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Comparison of the measurement of Pu and Am isotopes by AMS using fluoride and oxide anion beams

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ABSTRACT

^{239,240}Pu and ^{241}Am isotopes can be measured by Accelerator Mass Spectrometry (AMS) using iron oxide and neodymium fluoride matrices. This report summarizes the measurements of ^{239,240}Pu and ^{241}Am in oxide and fluoride matrices by isotope dilution using the same accelerator system and sample preparation techniques at A. E. Lalonde AMS Laboratory (AELL), University of Ottawa. The advantages of each method of Pu and Am isotope measurement are assessed by studying the sensitivity, detection limits, and precision of both techniques. Based the ease of sample preparation, efficiency of ionization, and sensitivity, the fluoride method has an edge. The separation of ^{239,240}Pu and ^{241}Am from the sample matrix using a single extraction chromatography column prepared with DGA resin, and their measurements by AMS in fluoride matrices, was tested using the low level certified reference material (IAEA-414). The measured concentrations of ^{239,240}Pu and ^{241}Am agreed with the concentrations in the standard reference material.

Introduction

The measurement of $^{239,240}Pu$ and ^{241}Am is important in view of nuclear safeguards and the occupational and public health concerns of the radiation hazards associated with their exposure and release into the environment. The increasing demand for fast, sensitive, and robust analytical techniques for actinides including $^{239,240}Pu$ and ^{241}Am is reflected in recent publications.[1-3] Low level detection of these isotopes (e.g. femto gram level) in environmental and bioassay samples has been achieved by combining thorough sample clean-up techniques and sensitive analytical methods.[4-6]Accelerator Mass Spectrometry (AMS) is one of the most sensitive methods for radioisotopes including actinide measurement. It has attracted considerable attention in recent years due to its high sensitivity as well as high throughput.[7-11] Unlike conventional mass analyzer/detectors where samples are normally ionized from aqueous media, AMS sputters a solid target to produce elemental or molecular anions. Therefore, $^{239,240}Pu$ and ^{241}Am that are extracted in aqueous media from samples (e.g. environmental, biological or mineral, usually with complex matrices) must be processed onto a solid target for insertion into the AMS sputter ion source. Co-precipitation is a fast and convenient method to separate any analyte from the aqueous solution. Iron hydroxide and titanium hydroxide have been used for the co-precipitation of $^{239,240}Pu$ and ^{241}Am.[12,13] The solids are then baked at high temperature (700 ºC) to yield oxides. The $^{239,240}Pu$ and ^{241}Am oxide samples are then dispersed in Al[12], Nb[13] or Ag[14] powders before being pressed into a target. $^{239,240}Pu$ and ^{241}Am can also be separated from the aqueous media by co-precipitation with Nd or Ce in dilute hydrogen fluoride solution.[15] The present authors have utilized the fluoride precipitation technique using Nd, and used PbF_2 powder to mix with the NdF_3 precipitate.[5,6,16]

^{239,240}Pu and ^{241}Am oxide anion (MO_n^-) beams are produced from a Cs^+ sputter ion source using the oxide samples. Similarly, ^{239,240}Pu and ^{241}Am fluoride anion (MF_n^-) beams are produced when the fluoride targets are placed in the Cs^+ sputter ion source. In a tandem AMS system, the negative ions are extracted from the source, and then accelerated into the positive voltage terminal of the tandem accelerator where several electrons are removed upon collisions with stripper gas, generally high purity Ar or He gas. The resulting positive atomic ions are accelerated further to exit the accelerator for mass analysis and particle counting and identification at MeV energies. Zhao[17]and Fifield[12]first measured actinides by AMS using targets made of iron oxide from which UO^- and PuO^- beams were extracted from Cs^+ sputter ion sources. In these earlier tests both U^{5+} and Pu^{5+} were selected for particle counting in gas ionization chambers. Subsequently, several other facilities have performed actinide measurements using isotope dilution techniques, again with oxide beams extracted from their cesium sputter ion sources.[13,14,18,19] However, Zhao et al.[16] later noted several potential advantages in the extraction of beams of fluoride anions from Cs^+ sputter-ion sources under certain conditions. First, they found stronger MF_n^- beams than MO_n^- when sputtered by a low Cs^+ flux. Second, in a sputter target made with a highly fluorinated matrix U and Th interferences were reduced because they form different fluoride compounds than Pu and Am. U and Th form predominantly MF_5^-, Pu forms mainly PuF_4^- and PuF_5^- with roughly equal probability. AmF_n^- forms roughly about 70% AmF_4^- and 30% AmF_5^- .[16] Following this trend the heavier actinides are expected to mostly form MF_4^-.

