Radiochemical determination of 241Am and Pu(alpha) in environmental materials.

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Radiochemical Determination of ^{241}Am and Pu(α) in Environmental Materials

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Americium-241 and plutonium determinations will become of greater importance over the coming decades as ^{137}Cs and ^{241}Pu decay. The impact of ^{137}Cs on environmental chronology has been great, but its potency is waning as it decays and diffuses. Having ^{241}Am and Pu as unequivocal markers for the 1963 weapon fallout maximum is important for short time scale environmental work, but a fast and reliable procedure is required for their separation. The developed method described here begins by digesting samples using a lithium borate fusion although an aqua regia leachate is also effective in many instances. Isolation of the Am and Pu is then achieved using a combination of extraction chromatography and conventional anion exchange chromatography. The whole procedure has been optimized, validated, and assessed for safety. The straightforwardness of this technique permits the analysis of large numbers of samples and makes ^{241}Am-based techniques for high-resolution sediment accumulation rate studies attractive. In addition, the technique can be employed for the sequential measurement of Pu and Am in environmental surveillance programs, potentially reducing analytical costs and turnround times.

Americium-241 is formed by the β decay of ^{241}Pu, which was released into the environment during atmospheric nuclear weapons' testing. Surface deposition of many radionuclides including ^{241}Pu and ^{137}Cs reached a maximum in 1963. Cs-137 has been widely used for dating sediment layers by comparing the ^{137}Cs profile in a core with known surface deposition history. However, the use of ^{241}Am in place of ^{137}Cs will prove beneficial due to the decay of the latter and because both ^{241}Am and parent ^{241}Pu are highly particle-reactive and are less likely to be affected by postdepositional redistribution. The half-life of ^{241}Am compared with ^{137}Cs (432.7 years and 30 years, respectively[1]), also makes its use viable for a much longer period of time. Such application of ^{241}Am for lake sediment dating has been reported[2] but has not been widely adopted partially as a result of the difficulties in rapidly and reliably isolating low levels of weapons' fallout-derived ^{241}Am from large numbers of sediment core subsamples. Pu isotopes can also be used for dating although their application has not been widely reported. Plutonium-239 + 240 will be present at similar activities to ^{241}Am. In addition, Pu isotopic analysis can be used to help establish the origin of the observed radionuclides and distinguish between weapons' fallout-derived signals and any local sources of contamination.[3]

In Europe, typical activities of ^{241}Am and Pu in estuarine sediments range from 0.5 Bq/kg in recent and 1950s' sediment to 5 Bq/kg at the 1963 deposition peak resulting from weapons' fallout. In the coastal areas of northwestern Europe, additional Am and Pu is derived from BNFL Sellafield and COGEMA La Hague. A number of approaches currently exist to determine ^{241}Am at these activities. γ-Spectrometric measurement of the 59.6-keV γ-photon associated with the decay of ^{241}Am requires little sample preparation, but sample throughput is slow and limits of detection are relatively high. Conventional γ spectrometry can achieve a typical detection limit (L_D) of 1 Bq/kg in soils and sediments (counting 20 g of sample in a well-type HPGe detector). Planar Ge detectors with their lower backgrounds can achieve an L_D of $\sim$0.1 Bq/kg although the method precision is poor owing to the low efficiency of the detectors. Samples also need to be counted typically for 3 days to achieve such activities, and this significantly limits sample throughput. Anticoincidence γ spectrometry is similar but is fairly specialized and expensive.

α-Spectrometric measurement of the 5.44 and 5.49 MeV ^{241}Am α emissions enable lower limits of detection to be achieved. The technique is also appropriate for the determination of ^{238}Pu and $^{239+240}$Pu (although it is not possible to distinguish between ^{239}Pu and ^{240}Pu as the two isotopes emit α particles of similar energies. Mass spectrometric techniques are required to distinguish these two isotopes[3]). α Spectrometry requires an efficient separation of the element of interest from the sample matrix to reduce interferences (particularly from U and Th decay chains) as well as to produce a final source of extremely low mass, minimizing attenuation of the α particles during measurement. Radiochemical separation of ^{241}Am followed by α spectrometry can provide highly precise data for 8−16 samples/week, depending on the number of detectors available (compared with a γ spectrometer that can measure 2 samples/week for concentrations less than 1 Bq/kg). Limits of detection are typically $\sim$0.01 Bq/kg for a 5-g sample size. However, the application of radiochemical analysis to large sample numbers is limited by the time required

(1) Jef-PC version 2.0. Joint evaluated file library. OECD/NEA database, Issy-Les-Moulineaux, France, 1997.

(2) Appleby, P. G.; Richardson, N.; Nolan, P. J. *Hydrobiologia* **1991**, *214*, 35−42.

(3) Taylor, R. N.; Warneke, T.; Milton, J. A.; Croudace, I. W.; Warwick, P. E.; Nesbitt, R. W. *J. Anal. At. Spectrom.* **2001**, *16*, 279−284.

for the separation and purification of ^{241}Am and Pu from environmental matrixes. In one review,[4] it was also noted that a number of separation schemes for Am routinely employed in commercial laboratories were unreliable, resulting in a wide range in chemical recoveries of ^{241}Am.

