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Integration of a hyphenated HPIC-ICPMS protocol for the measurement of transplutonium isotopic mass distributions for ^{252}Cf campaigns at Oak Ridge National Laboratory

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Abstract
Rapid measurement of transplutonium isotopic mass distributions during ^{252}Cf production campaigns at Oak Ridge National Laboratory is a critical need. Mass measurements for the isotopes of plutonium, americium, curium, and californium are routinely requested to support the α-hydroxy-isobutyrate runs for the purification and recovery of the heavy curium target material and final ^{249}Bk, ^{252}Cf, and ^{254}Es enriched isotope products. This paper presents the integration of an online high-pressure ion chromatography inductively coupled plasma mass spectrometry technique together with the protocol and chemistry that allows for rapid baseline separation and direct quantification of the transplutonium elemental concentrations and isotopic compositions.

Keywords Inductively coupled plasma mass spectrometry · High pressure ion chromatography · Transplutonium · Isotopic analysis · Californium · Berkelium · Einsteinium

Introduction

The High Flux Isotope Reactor (HFIR) uses intense neutron irradiation of mixed americium and heavy curium targets to produce transcurium isotopes. ^{252}Cf, the primary production isotope, is used for industrial, medical, and research applications. Every 2 years, as scheduled, ~ 200 mg of ^{252}Cf is produced together with ~ 20 mg of ^{249}Bk, micrograms of ^{254}Es, and picograms of ^{257}Fm [1]. The original Am/Cm source material, produced via multi-stage irradiation of plutonium at the Savannah River Site, has become rich in the heavy curium isotopes, ^{246}Cm and ^{248}Cm, through decades of activation and recovery cycles. A simplified route of activation pathways and beta-decays for the formation of the key isotopes is shown in Fig. 1, complete with highlighted isobars requiring separation for accurate quantification.

Chemical processing of the irradiated targets initially separates the actinide activation products, as well as the lanthanide fission products, from the remaining fission elements via batch solvent extraction utilizing di-2-ethylhexylphosphoric acid (HDEHP) [2]. This is followed by a lithium chloride-based anion exchange procedure to separate the lanthanides from the actinides [3, 4]. Subsequently, the individual actinides are separated from each other using

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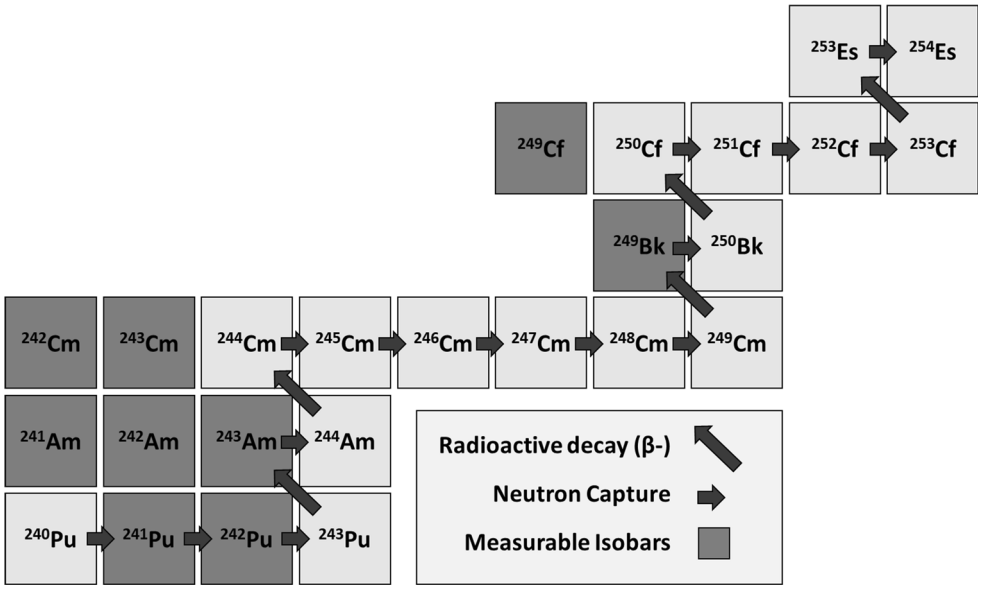

Fig. 1 Evolution chain of the initial plutonium material under neutron irradiation with ICP-MS measurable isobaric isotopes highlighted