The chemical separation and purification of ^{239,240}Pu and ^{241}Am are essential to eliminate interferences in their measurements by mass spectrometry. For example, ^{241}Pu and ^{241}Am are isobaric; and $^{238}UH^+$ interferes in $^{239}Pu^+$ measurements. Many techniques have been developed to separate Am and Pu including solid phase extraction,[20] ion-exchange and extraction chromatography.[21,22] ^{239,240}Pu and ^{241}Am are usually extracted in concentrated acid media from raw samples. However, the separation of ^{241}Am from the matrix is problematic as it is less selective in many chromatographic systems in highly acidic media. The present authors have introduced a fast and convenient separation method for ^{239,240}Pu and ^{241}Am by extraction chromatographic column using DGA resin.[5,6] DGA resins are extraction chromatographic materials in which the extractant system is N,N,N$^{/}$,N$^{/}$-tetra-n-octyldiglycolamide (DGA Resin, normal). It has high affinity for Am (III) and Pu (VI) in concentrated nitric acid (> 1 M) media. The adsorption coefficients are $>10^4$ and $>10^3$ for Am (III) and Pu (VI), respectively.[23] Am (III) can then be selectively desorbed from the resin in dilute hydrochloric acid, then the Pu can be quantitatively recovered from the resin by reducing the Pu (VI) to Pu (III) using $TiCl_3$ in dilute hydrochloric acid.[5,6] Pu and Am were co-precipitated with Nd in fluoride solution, and measured by an AMS system.

The objectives of this work were to compare the measurements of ^{239,240}Pu and ^{241}Am in oxide and fluoride matrices by isotope dilution (relative to ^{242}Pu and ^{243}Am, respectively) using the same accelerator system and sample preparation techniques at AELL, University of Ottawa. The advantages of each method are assessed in terms of sample preparation, measurement sensitivity, precision and detection limit and, the actinide separation and purification techniques used for these AMS measurements are tested using a low level certified reference material (IAEA 414).

Experimental

Reagents and materials

Standard solutions of Am and Pu were obtained from National Institute of Standards and Technology, USA. Titanium trichloride (10wt% $TiCl_3$ in 20~30 wt% HCl), neodymium nitratehexahydrate, hydrofluoric acid, ammonium hydroxide (28%), ferric chloride 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 (18 MΩ cm^{-1}) was used to prepare solutions obtained from a Milli-Q reverse osmosis water system. EXC cartridge (DGA resin normal, 2g cartridge, 50-100 mm particle size) was supplied by Eichrom Technologies Inc. (Lisle, IL. USA). Standard reference materials IAEA-414 (Irish and North Sea mixed fish) was obtained from International Atomic Energy Agency (IAEA), Vienna, Austria. Standard solutions of ^{243}Am (0.50 Bq g^{-1}), and ^{242}Pu (0.57 Bq g^{-1}) were obtained from (National Institute of Standards and Technology, USA). All other chemicals are of analytical grade and used without further purification.

Am and Pu separation

Pu and Am were extracted from the environmental samples by digestion in 16 M nitric acid and the isotopes were separated from the sample matrix by DGA resin column following the method published by Kazi et al.[5] Pu was maintained in oxidation state IV in the loading solution (8M HNO_3) by the addition of $NaNO_2$. This is essential for its separation from Am and other interfering cations by DGA resin because only Pu (IV) is retained on the DGA cartridge. The column was rinsed with 10 mL of each 8 M and 3 M HNO_3, followed by 10 mL 0.1 M HNO_3 to remove other cations such as Fe, Al and Ca that might interfere with the preparation of fluoride targets for AMS analysis. Then Am was eluted in 15mL of 0.1M HCl and subsequently the Pu on the column was reduced to Pu (III) and quantitatively eluted with 0.02 M $TiCl_3$ in 15 mL of 0.1 M HCl. The $TiCl_3$ in the eluting solution was used to reduce the Pu (IV) to Pu (III).

Co-precipitation in oxide matrices

^{242}Pu (6 pg) and ^{243}Am (1.6 pg) were added to each sample as tracers. Standards of ^{239}Pu (0.7pg), ^{240}Pu (0.7 pg) and ^{241}Am (0.16pg) were prepared to test the AMS system performance.

