



Americium and plutonium separation by extraction chromatography for determination by accelerator mass spectrometry



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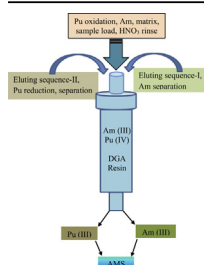
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HIGHLIGHTS

- Am and Pu were adsorbed and separated using a single extraction chromatography DGA column.
- Pu was eluted from the column completely using on-column reduction of Pu(IV) to Pu(III).
- ²⁴¹Am and ^{239,240}Pu measurements by accelerator mass spectrometry (AMS) agree with the certified values in two SRMs.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple method was developed to separate Pu and Am using single column extraction chromatography employing *N,N,N',N'*-tetra-*n*-octyldiglycolamide (DGA) resin. Isotope dilution measurements of Am and Pu were performed using accelerator mass spectrometry (AMS) and alpha spectrometry. For maximum adsorption Pu was stabilized in the tetra valent oxidation state in 8 M HNO₃ with 0.05 M NaNO₂ before loading the sample onto the resin. Am(III) was adsorbed also onto the resin from concentrated HNO₃, and desorbed with 0.1 M HCl while keeping the Pu adsorbed. The on-column reduction of Pu(IV) to Pu(III) with 0.02 M TiCl₃ facilitated the complete desorption of Pu. Interferences (e.g. Ca²⁺, Fe³⁺) were washed off from the resin bed with excess HNO₃. Using NdF₃, micro-precipitates of the separated isotopes were prepared for analysis by both AMS and alpha spectrometry. The recovery was 97.7 ± 5.3% and 95.5 ± 4.6% for ²⁴¹Am and ²⁴²Pu respectively in reagents without a matrix. The recoveries of the same isotopes were 99.1 ± 6.0 and 96.8 ± 5.3% respectively in garden soil. The robustness of the method was validated using certified reference materials (IAEA 384 and IAEA 385). The measurements agree with the certified values over a range of about 1–100 Bq kg⁻¹. The single column separation of Pu and Am saves reagents, separation time, and cost.

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1. Introduction

The investigation of the levels and behavior of radioactive actinides in the environment is necessary to assess their radiological and ecological effects. Isotopes of americium (Am)

and plutonium (Pu) are the most abundant long-lived actinides released into the environment from nuclear weapons tests, and accidental or authorized releases from nuclear activity [1–4]. About 15 PBq of ²³⁹⁺²⁴⁰Pu and 0.3 PBq of ²³⁸Pu have been globally released into the atmosphere from the test of nuclear weapons [1] and some sites have additional contamination from local sources. At most sites the majority of Am and Pu is found in soils and sediments [2,3]. Determination of Am and Pu in these environmental matrices by radioanalytical techniques poses challenges

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due to low concentration and matrix interferences. Thus sensitive analytical techniques and sample clean-up are needed for the accurate measurement of trace level actinides [5–12].

Alpha spectrometry (AS) is a sensitive and convenient radiometric technique often used for actinide isotopes because they are alpha emitting radionuclides. Mass spectrometric (MS) techniques also can be used in radionuclide measurements in environmental samples. The MS techniques include inductively coupled plasma mass spectrometry (ICP-MS), resonance ionization mass spectrometry (RIMS), thermal-ionization mass spectrometry (TIMS), glow discharge mass spectrometry (GDMS), and accelerator mass spectrometry (AMS) [13,14]. All these techniques require that the Am and Pu be separated from the matrix and concentrated before the decays or ions can be counted accurately [7]. Many techniques have been developed to separate Am and Pu including solvent extraction [8,9], solid phase extraction [10], ion exchange [11] and extraction chromatography [12]. Extraction chromatography (EXC) is particularly useful because it reduces sample preparation time, uses fewer reagents and solvents and often provides better separation selectivity over liquid–liquid extraction and ion exchange [5,6]. EXC can also be used (TRU-resin cartridge) in automated methods of Pu and Am separation [15]. The development of DGA resin solved a key issue; namely the efficient extraction of both Am and Pu from strongly acidic solutions [16]. Patented by the Eichrom Technologies [17], DGA Resins are extraction chromatographic materials in which the ingredient is either *N,N,N',N'*-tetra-*n*-octyldiglycolamide (DGA resin, normal) or *N,N,N',N'*-tetrakis-2-éthylhexyldiglycolamide (DGA resin, branched). Both forms of DGA have very high affinity for americium under concentrated nitric or hydrochloric acid media [16,17]. DGA resin has been coupled successfully with other resins (e.g. Anion, TRU, TEVA, and UTEVA) to extract and separate Pu and other actinides from sample matrices [12,18–25]. However, the use of two or more resins adds complexity, reagents and separation time [12,19,24], and consequently the cost of sample analysis is increased.