α-hydroxyisobutyric acid (α-HIB) cation exchange [5, 6]. Due to the high production costs and short half-lives of these isotopes, optimal recovery is crucial for a successful campaign. The Nuclear Analytical Chemistry and Isotopics Laboratories (NACIL) group, within the Chemical Sciences Division at ORNL, provides the radiochemical analytical support for these campaigns, striving to provide as much data to the production engineers as possible in a short time-frame. As many interferences exist in these complex isotopic and elemental mixtures (notably by the abundant curium isotopes), accurate interpretation of data is imperative. Traditional direct radiochemical measurements [7] are often not sufficient to accurately determine isotopic content of each sample, and thus, inductively coupled plasma mass spectrometry (ICP-MS) coupled with chemical separations is required.

Historically, it has been challenging to achieve baseline resolution using classical analytical gravimetric separation chemistries for the trivalent transcurium elements required to resolve isobaric overlaps and achieve accurate isotopic mass measurements [8–11]. Gourgiotis et al. [12] employed high pressure ion chromatography (HPIC) and demonstrated successful offline separations of curium, californium, and berkelium utilizing similar cation exchange chemistries as described above for chemical processing, using offline collected fractions to determine isotopic compositions. Similar methodologies have also been employed by the NACIL group since ^{252}Cf Campaign 76 (2013), but baseline separation of key isotopes for activity corrections, notably ^{242}Cm and ^{243}Cm, was difficult due to their low abundance and the need for baseline corrections. Determining the isotopic concentration of ^{242}Cm is key for accurate correction of the 6.11 MeV alpha peak to determine ^{252}Cf content in early stages of the separation process. Additionally, polyatomic interferences pose a problem when directly quantifying the isotopic composition and concentration of trace amounts of the heavy actinides Cf, Bk, and Es, the uranium and neptunium oxides being the most problematic. For accurate ^{249}Bk determination by ICP-MS, separation from the heavily abundant ^{249}Cf isotope is vital.

In this paper, by using hyphenated HPIC-ICPMS in conjunction with peak smoothing and fitting (available in the Thermo-Fisher Scientific™ Qtegra™ software), we show that online separations with direct isotopic analyses via determination of chromatogram peak areas is possible, reducing both the sample volume and analysis time required, in addition to the method detection limits. When coupled with certified plutonium and americium standards, the method can also be used to yield elemental concentrations, as well as isotopic compositions. This method has given the NACIL group a powerful analytical capability to provide rapid response during fast paced production campaigns to deliver these rare, and short-lived, isotope products.

Experimental

Equipment and software

A Thermo Scientific Dionex™ ICS-5000 + HPIC system coupled to a Thermo Scientific iCAP™ Q ICP-MS located in a radiological fume hood was used for this work (see Fig. 2). The HPIC system is comprised of an AS-AP autosampler, a gradient mixing pump (capable of

Fig. 2 Photo of the coupled HPIC-ICPMS system in a radiological fume hood

combining four different eluents in the same analysis), and a thermal compartment containing the injection loop and separation column, maintained at 35 °C for constant elution times and reproducibility. The ICP-MS employed a PFA-HS (Elemental scientific) nebulizer capable of nebulizing solutions of higher density and flow rates.

The HPIC-ICPMS method employs Thermo Scientific Qtegra Intelligent Scientific Data Solution^{TM} (ISDS) platform software. Qtegra ISDS utilizes peripheral drivers from Thermo Scientific Chromeleon^{TM} Chromatography Data System, enabling the simultaneous control of the ICP-MS and HPIC. The Chromeleon script used for the developed separation scheme is detailed in the ESI Appendix A. The chromatographic peak fitting and smoothing values used to determine peak area, found within the "Peak Detection" settings of the Qtegra software, can be found in the ESI Appendix B.

Reagents and standards

The eluent for the HPIC separation was prepared with trace metals basis grade chemicals and ultrapure water (18.2 MΩ cm) from a Millipore Milli-Q^{TM} water purification system (Millipore). Oxalic acid ($C_2H_2O_4$) (100 mM, 99.999% trace metals basis, Sigma-Aldrich Co) was dissolved in ultrapure water then buffered with ammonium hydroxide (NH_4OH) (20–22% as NH_3, Trace Metal Grade, Fisher Scientific) to a final pH of 4.5–4.7. The use of ammonium hydroxide as opposed to the traditional lithium and potassium hydroxide resulted in a "salt-less" eluent more suitable for analysis by ICP-MS. All samples containing plutonium were treated with hydroxylammonium nitrate ($NH_3OH.NO_3$) (24 wt% solution in H_2O, 99.999%, Sigma Aldrich).