Five mg iron as $FeCl_3$ in dilute HCl solution was added to each sample. NH_4OH was added to the sample to bring the solution pH to 9 to instigate the co-precipitation of the Am and Pu isotopes. The co-precipitate was washed, dried in an oven at 100^0C and baked at 700 ^{0}C in a muffle furnace in quartz crucible, recovered (~6 mg), and ground to prepare a target for AMS measurement. The co-precipitate of Am or Pu in iron oxide was mixed with Ag, Nb or Al powders. Each target contained nearly 8 mg of the mixed sample.

Co-precipitation in fluoride matrices

Another set of ^{242}Pu (6 pg) and ^{243}Am (1.6 pg) tracers and ^{239}Pu (0.7pg), ^{240}Pu (0.7 pg) and ^{241}Am (0.16pg) standards were prepared to co-precipitate in fluoride matrices.[5] One mL HF (28%) and 10 mg Nd as $Nd(NO_3)_2$ in solution were added to the sample to co-precipitate Am and Pu from the solution. The precipitate was washed, dried and ground to prepare a target for AMS measurement. The Pu or Am co-precipitate with NdF_3 was mixed with PbF_2 in a ratio of 1:7 (wt/wt). Each target contained 8 mg of the mixed sample.

AMS setup

The A. E. Lalonde Laboratory AMS system was described by Kieser et al.[11] The concentration of ^{241,243}Am and ^{239,240,242}Pu isotopes were measured by Accelerator Mass Spectrometry in oxide [12,17]and fluoride[16] matrices using similar procedures as reported by Cornett et al.[6] Pu and Am anions (MO^- or MF_4^-) were extracted at 35keV energies from a Cs sputter ion source (Model SO-110, High Voltage Engineering Europa)[11] and analyzed as Pu^{3+} or Am^{3+} after the tandem accelerator operated at terminal voltage 2.5 MV. The analytes were counted by a dual anode dE/dx gaseous ionization detector. The Lalonde laboratory detector is an enclosed volume of isobutene gas in a chamber which is separated from the high vacuum beam line by a 75 nm thick SiN membrane window. This detector reduces the energy of the analyte ions in 10 mbar of isobutane; the electrons produced by the passage of the ions through the gas in two sequential regions of the detector are collected on anodes and provide voltage signals that are proportional to the energy lost by the ion in that region. The coincidence of signals from both anodes provides noise-free single ion counting and the energy loss information provides elemental and charge state identification. The AMS operating parameters used for the actinide measurements are summarized in Table 1.

Results and discussion

Measurements using oxide and fluoride anion beams

The AMS measurements of ^{239,240,242}Pu and ^{241,243}Am usually use MO^- anions. ^{239,240,242}Pu and ^{241,243}Am isotopes in iron oxide are mixed with fine powders of Al, Nb or Ag to form the sputter target.[12-14] The metal powders are used as binders to ensure good electrical and thermal conductance of the sputter target. The oxide ion beams of Pu and Am from targets without metallic binders are potentially unstable.[12-14] The iron oxide to metallic powder weight ratios used in this work were kept the same as those published. Ratios of iron oxide to Al, Nb and Ag powders were 1:4, 1:1 and 1:1 by weight, respectively. The oxide anions of Pu and Am (PuO^- and AmO^-) are extracted from the ion source, accelerated and electrons stripped to produce Pu^{3+} and Am^{3+}ions for analysis. A measured amount of sample is pressed in a Cu target holder, so that the amount of Pu and Am isotopes loaded in each target can be estimated. A target is typically measured for longer than an hour, with each isotope sequentially selected for counting for a pre-set duration (2 to 10 seconds), with 2 seconds used for settling after each switch. The number of counts that have been collected for ^{242}Pu and ^{243}Am from the targets are normalized to counts/sec/fg to compare the sensitivity of the measurements (Table 2).

The use of fluoride matrices in AMS measurements of Pu and Am has been reported earlier by our group[5,6,16] The co-precipitate of Pu/Am and NdF_3 is mixed with PbF_2 in a ratio of 1:7 (by wt.), which is pressed into a copper target holder. Being one of the best ionic conductor when heated, the PbF_2 matrix ensures electrical conductivity of the sputter target, and serves as a supply of fluorinating reactants to enhance the formation of halide anion beams of Pu and Am (PuF_4^- and AmF_4^-).[16] Like the oxide targets, the amount of Pu and Am isotopes in each target is estimated by loading a weighted amount of sample in the target. The measurement procedures are similar to those for oxide measurements. The ionization and ion source extraction efficiency for actinide measurements using fluoride anion is estimated by counting the atoms on a target until target exhaustion. The ionization and source extraction efficiency for using fluoride matrices using our AMS system is 1%. Similarly, for using oxide matrices this is estimated to be 0.1%.