To permit the routine application of α-spectrometric measurement of ^{241}Am and Pu in sediment accumulation rate studies, it was decided to develop a more robust chemical separation technique. Such a method required a convenient procedure for sample dissolution followed by a simplified chemical separation scheme that would permit the separation of Am and Pu from a wide range of other elements and radionuclides present in the sediment. Croudace et al.[5] reported the use of lithium borate fusions coupled with extraction chromatographic separation for the rapid isolation of Pu and U in environmental samples, and this approach was therefore chosen and developed for the isolation of Am. The application of commercially available extraction chromatographic resins permits the selective preconcentration and separation of many actinides. In particular, TRU resin has been used for the isolation of Pu and Am[6-8] from environmental matrixes although in most reported methods a number of chemical preconcentration stages have been included prior to the column separation stage, increasing the complexity and time scale of the method. However, by coupling the lithium borate fusion with a combined isolation of Pu and Am on the TRU column, and eliminating further preconcentration stages, it is shown that a more streamlined and robust methodology is obtained.

EXPERIMENTAL SECTION

Reagents. All reagents were analytical grade or above. Anion-exchange resin and TRU resin were supplied by Hichrom Industries and used without any further purification. Lithium tetraborate was supplied by Engelhard. Ammonium thiocyanate, ascorbic acid, and PEG-2000 were supplied by Aldrich Chemicals (Gillingham, U.K.). Certified ^{242}Pu and ^{243}Am tracers were supplied by AEA Technology (Harwell, U.K.). Sodium nitrite was supplied by Merck Chemicals (Poole, U.K.). All other reagents were supplied by Fisher Scientific (Loughborough, U.K.).

Thirty-milliliter Pt−Au (5%) dishes were used for the fusions and were supplied by Engelhard. The dishes were made using grain-stabilized Pt−Au alloy. However, fusions can also be effectively and cheaply carried out using graphite crucibles and this procedure is now adopted in this laboratory. α-Spectrometric measurements were performed using an EG&G Octete PC α spectrometer fitted with ion-implanted Si detectors. γ-Spectrometry measurements were performed using Canberra well-type HPGe detectors.

Safety. Ammonium thiocyanate may react violently with strong oxidizing agents and with strong acids. Care must be taken to avoid contact with either of these material types. All operations involving NH_4SCN and its solutions were performed in a fume cupboard. Quenching of the fused melt in water should be performed with care to prevent the hot melt from coming in direct contact with the beaker (see below). Large amounts of heat are dissipated at this stage, and the beaker should be placed on a heat-resistant surface. There are no specific procedures required for preparing and handling 1 M HNO_3−MeOH although care must be taken to ensure that significantly more concentrated HNO_3 is not inadvertently added to the methanol.

Methodology. (1) Separation of Pu and Am from the Sample Matrix. Soils and sediments were oven-dried at 110 °C overnight prior to ignition. Approximately 5 g of ignited material was intimately mixed with 7 g of lithium tetraborate flux, and the mixture was accurately spiked with ∼50 mBq of ^{242}Pu and ^{243}Am tracers. Samples were fused at 1100 °C, and the fused melt was quenched by pouring into 50 mL of water in a borosilicate beaker (care is required to safely perform this procedure). A Pt lid is placed at the bottom of the beaker and the melt poured onto the lid, care being taken to avoid direct contact between the melt and the beaker. This prevents thermal shock and subsequent shattering of the beaker. Although it is advisable to perform this pouring procedure behind a safety screen, the operation has been routinely performed in this laboratory without any breakages. An 11-mL aliquot of 16 M HNO_3 was added to produce a 3 M HNO_3 solution. A 1-mL aliquot of 0.1 M PEG-2000 was also added to enhance the precipitation of colloidal silica that will form from the fusion of silicate materials. The frothy glass was then dissolved by warming the solution overnight at 40 °C with constant stirring. The resulting mixture contained a white precipitate of silica and excess boric acid which were both removed by filtering through a Whatman GFA filter supported on a Whatman No. 540 paper filter. The residue was thoroughly washed with 20 mL of 3 M HNO_3 to ensure efficient removal of any occluded solution.

Five grams of ascorbic acid was added to the 3 M HNO_3 solution to reduce Fe^{3+} to Fe^{2+}, and this quantity was sufficient for typical soils and sediments. The solution was then loaded onto a 5 × 0.5 cm TRU column previously conditioned with 3 M HNO_3. The column was washed with 10 mL of 3 M HNO_3 followed by 10 mL of 2 M HNO_3−0.1 M $NaNO_2$. Am was eluted with 20 mL of 4 M HCl after which Pu (along with other tetravalent actinides) was eluted with 20 mL of 1 M HCl−0.02 M HF. Both eluent fractions were evaporated to dryness prior to further purification.

(2) Purification of Pu. The Pu fraction was dissolved in 2 mL of aqua regia and evaporated to incipient dryness. This was repeated to ensure complete removal of traces of HF. The residue was dissolved in 5 mL of 9 M HCl, and a couple drops of concentrated HNO_3 were added. The solution was transferred to a 2 × 0.7 cm anion-exchange column along with 9 M HCl washings. The column was washed with 20 mL of 9 M HCl followed by 10 mL of 8 M HNO_3 and 10 mL of 3 M HNO_3 to elute traces of U. The column was then washed with 10 mL of 9 M HCl, and the Pu was eluted with 20 mL of 9 M HCl + NH_4I. The Pu eluent was evaporated to ∼10 mL, and 3 mL of concentrated HNO_3 was added to decompose the NH_4I, liberating I_2. This solution was evaporated to dryness, and the residue was reserved for α source preparation.