A mixed actinide sample of plutonium, americium, curium, berkelium, californium, and einsteinium was prepared using process samples from the Cf-252 campaign 78 (completed in 2017). A mixed Pu/Am/Cm process sample, a purified ^{249}Bk sample, and a purified ^{253}Es/^{254}Es sample were combined with an in-house certified ^{249}Cf/^{251}Cf isotopic standard to ensure all actinides were at a detectible level. The isotopes monitored in the separation scheme and their predetermined isotopic abundances are given in Table 1.

Isotopic and separation QA standards were CRM-137, a certified plutonium isotopic standard (NBL, unseparated from ^{241}Am ingrowth), an in-house verified americium working reference material (WRM) comprised of ^{243}Am (counting standard, Eckert and Zeigler Isotope Products, concentration verified via isotope dilution using a Thermo Fisher Neptune multi-collector MC-ICP-MS, an in-house verified ^{241}Am source, and an in-house verified ^{249}Cf/^{251}Cf isotopic WRM standard. Data from an americium/curium "rework" sample for ^{242}Pu/Am/Cm and ^{243}Am/Cm is also reported.

Separation scheme

Samples were injected onto a Dionex CS5A column (fitted with a CG5A guard column) via a 50 µL injection loop. The CS5A column is a next generation, duel functionality column with mixed sulfonic acid cation exchange sites and tetra-alkylammonium anion exchange sites and a loading capacity of 40 µequivalents/column. Each injected sample was separated using a 40-min isocratic elution profile using oxalic acid (100 mM, buffered to pH 4.5–4.7 with NH_3OH) at a flow rate of 1 mL min^{-1}. Post column, an inline t-piece allowed for the eluent to be acidified by a pumped addition of 2 M HNO_3 at a flow rate of 0.1 mL min^{-1} prior to nebulization and analysis via ICP-MS.

Results and discussion

Actinide separation

The isocratic oxalic acid (100 mM) separation scheme was chosen for the efficient separation of plutonium, americium,

Table 1 The measured isotopes of plutonium, americium, curium, berkelium, californium, and einsteinium with their predetermined isotopic abundances

Plutonium (atom%)[a]	Americium (atom%)	Curium (atom%)	Berkelium (atom%)	Californium (atom%)	Einsteinium (atom%)[b]
^{240}Pu (100)	^{241}Am (9.9)	^{244}Cm (77.1)	^{249}Bk (100)	^{249}Cf (52.2)	^{253}Es (~ 96%)
	^{243}Am (90.9)	^{245}Cm (8.1)		^{250}Cf (11.9)	^{254}Es (~ 4%)
		^{246}Cm (13.5)		^{251}Cf (35.9)	
		^{247}Cm (0.3)			
		^{248}Cm (1.0)			

[a]Decay product from ^{244}Cm monitored only

bDue to short half-life of ^{253}Es exact isotopic contributions are given as estimates at time of mixing

curium, berkelium, californium, and einsteinium, in addition to acquiring consistent gaussian peak shapes and minimal peak tailing. The trivalent actinides likely elute as the $[Ac^{3+}(C_2O_4^{2-})_2]^-$ anions, which have been shown to readily form [13], although $[Ac^{3+}(C_2O_4^{2-})_3]^{3-}$ species have also been reported [13]. Plutonium is the exception, with a readily available Pu(IV) oxidation state—it is known to easily oxidize in oxalate solutions [14]. This will likely result in plutonium forming the $[Pu^{4+}(C_2O_4^{2-})_2]$ neutral species as soon as it is injected onto the column, having been removed from the reducing environment of the hydroxylamine nitrate. Figure 3 illustrates the elution profile of the mixed Pu/Am/Cm/Bk/Cf/Es sample, with single *m/z* traces for each element highlighted for figure clarity.

The actinides eluted as expected, in order of decreasing ionic radii: Pu, Cm, Am, Bk, Cf, then Es. Six individual injections were analyzed, limited by the quantity of einsteinium and berkelium available for this study. The elution times, defined as the time the peak apex was measured, and 2σ standard deviation uncertainties of the six replicate injections were; plutonium 101(1) s, americium 899(7) s, curium 1027(6) s, berkelium 1594(7) s, californium 1907(5) s, and einsteinium 2056(10) s. These elution times, however, will be heavily dependent on the pH of the oxalic acid eluent. Figure 4 shows the 6 individual chromatographic peaks attributed to ^{144}Cm indicating, not only the reproducibility in peak retention times, but also of peak shape and height. The uncertainty of the peak area is largely dependent on the 50 µL sample injection loop and the concentration of the isotope in the sample.