The amount of Pu and Am in the targets ranged from 2 to 5 pg for ^{242}Pu and 0.2 to 1 pg for ^{243}Am. The count rate of ^{242}Pu and ^{243}Am ranged from 5 to 9 and 4 to 8 counts per second per picogram (cps/pg) in oxide matrices, respectively. In fluoride matrices, the cps/pg for ^{242}Pu and ^{243}Am ranged from 80 to 130 and 107 to 172 cps/pg, respectively. The sensitivities reported in Table 2 were measured in several experiments (n = 4) and although the sensitivity depends on the actual ion source settings, the sensitivity with the oxide technique was consistently lower than the sensitivity in tests that were performed using fluoride matrices in our SO110 ion source. The fluoride method using PbF_2 matrices provide an order of magnitude more cps/pg for both ^{242}Pu and ^{243}Am (Table 2). This result for ^{242}Pu and ^{243}Am measurements is in agreement with our previous work using the same AMS system at University of Ottawa.[6]

The process blank and the detection limit of ^{239,240}Pu and ^{241}Am were determined by isotope dilution and they were influenced by trace amounts of these actinides in reagents used in the preparation of the samples. Table 3 summarizes the measurements of blanks in oxide and fluoride matrices. The blanks in both oxide and fluoride matrices range from 0.4 to 1.2 femto grams (fg) level. Based on the process blank measurements and assuming a normal distribution in concentrations, the detection limits are calculated for each isotope using the following relation.[24]

$$L_d = 1.645 \text{ x } 2(\sigma_0)$$

where σ_0 is the uncertainty of the blank measurements in fg. The detection limit of ^{240}Pu in fluoride matrices is relatively higher (1.5fg). The lowest detection limits for ^{239,240}Pu and ^{241}Am using oxide matrices were obtained with Al binders. The higher sensitivity that has observed using Al binder was expected as Al-powder served as both electrical and thermal conductor.[12] Al binder also produced a higher temperature from the exothermic reaction with iron oxide on Cs sputtering which enhances the ionization of Pu and Am. The combination of PbF_2 with the co-precipitate of Pu and Am with NdF_3 provided the lowest detection limits for the ^{239,240}Pu and ^{241}Am.

Based on these ^{239,240,242}Pu and ^{241,243}Am measurements by AMS in oxide and fluoride matrices using the same operation conditions with SO-110 Cs sputter source, the fluoride anion beam method gives more than 1 order of magnitude better sensitivity (cps/pg) over the oxide anion method. The only difference in operation conditions is that the production of the oxide anion requires a strong Cs^+ flux. Though similar detection limits for ^{239,240}Pu and ^{241}Am are observed in both methods, the fluoride method does not require the use of a large flux of Cs^+ sputter beam. This is an advantage when the ion source in an AMS system cannot be producing a large Cs^+ beam. Another advantage of using the fluoride matrices is its relatively simple sample preparation steps. Quantitative isotope recovery has been tested for actinide co-precipitation with NdF_3.[5,6,15] This method does not need sample baking at high temperature (700 ^{0}C) where sample loss and inconvenience in sample handling may be a concern.[25]

In this work we also measured ^{239,240,242}Pu and ^{241,243}Am isotopes extracted from certified reference material (IAEA 414), and ^{239,240}Pu and ^{241}Am in standards with known activities using fluoride matrices to validate the separation and the measurement method. The isotope concentrations ranged from 3 fg to 5 pg per target in these measurements (Fig. 1). The measured values of ^{239,240}Pu and ^{241}Am in each case agreed with the certified values. The measured values fall on a 1:1 line within the statistical uncertainty of the measurements (Slope = 0.993 ±0.023 and intercept -0.002 ± 0.047). The external error is shown by the error bars ($\pm\sigma$) in the Fig.1. It was less than the size of most of the symbols shown in Fig.1. The ^{241,243}Am and ^{239,240,242}Pu measurements made in this study using fluoride and oxide anions were compared with published results that used oxide anion beams (Table 4). ^{242}Pu measurement in the present work using oxide mixed with Nb powder produced a sensitivity (9±4 cps/pg), which is in line with the sensitivity reported by most laboratories. Only the ETH laboratory has higher oxide count rates per picogram as the actinide transmission efficiencies were well optimized in the small AMS system developed there.[10,26,27] The count rates measured using the fluoride method are 10 fold greater than those using the oxide method using the same accelerator system at A. E. Lalonde AMS, and comparable to the best values found with the oxide anion beam at ETH. Similar increases in ^{243}Am count rates per picogram using fluoride method over oxide method were also observed in the current study. The measurements of ^{241}Am by AMS is not yet common. Only recently, Christl et al. have reported the measurements of ^{243}Am in iron oxide and titanium oxide in a range of 18.4 to 87.6 cps/pg.[27] The detection limits for ^{239,240}Pu and ^{241}Am are a few femtogram or less in all laboratories (Table 4).