(3) Purification of Am. The Am fraction eluted from the TRU resin column was evaporated to incipient dryness and the residue was dissolved in 2 mL of 1 M HNO_3−93% methanol. This solution was loaded along with 2 mL of beaker rinsings onto a 2 × 0.7 cm

(4) Warwick, P. E.; Croudace, I. W.; Carpenter, R. *Appl. Radiat. Isot.* **1996**, *47*, 627−642.
(5) Croudace, I. W.; Warwick, P. E.; Taylor, R. N.; Dee, S. J. *Anal. Chim. Acta* **1998**, *371*, 217−225.
(6) Ham, G. J. *Sci. Total Environ.* **1995**, *173/174*, 19−22.
(7) Horwitz, E. P.; Dietz, M. L.; Chiarizia, R.; Diamond, H.; Maxwell, S. L.; Nelson, M. R. *Anal. Chim. Acta* **1995**, *310*, 63−78.
(8) Cadieux, J. R.; Reboul, S. H. *Radioact. Radiochem.* **1996**, *7* (2), 30−34.

anion-exchange column that had been previously conditioned with 1 M HNO_3−93% methanol. The column was washed with 10 mL of 1 M HNO_3−93% methanol followed with 40 mL of 0.1 M HCl− 0.5 M NH_4SCN−80% methanol to remove light rare earth elements. The column was then washed with 10 mL of 1 M HNO_3− 93% methanol, and the Am was eluted with 10 mL of 0.5 M HCl. This solution was evaporated to dryness prior to α source preparation.

(4) α Source Preparation. α Sources were prepared by electrodeposition onto a 27-mm stainless steel disk from an oxalate medium.[9] The sample was dissolved in 1 mL of 1 M HCl and transferred to a plating cell along with 10 mL of 2% ammonium oxalate solution. The actinides were electrodeposited at 12 V/400 mA for 105 min. Two drops of ammonia were added, and the current was disconnected. The disks were rinsed with Milli-Q water and dried on a warm hot plate prior to counting on the α spectrometer.

(5) Determination of Distribution Coefficients, k_D. Distribution coefficients for Am on TRU resin were determined by spiking a known amount of the radionuclide into ∼10 mL of the solution under test. The total mass of the solution was noted, and 0.05 g of TRU resin was added. The mixture was shaken for 2 h to attain equilibrium. The resin was then removed by filtration through a 0.2-μm membrane filter. The amount of the radionuclide per gram of solution was determined using γ spectrometry, and the corresponding amount of the radionuclide retained on the resin was calculated along with the distribution coefficient.

DISCUSSION

Fusion of Sample. The sample fusion technique is similar to that described by Croudace et al.[5] for use in the isolation of Pu and U from soil matrixes, but in this study, the glass is dissolved in 3 M HNO_3 rather than 8 M HNO_3. The use of more dilute HNO_3, though resulting in a slower dissolution of the glass, limits the oxidation of the ascorbic acid that is subsequently added but is still sufficiently high to permit the retention of both Pu and Am on the TRU column. The application of the lithium borate fusion permits the complete dissolution of potentially intractable materials and thus ensures the dissolution of radionuclides, such as Pu, that may form refractory oxides. The lithium borate fusion is preferable to the more conventional HF digestion or fusion with potassium fluoride on safety grounds. In addition, the lithium borate fusion procedure results in a solution that may be loaded directly onto the TRU column with no further adjustment in acid strength or additional preconcentration stages. However, an HNO_3, HCl, or aqua regia digest may be equally efficient for the extraction of Am.