Using peak area for online isotopic analysis

The isotopic compositions of the separated actinides were quantified via the calculated peak areas from the chromatogram. Figure 5 shows the individual chromatograms for the americium, curium, and californium masses, after chromatogram smoothing and defining the retention time of each element the Qtegra peak fitting software calculates the peak areas, which can then be compared.

The method reproducibility was assessed to determine the precision of the analysis. The precision is defined as the 2σ standard deviation of six replicates over the period of 3 days. As can been seen in Table 2, a 1–2% precision was obtained for the major isotope ratios of americium, curium,

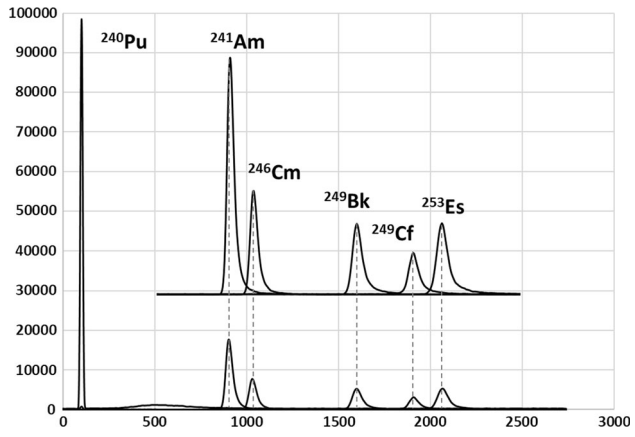

Fig. 3 The elemental separation of plutonium (^{240}Pu), americium (^{241}Am), curium (^{246}Cm), berkelium (^{249}Bk), californium (^{249}Cf), and einsteinium (^{253}Es)

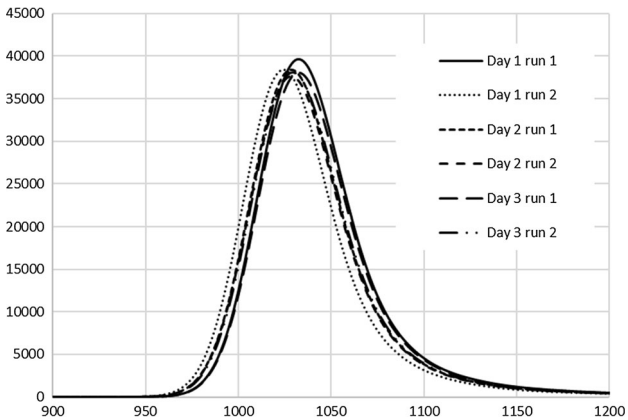

Fig. 4 The 6 individual *m/z* 144 chromatograms for peak at *t* = 1027 (^{144}Cm)

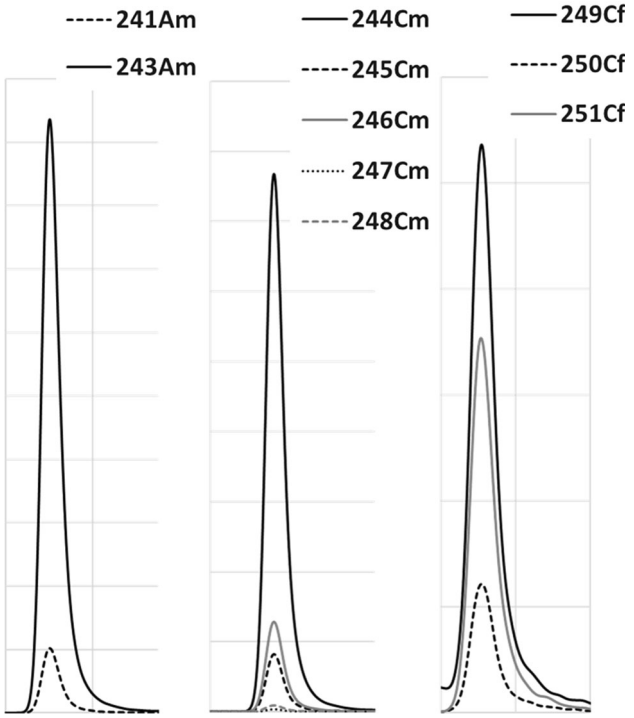

Fig. 5 Peaks for the individual chromatograms for *m/z* 241 and 243 at t = 899 (left), *m/z* 244, 245, 246, 247, and 248 at t = 1027 (center), and *m/z* 249, 250 and 251 at t = 1907 (right). Determined to be americium, curium, and californium respectively