Pu and Am measurements in certified reference material (IAEA 414)

The mixed fish from the Irish Sea and North Sea (IAEA 414) is a certified reference materials with a very low ^{241}Am concentration (0.427 Bq/kg).[28] The measurement of Pu isotopes in environmental samples by AMS has been reported by several laboratories, but there are so far only a few ^{241}Am measurements by AMS.[5,6,25,27] We tested our fluoride procedures by analyzing ^{239,240}Pu and ^{241}Am in this mixed fish sample (Table 5). The measured values obtained by extraction, single column (DGA) separation and detected by AMS using fluoride media, are in excellent agreement with the certified values in the SRM.

Conclusions

AMS measurements of ^{239,240}Pu and ^{241}Am using two different anions, MO^- and MF_4^-, have been systematically studied and compared using the same chemical extraction procedure and AMS system at the A. E. Lalonde AMS Laboratory. Enhancement of Pu and Am ionization and count rates were observed using the fluoride method due to the addition of excess fluorine from the PbF_2 matrices. Higher count rates for ^{243}Am (140±30 cps/pg) open possibilities to measure low (fg/g) levels of Am isotopes.^{239,240}Pu and ^{241}Am in the low level standard reference material (IAEA 414) have been separated using a DGA column and measured using the fluoride precipitation method. The measured concentrations agree well with the certified values.

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Table 1 Comparison of AMS operation conditions for the measurement of Pu and Am by the fluoride and oxide methods using the SO-110 ion source at A. E. Lalonde AMS Laboratory.

Parameter	Fluoride	Oxide
Actinide anions	MF_4^-	MO^-
Cs^+ energy	7 keV	7 keV
Cs^+ flux as indicated by typical $^{12}C^-$ current from graphite target	≤ 2 μA (before inserting 1st PbF_2-matrix target)	≤ 50 μA
Total energy of extracted anions	35 keV	35 keV
Terminal voltage	2.5 MV	2.4 MV
Positive ion detected	M^{3+}	M^{3+}
Low energy beam line transmission efficiency (estimate)	~70%	~70%
Accelerator and high energy main magnet transmission efficiency	~13%	~13%
High energy beam line transmission efficiency after main magnet	~95%	~95%

Table 2 Pu and Am efficiency measured by AMS using oxide and fluoride precipitates dispersed in various binders. Isotope count rates in each target are normalized to 1 fg of the spiked tracer.

Matrices	Sample[a]	Isotopes added/ target, fg		Isotopes measured, cps/fg [b]	
		^{242}Pu	^{243}Am	^{242}Pu	^{243}Am
Iron oxide	Oxide: Al (1:4)	2196	218	0.005±0.001	0.008±0.001
Iron oxide	Oxide: Nb (1:1)	2682	752	0.009±0.004	0.004±0.001
Iron oxide	Oxide: Ag (1:1)	4388	1043	0.005±0.001	0.005±0.001
Fluoride	Fluoride: PbF_2 (1:7)	4708	1225	0.11 ±0.02	0.14±0.03

[a] The ratios are in wt/wt%, [b] Average of 3 targets measured.

Table 3 Pu and Am measured in reagent blanks prepared using oxide and fluoride matrices mixed with Al, Nb and Ag in the weight ratios shown in the table. The uncertainties quoted are within 1σ based on 4 replicates.

Method	Sample	^{239}Pu(fg)	^{240}Pu(fg)	^{241}Am(fg)
Iron oxide	Oxide: Al (1:4)	0.56±0.13	0.17±0.11	0.45±0.09
Iron oxide	Oxide: Nb (1:1)	1.34±0.31	0.25±0.10	0.79±0.22
Iron oxide	Oxide: Ag (1:1)	1.24±0.48	0.34±0.14	0.65±0.31
Fluoride	Fluoride: PbF_2 (1:7)	1.14±0.47	0.57±0.10	0.37±0.09

Table 4 Comparison of AMS measurements of Pu and Am using MF_4^- and MO^- anions. The precisions shown are the relative standard deviations in %.