Retention of Am and Actinides on TRU Resin. TRU resin is a commercial extraction chromatographic resin consisting of an octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide− tributyl phosphate mixture coated onto an inert polyacrylamide support. The resin has a high affinity for all tri- and tetravalent actinides in nitric acid solutions. In general, distribution coefficients increase with nitric acid concentration. However, k_Ds for
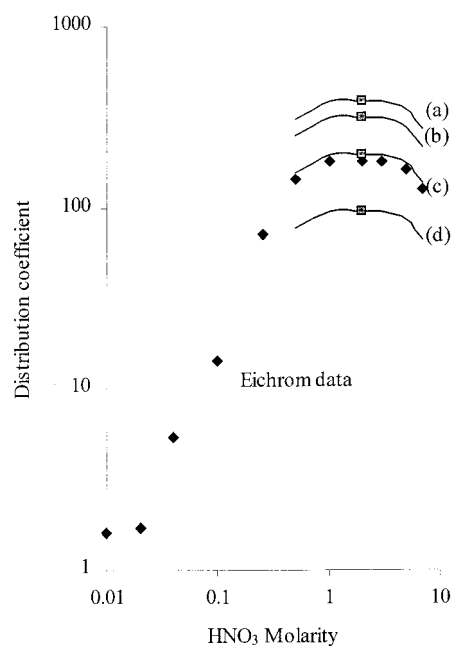
(9) Bains, M. E. D. The determination of plutonium, enriched and natural uranium in faeces. In *The determination of radionuclides in materials of biological origin*; Holmes, A., Ed.; Proceedings of the symposium held at AERE Harwell 20/21 April 1967. Report AERE -R5474. AEA Technology: Harwell, Oxfordshire, U.K., 1967.
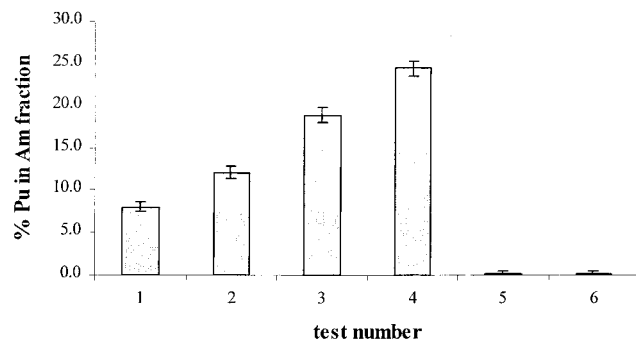
Figure 1. Distribution coefficients for Am on TRU for different media: (a) 2 M HNO_3 saturated with lithium borate; (b) 5 g of sediment fused with lithium borate, dissolved in 2 M HNO_3, and Fe(III) reduced with ascorbic acid; (c) 2 M HNO_3; (d) as for (b) but with no ascorbic acid added. Eichrom K' data were converted to distribution coefficients using the relationship $k_D = K' v_m/v_s$, where $v_m/v_s = 0.223$ for TRU resin[7]). The solid lines are theoretical extrapolations of the measured data points, assuming a similar k_D acid dependency curve to the Eichrom published data.

Am reach a maximum of ∼200 in 2−3 M HNO_3 and then decline at higher acid concentrations. In HCl media, the resin exhibits high distribution coefficients for tetravalent actinides but trivalent Am is not retained.[7]

Measurement of the distribution coefficient for Am on TRU in a number of media indicated that the k_D doubles when loading occurs in a saturated solution of lithium borate in nitric acid compared with k_Ds in identical HNO_3 concentrations (Figure 1). Uptake of Am on TRU was lower from a soil digest (containing 5 g of soil and 7 g of lithium tetraborate fused and dissolved in 100 mL of 3 M HNO_3). However, this decrease was counteracted through the addition of ascorbic acid, confirming that the reduction in extracted Am is due to competition between Fe(III) and Am(III) for the TRU resin complexant. Ascorbic acid effectively reduces Fe(III) to Fe(II), preventing Fe from competing with the Am. Although the application of ascorbic acid prevents Fe uptake, its use limits the acid strength that can be employed. Ascorbic acid is rapidly oxidized in HNO_3 solutions greater than 6 M (and even in more dilute solutions it may be expected that slow oxidation will still occur). A 3 M concentration of HNO_3 was chosen because the rate of oxidation was such that no visible signs of ascorbic acid decomposition were observed during the separation. In addition, the k_D for Am is sufficiently high to permit an efficient separation of Am from the bulk fusion solution, particularly with the increase in k_D observed in the presence of saturated lithium borate. The decline in k_D with decreasing HNO_3 concentration may be overcome through the addition of $Al(NO_3)_3$, and k_Ds as high as 2000 have been reported for Am uptake on TRU from a solution of 0.1 M HNO_3−0.5 M $Al(NO_3)_3$ compared with

Figure 2. Effect of the column washing regime on the coelution of Pu with Am: (1 + 2) columns eluted with 20 mL of 4 M HCl directly after loading; (3 + 4) columns washed 10 mL of 2 M HNO_3 and then eluted with 20 mL of 4 M HCl; (5 + 6) columns washed with 10 mL of 2 M HNO_3 and 10 mL of HNO_3 + $NaNO_2$ prior to elution with 20 mL of 4 M HCl.

~100 for 0.1 M HNO_3 alone. However, the dissolution of the fused melt is slow at such a low acid strength and 3 M HNO_3 was chosen for all further work. At this acid concentration, the addition of $Al(NO_3)_3$ had a negligible effect on the k_D.

The increase in k_D of Am on TRU resin from HNO_3 saturated with lithium tetraborate was of particular interest. Similar enhancements have also been seen for U and Th on UTEVA resin by the authors. Such increases in k_D for Am on TRU resin were not observed for comparable concentrations of lithium nitrate and boric acid, showing that the enhancement was not directly linked to the specific presence of either the Li^+ or BO_3^- ions. A slight increase in k_D was observed for solutions containing $LiNO_3$, but the effect was not of a comparable magnitude and more likely resulted from the increase in NO_3^- ions in solution. The elevation in k_D observed for HNO_3 saturated with lithium borate was most likely due to the presence of the high solute content of the solution promoting the extraction of Am from the aqueous to the organic phase or a interaction between the Am and complex species present in solution. Further work is required to elucidate this mechanism.

Following sample loading and column washing in 3 M HNO_3, the column is washed with 2 M HNO_3–$NaNO_2$. During this washing stage, any Pu(III) formed by the reduction of Pu(IV) with ascorbic acid is reoxidized to Pu(IV). This prevents any Pu(III) from coeluting with the Am in 4 M HCl. The omission of this stage may result in up to 25% of Pu coeluting with the Am (Figure 2).