There are methods used to separate Am, Pu and other actinides in environmental samples by single column anion exchange [26], and extraction chromatography [27–29]. But none of the column materials showed high affinity for Am. Goodall and Lythgoe [27] has reported an isolation of Pu from other actinides using UTEVA resin and on-column reduction of the analyte with ascorbic acid, analyzed by TIMS following a wet ash decomposition of the acid residue. This innate affinity of Am for DGA resin with a high *k* (adsorption coefficient) value ($>10^4$) in concentrated HNO_3 [16,17] can be exploited to separate Am from other actinides. In this paper a new method for separating Am and Pu using EXC is described using a single cartridge with DGA resin. This method uses the combined effects of the oxidation–reduction properties of Pu, the tendency for Am to form nitro complex, and the strong binding capacity of DGA resin for Am and Pu in 8 M nitric acid media [16,22]. This technique can be used for alpha and mass spectrometry analyses. The major interferences (Ca^{2+} , Fe^{3+} , Al^{3+}) in this separation process were eliminated by optimizing the HNO_3 concentration and volume for the adsorption and recovery of Am and Pu on the resin. Then the method was tested using spiked samples, contaminated river sediments and certified reference materials analysis.

2. Experimental

2.1. Reagents and materials

Standard solutions of ^{243}Am (0.50 Bq g^{-1}), ^{236}Pu (0.875 Bq g^{-1}), and ^{242}Pu (0.57 Bq g^{-1}) were obtained from (National Institute of Standards and Technology, USA). Titanium trichloride (10 wt% TiCl_3 in 20–30 wt% HCl), neodymium nitrate hexahydrate, hydrofluoric acid and sodium nitrite were purchased from Sigma–Aldrich,

Canada. Analytical grade hydrochloric acid and nitric acid were obtained from Fisher Scientific, Ottawa, ON. Ultrapure water was used for the preparation of eluents and the dilution of samples obtained from a Mili-Q purification system (Milipore, Bedford, MA). EXC cartridges (DGA resin, normal, 2 g cartridge, 50–100 mm particle size), and polypropylene membrane filters (0.1 μm thickness) were supplied by Eichrom Technologies Inc. (Lisle, IL, USA). Standard reference materials (SRM) IAEA-384 (Fangataufa Lagoon sediment) and IAEA-385 (Irish Sea sediment) were obtained from International Atomic Energy Authority (IAEA), Vienna, Austria. Sediment samples were collected from adjacent to Chalk River Laboratories. Soil samples were collected from plant beds at the University of Ottawa.

2.2. Instrumentation

Samples were analyzed for $^{241,243}\text{Am}$ and $^{238,239,240,242}\text{Pu}$ by alpha spectrometry using an Ortec 576A alpha spectrometer coupled to an Ortec Spectrum Master 920-8 Multichannel Buffer. Counting times varied between 2–100 h for each sample to enable the collection of a sufficient number of counts. The detector efficiency (26%) was determined using certified samples of Pu and Am prepared in the same counting geometry. ^{241}Am also was measured using a PerkinElmer Wizard II NaI gamma spectrometer at University of Ottawa. $^{241,243}\text{Am}$ and $^{239,240,242}\text{Pu}$ isotopes were measured by accelerator mass spectrometry (AMS) (IsoTrace Laboratory) using the procedures reported by Zhao et al. [30]. In this procedure, Pu was co-precipitated with NdF_3 (~8 mg) and then mixed with PbF_2 powder in 1:7 ratios to form a sputter target. The IsoTrace AMS system uses electronic controls to automatically adjust the terminal voltage and all high-energy electric analyzers, along with the injection magnet bouncer. Measurements of Pu^{3+} at a 0.85 MV terminal voltage showed that the $^{239,240,242}\text{Pu}$ isotopes can be detected with a low background, high efficiency and a 1 fg detection limit [30].

2.3. Sample pre-treatment

Sample pre-treatment and separation strategies are summarized in Fig. 1 and described in detail in Table 1. 1–10 g of solid sample was

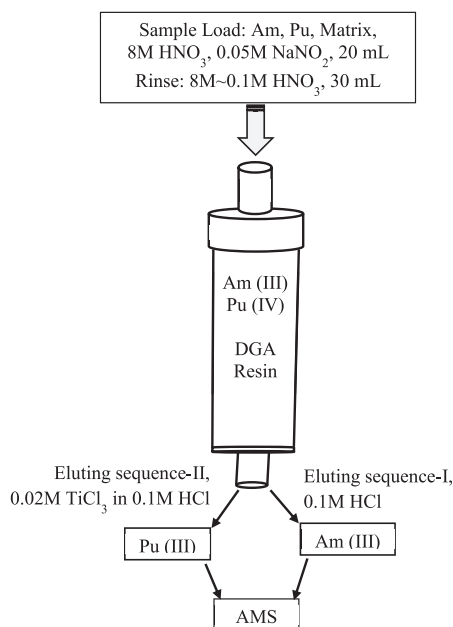


Fig. 1. Separation of Pu and Am using DGA resin.

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