600	800	900	1200
Am(%)	24	39	64	87	89	81
Pu(%)	15	34	55	68	84	78

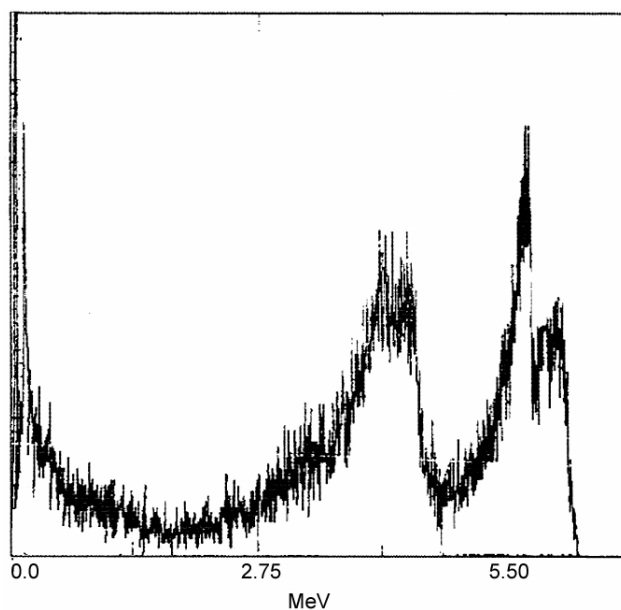


Fig. 1 — α -Spectrum of mixed 0.5 Bq g $^{-1}$ americium (appearing at 5.8 Mev) and 0.25 Bqg $^{-1}$ plutonium (appearing at 4.7 Mev).

To the sample solution (either americium or plutonium), 2 mL of 0.36 M NaHSO $_4$ was added and heated to near dryness. After fuming, the beaker was allowed to cool and washed with 2 mL of distilled water. Six mL of 0.075 M H $_2$ SO $_4$ and a few drops of thymol blue indicator were added. The color solution became salmon-pink by aqueous ammonia solution (1:1, v/v H $_2$ O). Then the solution was transferred to the electroplating cell.

Results and discussion

The chemical separations of low level americium and plutonium in soil samples are difficult and time consuming. A column extraction chromatography was used at a flow rate of 1 mL per min to separate Pu and Am from matrix and interfere elements. The technique is simpler than the earlier ion-exchange technique, with less liquid waste and higher accuracy.

The alpha-energy calibration and measurement of counting efficiency of the instrument were performed by using a standard planchette source, including plutonium and americium.

Table 2 — Electrodeposition yields of ^{241}Am and ^{239}Pu as a function of time. (Am=2 Bqg $^{-1}$, Pu=0.5 Bqg $^{-1}$, current=900 mA)

Time (min)	20	40	60	80	90	120	140
Am (%)	18	43	76	84	90	91	90
Pu (%)	14	40	69	74	86	86	85

Table 3 — Electrodeposition recovery of ^{241}Am and ^{239}Pu in soil samples

Sample code	^{241}Am			^{239}Pu		
	Added (Bqg $^{-1}$)	Found (Bqg $^{-1}$)	Yield (%)	Added (Bqg $^{-1}$)	Found (Bqg $^{-1}$)	Yield (%)
KIN1	2	1.65	86	1	0.81	81
KIN2	2	1.65	82	1	0.80	80
KIN3	2	1.70	85	1	0.78	78
KIN4	2	1.8	90	1	0.84	84

The electrodeposition studies were carried out after adjusting buffer of the solutions (pH 2 – 2.5). Applied current and deposition time were also studied. Table 1 shows the electrodeposition yield of the ^{241}Am and ^{239}Pu as a function of current intensity. The deposition yield increases until 900 mA for both nuclides. At high current intensity (more than 1000 mA), the solution volume decreases by overheating and a change in pH causes a decrease in the electrodeposition efficiency. Also, if applied current is reduced to less than 400 mA, the deposition yield decreases sharply. Table 2 shows americium and plutonium deposition as a function of time at a fixed current. The deposition yield showed a fixed yield beyond 90 min.

Experimental solution samples containing both Am and Pu were added to soil samples and analyzed by this approach to check the separation efficiency by small column chromatography and measurement using electrodeposition prior to alpha-spectroscopy determination. (Fig. 1).

In order to determine chemical recovery of Am and Pu, the filtrate from digestion of soil samples was spiked with a known activity of either americium or plutonium. Table 3 shows an acceptable recovery of both nuclides in soil samples.

Under the optimized conditions, the reproducibility of the method was checked by performing 5 replicate determinations of standard ^{241}Am over a period of 5 consecutive days. The relative standard deviation of the method was 0.9% which is within the acceptable limits^{14,15}.

References

- 1 Mietelski J W, Dorda J & Was B, *Appl Radiat Isot*, 46(11) (1996) 1203.
- 2 Remeikis V, Gvozdaite R, Druteikiene R, Plukis A, Tarasiuk N & Spirkauskaitė N, *Nukleonika*, 50(2) (2005) 61.
- 3 Knatko V A, Asimova V D, Yanush A E, Golikov Yu N & Bondar Ya I, *J Environ Radioact*, 83 (2005) 49.
- 4 Bondar Y I, Zabrodsk V N & Kalinina V, *Distribution of the Transuranium Elements in Radiobiology* (National Academy of Sciences of Belarus, Minsk) 2002, p.14.
- 5 Alloway B J, *Heavy Metals in Soils* (Blacki, London) 1995.
- 6 Becker J S & Dietze H J, *J Anal Atom Spect*, 14 (1999) 1493.
- 7 Hardy E P, Krey P W & Volchok H L, *Nature*, 241 (1973) 444.
- 8 Druteikiene R, *Investigation of Pu Spreading in the Environmental System*, Doctoral Thesis, Institute of Physics, Vilius, Russia 1999.
- 9 Perna L, Betti M, Moreno J M B & Fuoco F, *J Anal At Spectrom*, 16 (2002) 26.
- 10 Goudall P & Lythgoe L, *Analyst*, 124 (1999) 263.
- 11 Suplinka M, *Nukleonika*, 47(2) (2002) 45.
- 12 Salar Amoli H, Barker J & Flowers A, *J Radioanal Nucl Chem*, 268(3) (2006) 497.
- 13 Salar Amoli H & Barker J, *J Radioanal Nucl Chem*, 273(2) (2007) 281.
- 14 Bajo S & Eikenberg J J, *J Radioanal Nucl Chem*, 242(3) (1999) 745.
- 15 Joe K, Lee C H, Song B C, Jeon Y S, Kim W H & Suh J K, *Bull Korean Chem Soc*, 24(59) (2003) 657.