Decontamination of Am from Potential Interferences. A number of radionuclides emit α particles with energies similar to those of either ^{243}Am or ^{241}Am (Figure 3). If present in the final source, these nuclides will interfere with the precise measurement of ^{241}Am and it is therefore vital that these radionuclides are efficiently separated from Am during the chemical purification stages. Interfering radionuclides that will potentially be present in the sample include ^{232}U (a tracer commonly used in U measurements), ^{228}Th (daughter of ^{232}U and a naturally occurring isotope of Th), ^{238}Pu, ^{239}Pu, ^{240}Pu, and naturally occurring ^{210}Po. These radionuclides are all retained on the TRU column from 3 M HNO_3 and 4 M HCl and therefore do not coelute with Am. ^{242}Cm and ^{244}Cm will follow Am in many chemical separation schemes but will not interfere with the measurement of ^{241}Am.

With further optimization to prevent fractionation of Am and Cm, it is possible that the technique may be suitable for the simultaneous measurement of Am and Cm α-emitting radionuclides.

Elution of Pu from the TRU Column and Subsequent Purification. Attempts to preferentially elute Pu with a dilute oxalate solution[10] were unsuccessful as both U and Th coelute with Pu. In addition, the oxalate in the residue must be destroyed prior to any further chemical purification of the Pu. Reduction of Pu(IV) to Pu(III) and subsequent elution from the TRU column was attempted using NH_4I–9 M HCl. However, only a small percentage of Pu was eluted. The mixture 1.0 M HCl–0.02 M HF rapidly eluted Pu from the TRU column although Th and U were coeluted. However, the removal of this eluent and subsequent purification of Pu is straightforward and this eluent was therefore chosen for routine use.

Purification of Pu is achieved using conventional anion-exchange chromatography. Any residual HF remaining from the TRU resin eluent will significantly reduce the uptake of Pu on the anion column and a double aqua regia attack on the residue with evaporation is critical prior to the dissolution using 9 M HCl.

Pu and U are retained on a 2 × 0.7 cm Eichrom 1 × 8 anion-exchange column with distribution coefficients for Pu and U in 9 M HCl of >10^3. Th is not retained under these conditions. The column is washed with 8 M HNO_3 and 3 M HNO_3 to remove U. However, even in 3 M HNO_3, with the k_D ~ 5 for U and the k_D ~ 500 for Pu, tailing of U and incomplete separation of U from Pu may still occur. Following the HNO_3 washes, the column is converted to the chloride form by washing with 9 M HCl. Both Pu and any residual U are strongly retained. Elution of Pu may be achieved using a variety of reagents including 1 M HCl–H_2O_2, 1 M HCl–0.01 M HF, and 9 M HCl–NH_4I. HCl–NH_4I was chosen as, unlike the other eluents, it will not coelute any residual U still present on the column with the Pu.

During initial studies, Pu was loaded onto the column using 8 M HNO_3 whereby U, Th, and Pu are all retained. Th was subsequently eluted with concentrated HCl. Using this approach, traces of Th were often detected in the final Pu fraction during routine analyses. By loading the Pu in 9 M HCl, Th is not initially retained on the anion resin resulting in better separation of Th from Pu.

Purification of Am from Rare Earth Elements. As well as interference from α-emitting radionuclides, the ^{241}Am α spectrum may also be degraded by the presence of significant quantities of rare earth elements (REEs) that are also retained on TRU resin from 2 M HNO_3 and subsequently coeluted with Am. Approximately 100 μg of REEs is required to noticeably degrade the α spectrum (Figure 4). For most sample types, the concentrations of REEs are sufficiently low that their presence on the final α source does not result in significant degradation of the α spectrum. However, many soils and sediments contain ΣREE concentrations of typically 80–90 ppm,[11] and REEs must be separated from the Am prior to α source preparation.

Anion-exchange chromatography using HNO_3–MeOH or NH_4SCN–MeOH have been widely used for the separation of Am