Table 2 The measured isotopic ratios for americium, curium, and californium, with the calculated 2σ uncertainties for 6 replicates measured over 3 days

Isotope ratio	Average measured ratio (2σ STD)
^{241}Am/^{243}Am	0.109(1)
^{254}Cm/^{244}Cm	0.108(2)
^{246}Cm/^{244}Cm	0.170(3)
^{247}Cm/^{244}Cm	0.0045(3)
^{248}Cm/^{244}Cm	0.0113(3)
^{250}Cf/^{249}Cf	0.236(5)
^{251}Cf/^{249}Cf	0.704(6)

and californium. Also, good recovery was observed for the in-house certified standards, with ^{241}Am/^{243}Am being 101(2)%, and ^{249}Cf/^{251}Cf being 100(1)%.

Decay-corrected isotopic analysis of einsteinium

Due to the short half-lives of ^{253}Es and ^{254}Es, over the 48 h analysis period, it was not possible to use standard deviation of the replicates to assign uncertainties. To calculate recoveries, the first determined isotopic ratio was termed T = 0, and a decay-corrected ratio was calculated for each

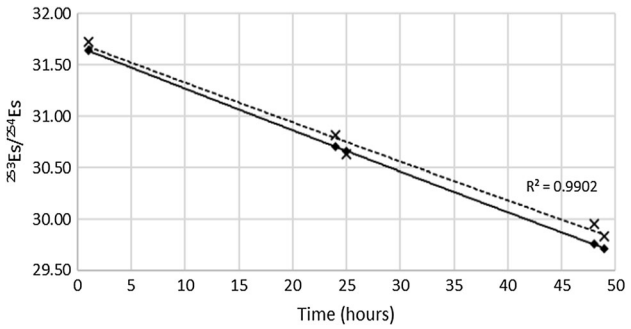

Fig. 6 The calculated (◆) and observed (×) ^{253}Es/^{254}Es ratios for each of the six replicates plotted against the time of analysis2

analysis time, based on the half-lives of ^{253}Es and ^{254}Es [20.47(3) and 275.7(5) days, respectively]. Figure 6 depicts the calculated vs. observed ^{253}Es/^{254}Es ratio over time, with recoveries ranging from 99 to 101%. For each injection, the mass of ^{253}Es and ^{254}Es analyzed was ∼ 5 pg and 250 fg, respectively.

Online concentration analysis of Berkelium

The concentration of the ^{249}Bk in the separated actinides was quantified via use of standard bracketing, using the ^{243}Am tracible standard and a semiquantitative approach with the resulting peak areas. Given that the ICP-MS response to the high mass elements have been determined to be equal (flat response curve in the high mass region) the approach of employing an actinide with similar chemistry and ionization efficiency has been used within the NACIL group for over a decade for direct concentration analysis of actinides. Previous applications include analyses ranging from ^{225}Ac to ^{252}Cf, as a secondary measurement, to the primary radiochemical mass determinations using activity yielding recoveries of > 95%. The recovery of berkelium for the separated test samples was 98(6)%, based off an offline concentration of the purified ^{249}Bk source, determined using liquid scintillation counting and gross beta analysis, verified via semi-quantitative standard bracketing ICP-MS.

Certified reference material analysis

An unseparated CRM-137 plutonium isotopic standard, with ca. 2 wt% ^{241}Am ingrowth, was used as an isotopic and separation laboratory quality control to bracket the samples and monitor whether a mass bias is observable using the online isotopic analysis. Table 3 displays the average measured isotopic ratios, with 2σ standard deviation recoeries, for six replicate standards. The major ratio, ^{239}Pu/^{240}Pu, showed an uncertaianty comparable to that of the major ratios observed for americium, curium and

Table 3 The measured isotopic ratios for the separated CRM-137 plutonium fraction, with the calculated 2σ uncertainties for six replicates measured over 3 days