Parameter	ANU [12]	LLNL [13]	VERA [14,29]	ANSTO [30]	ETH [26, 27]	This study	This study
Ionization method	Oxide anion	Oxide anion	Oxide anion	Oxide anion	Oxide anion	Oxide anion	Fluoride anion
^{242}Pu Sensitivity (cps/pg)	0.24±0.14	-	13.5	-	170	9±4	110±20
^{243}Am Sensitivity (cps/pg)	-	-	-	-	53	8±1	140±30
^{239}Pu Detection Limit (fg)	0.2	0.2	-	3.2	0.4	1.5	1.5
^{240}Pu Detection Limit (fg)	0.5	0.3	-	0.5	0.4	0.5	0.3
^{241}Am Detection Limit (fg)	-	-	-	-	0.12	1.5	0.3
^{239}Pu Precision (%)	7.5	4.6	3.2	3.4	2.4	7.4	0.82
^{240}Pu Precision (%)	9.2	4.6	3.6	3.1	2.1	8.5	1.3
^{241}Am Precision (%)	-	-	-	-	-	6.5	2.3

Table 5 Measurements of Pu and Am in IAEA-414 (Mixed Fish from the Irish Sea and North Sea) by AMS using fluoride matrices following the DGA resin separation. Number of samples, n = 6

Isotope	Measured, mBq/g	Certified, mBq/g
^{239}Pu	0.066± 0.001	0.066± 0.009
^{240}Pu	0.047± 0.004	0.047± 0.003
^{241}Am[a]	0.404± 0.121	0.427± 0.006

[a] Certified value corrected for in growth of ^{241}Am from ^{241}Pu

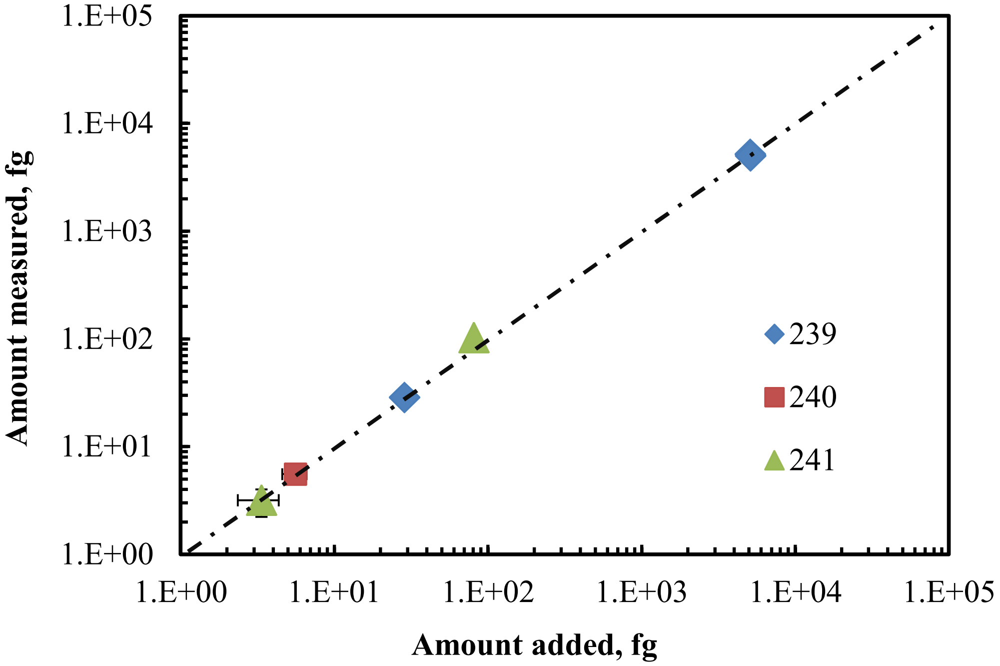

Fig. 1 Measurements of ^{239,240}Pu and ^{241}Am concentrations in standards and certified reference materials (IAEA 414). The data point represents amount of isotope per AMS target. The uncertainty is shown for all samples but it is smaller than the data points for most measurements.

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The co-precipitation of actinides using NdF_3 provides a robust and sensitive alternative method of preparing and analyzing actinide samples by accelerator mass spectrometry