(10) *Eichrom Americium, plutonium and uranium in water*; Analytical procedures, ACW03, rev 1.3. Eichrom Industries, 1995.
(11) Taylor, S. R.; McClennan, S. M. T*he continental crust: its composition and evolution*; Blackwell Scientific: Oxford, U.K., 1985.
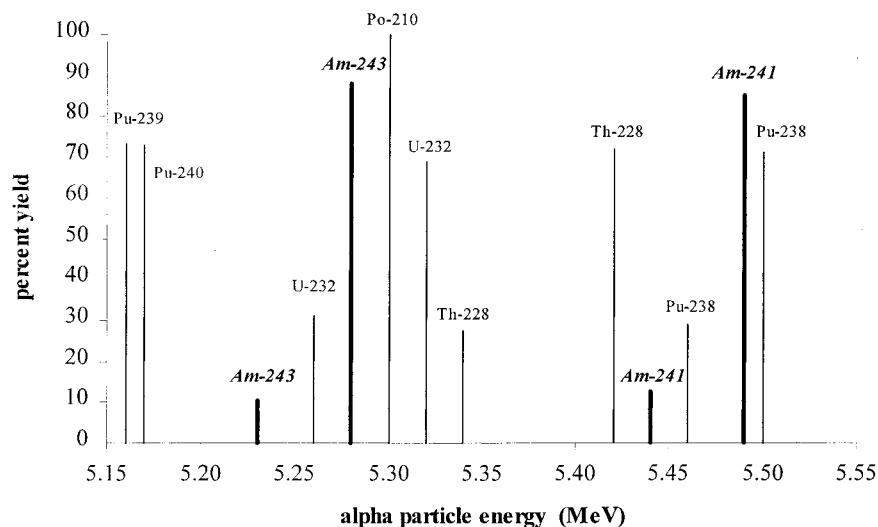
Figure 3. α Energies and yield for potential interfering radionuclides (α decay data from ref 1).
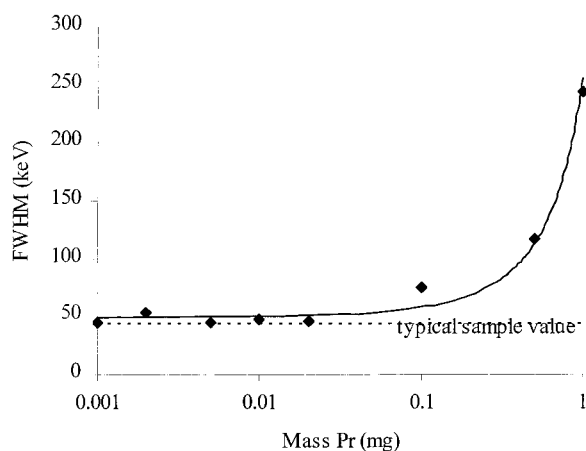

Figure 4. Effect of Pr on the measured full width at half-maximum (fwhm) of the ^{241}Am α peak. Solutions of ^{241}Am were spiked with a known mass of Pr (a proxy for any REEs), electrodeposited, and then counted on an EG&G Octete-PC α spectrometer; the dotted line represents the typical fwhm values of ^{241}Am isolated from soil and sediment samples indicating effective removal of REEs.
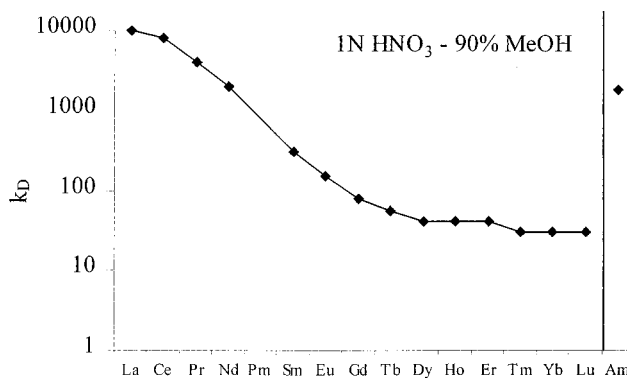

Figure 5. Uptake of rare earth elements on anion-exchange resin from 1 N HNO$_3$−90% MeOH. (Data compiled from ref 19—although the data presented are for a slightly different composition of HNO$_3$−MeOH than that used in the current study, the plot demonstrates the relative behavior of the REEs in this type of system.)

Table 1. Decontamination Factors for Key α Emitters[a]

	contaminants				
	Po	Th	U	Pu	Am
Pu fraction (elution with NH$_4$I/HCl)	10^3	$>5 \times 10^2$	8×10^3		$>10^3$
Pu fraction (elution with H$_2$O$_2$/HCl)	10^3	nd^b	5×10^3		$>10^3$
Am fraction (no second purification)	10^2	6×10^3	10^4	$>5 \times 10^2$	
Am fraction (second purification)	10^3	8×10^3	8×10^3	$>3 \times 10^2$	

[a] The decontamination factor (DF) is defined as DF = M_{init}/M_{final}, where M_{init} is the mass of the element in the sample and M_{final} is the mass of the element in the purified fraction. ">" Values represent a mass of element in the final fraction that is below the limit of detection. The limit of detection is then used to calculate a threshold value. ^{b} nd, not determined.

from rare earth elements.[12−15] The adopted scheme was based on a method described by Yamato.[16] Am and light REEs are loaded onto an anion-exchange column in 1 M HNO$_3$−93% MeOH (Figure 5). Heavy REEs (above Gd—see Figure 6) are eluted at this stage with Lu eluting the most rapidly. A small proportion of Eu is also eluted during the initial load and washing in HNO$_3$−MeOH. The column is then washed with a mixture of 0.1 M HCl−0.5 M NH$_4$-SCN−83% v/v methanol, which strips light REEs, along with the remainder of the Eu and Sm. La is eluted rapidly during this washing stage with the elution times becoming progressively slower for the heavier REEs up to Nd. The column is then washed with a further portion of 1 M HNO$_3$−93% v/v MeOH, effectively removing traces of NH$_4$SCN. Finally Am is eluted with 0.5 M HCl.

A small fraction of REEs was detected in the final Am eluent, consisting of 10−20% of the light REEs and 1−2% of the heavy REEs. No breakthrough of Am was observed in any of the load and wash fractions.