	Atom%	Ratio	Averaged measured ratio (CRM-137)	Decay corrected certificate value ratio (CRM-137)	Recovery from certificate value (2σ STD)
^{238}Pu	0.21	238/240	0.0111	0.0112	99(3)%
^{239}Pu	79.19	239/240	4.17	4.15	100(1)%
^{240}Pu	18.87				
^{241}Pu	0.49	241/240	0.0259	0.0257	101(2)%
^{242}Pu	1.24	242/240	0.0651	0.0649	100(3)%

Table 4 The measured isotopic ratios for the separated *m*/*z* 242 and 243 peaks relative to the major isotope, with calculated 2σ uncertainties for six replicates measured over 3 days also given

Isotope ratio	Average measured ratio (2σ STD)
^{242}Cm/^{244}Cm	0.000164(6)
^{243}Cm/^{244}Cm	0.00034(3)
^{242}Am/^{243}Am	0.00026(1)
^{242}Pu/^{240}Pu	0.010(1)

californium in the sample (^{241}Am/^{243}Am, ^{246}Cm/^{244}Cm, and ^{251}Cf/^{249}Cf). No measurable mass bias is observed, and good recovery is shown for isotopes with < 1 atom% contribution.

Proof of concept analyses

This method was applied to analyze the isotopic composition of the recycled Cm/Am target material from Campaign 78 in December of 2017. Six samples of oxide were dissolved and analyzed using the developed separation and direct isotopic analysis method. The 2σ STD uncertainties for the major isotopes were ∼ 1–2% for americium, curium and plutonium with the Cm: Am: Pu mass ratio of 150:10:1. Table 4 shows the measured ratios for the *m*/*z* 242 and 243 isotopes, with the chromatogram of the *m*/*z* 242 trace illustrated in Fig. 7. Even at these low levels (the injection masses for the 242 isotopes were ∼ 250 fg ^{242}Pu and ^{242}Am, and ∼ 500 fg ^{242}Cm), the peaks are well defined with clear separation. The uncertainties for the isotopic ratios for the triplicate analysis reflect the low isotopic abundance of these analytes.

The mixed Cm/Am (with trace plutonium) oxides were also analyzed via traditional radiochemical methods, yielding pulsed alpha ratios for ^{242}Cm (6.11 MeV) and ^{244}Cm (5.80 MeV), as well as a gamma number for ^{243}Cm. After an activity to mass conversion, the ^{242}Cm/^{244}Cm ratio was determined to be 0.00018(1) and the ^{243}Cm/^{244}Cm ratio to be 0.00034(7). The online isotopic data were acquired 10–12 days after the radiochemical isotopic data, and the ^{243}Cm/^{244}Cm ratios show good agreement. A 12-day decay correction to the radiochemical data yields a ^{242}Cm/^{244}Cm ratio of 0.00017(1), which is well within the statistical uncertainty of the 0.000164(6) observed using this method.

Conclusions

The timely and precise measurement of the isotopic compositions of the actinides, in particular those for americium, curium and californium, was the primary goal of this work. What once took the NACIL labs up to a week to achieve via manual cartridge-based resin separations, followed by offline isotopic measurement by ICP-MS (involving multiple manual isotopic corrections due to inefficient separations), can now be done in under an hour. The amount of material required is smaller, the dose exposure of the operator is significantly reduced, and the method is 1–2

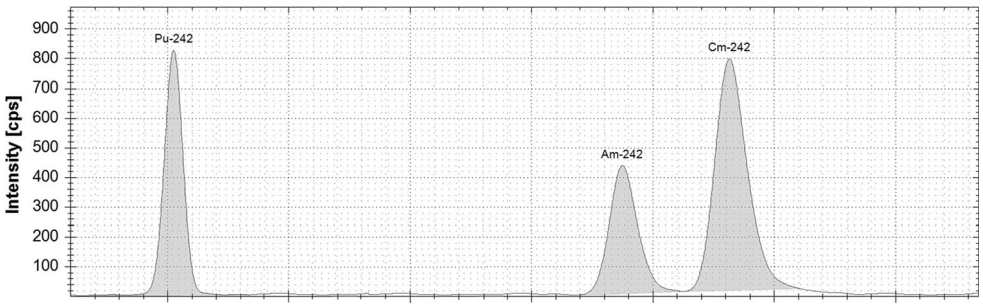

Fig. 7 The *m*/*z* 242 chromatogram with the elementally separated ^{242}Pu, ^{242}Am, and ^{242}Cm peaks

orders of magnitude more sensitive, depending on the nature of the sample.

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