Overall Assessment of the Methodology. Application of the method to routine analysis of ^{241}Am has shown typical chemical recoveries for a range of sample types, including sediments, soils,

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Load 2ml | 1M HNO₃ - 93% MeOH

$$ \text{1M HNO}_3 \text{ - 93\% MeOH} $$

Elution of heavy REEs

(light REEs and Am retained on the column)

percentage eluted

fraction number

0.1M HCl - 0.5M NH₄SCN - 80% MeOH — 1M HNO₃ - 93% MeOH
2ml aliquots — 2ml aliquots

Elution of light REEs
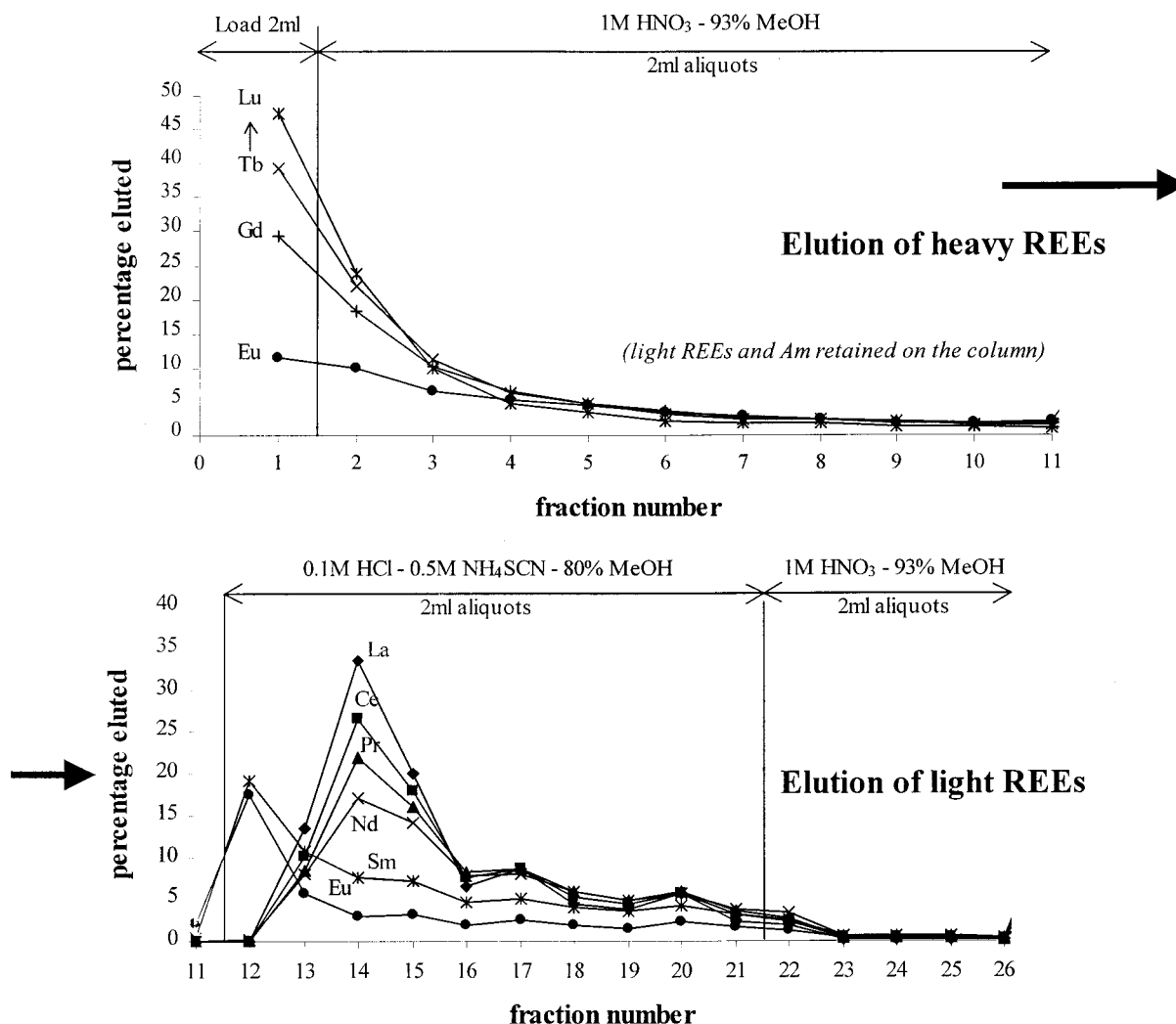
percentage eluted

fraction number

Figure 6. Elution profiles for light and heavy rare earth elements. With a *2* × 0.7 cm 100−200 mesh 8% cross-linked anion-exchange resin column. No breakthrough of Am was observed. Am was quantitatively eluted with 10 mL of 0.5 M HCl.

Table 2. Analysis of Reference Materials for ^{241}Am and $^{239+240}$Pu^a

reference material (date)	sample type	mass analyzed (g)	certified ^{241}Am (range)	measd ^{241}Am	certified $^{239+240}$Pu (range)	measd $^{239+240}$Pu
IAEA 134 (1−1−1992)	cockles	1.5	38 (35−39)	36 ± 2	15 (14−16)	14 ± 1
IAEA 135^b (1−1−1992)	sediment	0.1	318 (310−325)		213 (205−226)	217 ± 15
	(corrected for ^{241}Am ingrowth)		359 (351−366)	352 ± 24		
IAEA 367 (1−1−1990)	sediment	1.0	26 (24−28)	24 ± 2	38 (34−40)	34 ± 3

^{a} Values in parentheses represent the range of the certified value at the 2σ confidence level. Uncertainties on measured values are at the 2σ confidence level. ^{b} Results for IAEA-135 represent repeated analysis of the reference material ($n = 5$) over a 12-month period by two analysts using different ^{242}Pu spikes.

and biota, to be between 60 and 90%. Recoveries of Pu were generally slightly lower at typically 60%. The majority of the losses appear to occur during the filtering stages where some of the solution remains occluded within the gelatinous silica/boric acid precipitate. Similar losses to silica precipitates have been reported by Burnett et al.[17] Decontamination factors were high with values typically between 10³ and 10⁴ for U, Th, and Po in the Am and Pu

(17) Burnett, W. C.; Corbett, D. R.; Schultz, M.; Horwitz, E. P.; Chiarizia, R.; Dietz, M.; Thakkar, A.; Fern, M. *J. Radioanal. Nucl. Chem.* **1997**, *226*, 121− 127.

fractions (Table 1). Inspection of Pu and Am α spectra did not indicate the presence of any interfering α emitters. Typical full width half-maximums (fwhm) for $^{239+240}$Pu and ^{241}Am were similar to those obtained from plated standard solutions (∼50 keV−Figure 4) showing that attenuation of α particles as a result of residual material on the final source was limited. Analysis of IAEA reference materials for ^{241}Am generally gave results that were higher than the certified values due to the ingrowth of ^{241}Am from ^{241}Pu. Analysis of IAEA135 for ^{241}Pu by liquid scintillation counting[18] showed that the reference material contained 3610 Bq/kg
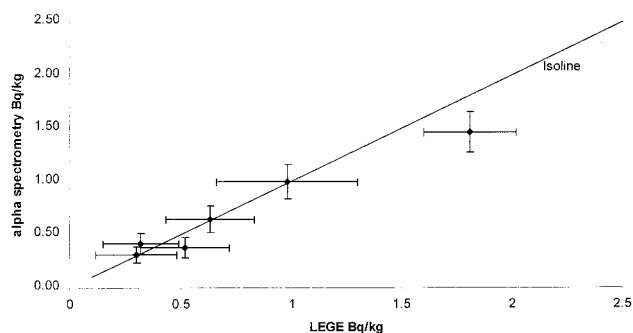
Figure 7. Comparison between LEGE and α spectrometric analysis. LEGE analysis performed on 20 g of sample counting for 300 000 s. α-Spectrometric measurement performed on 5 g of dry sample counting for 166 000 s.

^{241}Pu (decay corrected to the reference date). When the certified ^{241}Am value of 318 Bq/kg is corrected for ^{241}Am ingrowth (activity in June 2000), the reference value becomes 359 Bq/kg, which is in good agreement with the measured value. Plutonium-241 activities in the other reference materials were below the detection limits, and a similar correction could not be made. Analysis of IAEA reference materials confirmed that the method was achieving the desired degree of accuracy (Table 2). In addition, the time required for analysis of a batch of eight samples is typically 2.5 days compared to 4−5 days for a conventional Am separation.

A comparison between ^{241}Am activities in sediment obtained by low-energy germanium γ spectrometry (LEGE) and this technique shows generally good agreement between the two techniques (Figure 7). However, the uncertainties on the α-spectrometric measurements are approximately half the LEGE uncertainties even though the count times were shorter and sample masses analyzed were smaller. In addition, α spectrometry has been successfully used to measure ^{241}Am activities in sediments below the detection limit of the LEGE.

CONCLUSIONS

The combination of a lithium borate fusion with extraction chromatography results in a separation scheme that is both rapid and robust. The lithium borate fusion provides a safe and efficient method for sample digestion. The solution arising from this may be loaded directly onto the TRU column and removes the need for many intermediate chemical separation stages ensuring consistently high chemical recoveries. In addition, the presence of high concentrations of lithium borate has been found to enhance the uptake of Am on the TRU resin column. The combination of TRU and anion-exchange chromatography results in high-quality sources for α spectrometry even for samples containing relatively high levels of rare earth elements. The overall method is rapid and amenable to scaling up with sample batches of 8−16 permitting the application of this technique to routine ^{241}Am dating of sediment layers.

Although the method has been specifically evaluated for the analysis of ^{241}Am and Pu in sediments, additional investigations have shown that the technique is also suitable for the determination of ^{241}Am and Pu in a wide range of marine and terrestrial biota as well as soils. The methodology may therefore be applied for environmental monitoring surveys again increasing sample throughput while reducing the number of samples requiring repeat analysis.

(18) Oh, J.-S. The migration and accumulation of radionuclides in the Ravenglass Saltmarsh, Cumbria, UK. Ph.D. Thesis, University of Southampton, UK, 1999.

(19) Ballestra, S. *Artificial radioactivity and marine environment: study of the transuranium elements plutonium-238 (239+240) 241 and americium-241 in the Mediterranean*; RFP-trans-392. Rockwell International Corp.: Golden, CO, 1983.