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Technical Note:

An Alternative Method for Chronometric Determinations Involving Curium

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Abstract

A method for quantifying ratios of isotopes of plutonium (Pu), americium (Am), and curium (Cm) using inductively coupled plasma mass spectrometry (ICP-MS) is described that does not require radiochemical separations or a chemical yield monitor. This approach provides more rapid analysis, which is important for chronometric applications related to nuclear forensics analysis. To demonstrate its utility, we used it to quantify the ingrowth ^{240}Pu ($t_{1/2}$ = 6563 years) from ^{244}Cm ($t_{1/2}$ = 18.10 years) in a solution of unknown “age” (e.g. time since last separation). Results are compared to similar samples for which the time since separation was known. In addition, alpha spectrometry was used to validate the ICP-MS measurements. In this case, ^{238}Pu and ^{241}Am were used as chemical yield monitors for ^{240}Pu and ^{244}Cm, respectively. The relative standard deviation for the isotope ratio method using ICP-MS was slightly greater than the traditional radiometric approach, but sufficient for this application. Measured activity ratios of ^{240}Pu and ^{244}Cm provided an age for the unknown sample that linked it to research activities involving the production of curium isotopes for thermoelectric heat sources during the late 1970’s.

1.0 Introduction

Simultaneous measurement of plutonium and trans-plutonium isotopes is necessary for applications ranging from environmental monitoring and radioactive waste management,[1 2 3 4 5 6] to nuclear forensics and nuclear safeguards,[7 8 9 10] to bioassay,[11 12 13] and basic nuclear physics research.[14 15 16 17] While traditional radiometric methods using yield tracers provide quantitative isotopic information, they typically require labor intensive separations that can reduce overall sample throughput for routine analyses. Using isotope ratio approaches, atomic spectrometry via inductively coupled plasma mass spectrometry (ICP-MS) offers an opportunity to provide isotopic information with reduce sample processing time. However, technical details for such methods involving the trans-plutonium isotopes are limited. In addition, reference materials to validate methods for these elements and isotopes are generally not available.

To support research activities on minor actinide transmutation and actinide neutron cross section measurements, Gourgitis et al. reported on the quantification of isotopic signatures for curium (Cm), californium (Cf), and berkelium (Bk) in a matrix dominated by Cm using quadrupole ICP-MS; they obtained very low uncertainties for Cm as required for this application.[14 18] One of the primary contributors to the uncertainty was hydride formation, which they successfully addressed. Similarly, Krachler et al recently reported an atomic spectrometry method for determination of americium (Am) in the presence of Cm and plutonium (Pu) in spent nuclear fuel matrices using a combination of inductively coupled plasma optical emission spectrometry (ICP-OES) and sector field ICP-MS.7 In the absence of a certified reference material for Cm, they validated their results using traditional radioanalytical chemistry.

The sample matrices for these ICP-MS methods are unique nuclear materials that, while challenging from a sample analysis perspective, are not representative of the broader array of sample matrices expected for environmental monitoring and nuclear forensics. In addition, some of these applications are more tolerant of larger analytical uncertainties. Rather, minimized analytical uncertainty must sometimes be balanced against increased sample throughput. One example of a nuclear forensics application is the estimation of the time since separation of a parent radionuclide from its progeny. Such determinations can be useful in elucidating the source and age of unknown legacy radioactive materials.[19 20 21 22] For the actinide isotopes, such common radiogenic relationships include ^{244}Cm and ^{240}Pu (α-decay, $t_{1/2}$ = 18.10 years), ^{241}Pu and ^{241}Am (β-decay, $t_{1/2}$ = 14.35 years), and ^{241}Am and ^{237}Np (α-decay, $t_{1/2}$ = 432.2 years). Although these progenitor relationships are well known, we know of no previous publications in the open literature of their application to nuclear forensics, age dating, and determination of provenance. Knowledge of the activities or number of atoms of both the parent and progenitor radionuclides allows determination of the time since separation between the radiogenic pairs, assuming the activity of the progeny is zero immediately following separation. Furthermore, the use of activity ratios of isotope pairs in such radiogenic relationships allows bypass of specific isotope quantification, which can speed overall analysis time.

In this study, the parent-progenitor relationship between ^{244}Cm and ^{240}Pu for three samples has been determined; two of the samples were of known origin whereas the origin of the third was unknown. The decay diagram for ^{243}Cm and ^{244}Cm are provided in the Electronic Supplementary Information (ESI) accompanying this paper (Figure ESI-1). At the time of acquisition, the provenance of the unknown sample was in question, but believed to be linked to research activities dating back to the 1970's on the potential use of ^{244}Cm as a thermoelectric heat source for deep space exploration and as an intermediate target for ^{252}Cf production; historical details about these research activities are provided in the ESI. The solutions studied were chemically pure, allowing reliance on a single parent-daughter relationship (e.g. ^{244}Cm and ^{240}Pu). For two of these solutions, this single relationship was investigated by two separate analytical methods: radiochemical separation followed by alpha spectrometry and isotope ratio ICP-MS determination. One of these two solutions had known quantities of ^{244}Cm, allowing us to validate our method, similar to the approach of Krachler et al.7. This method offers distinct advantages over traditional radiochemical analysis as it does not require radiochemical separations or a chemical yield monitor, allowing for more efficient overall sample processing.

2.0 Experimental

2.1 Samples and reagents

Three different ^{244}Cm solutions were used in this study. The first one was a solution that was received from the Savannah River Site (Savannah River National Laboratory, SC) and had been stored in the laboratory for decades, with no information about the last separation date or the isotopic composition. This solution was the unknown, and is referred to as Sample 1. The second was a Standard Reference Material (SRM 4320A) obtained from NIST (National Institute of Standards and Technology, Gaithersburg, MD). This was a ^{244}Cm radioactivity standard solution for which the massic activity of Cm and the reference date for separation were well known; however, the reported quantity of ^{240}Pu had an associated relative standard deviation (RSD) of approximately 50%. This SRM is no longer available from NIST so that ^{240}Pu could not be re-measured to reduce this uncertainty. Although the ^{240}Pu uncertainty was somewhat large, such samples containing transplutonium isotopes are rare, and it served as a useful sample for testing this chronometric method. This solution is referred to as Sample 2. The third ^{244}Cm solution was obtained from Eckert & Ziegler Analytics (Atlanta, GA), and the isotopic composition of this sample was well known [Eckert & Ziegler Analytics, personal communication], although the reported activities were not certified values. Since no isotopic standard for curium was commercially available at the time of this study, this third sample served as an informal reference material for our work, and is referred to as Sample 3. All reagents used in this study were of analytical grade and used without further purification. Deionized water was purified with LABCONCO Water Pro PS system (Kansas City, MO).

2.2 Sample preparation

For the ICP-MS method, Cm solutions were diluted by volume with 2 M nitric acid (JT Baker) and stored in 2 mL plastic vials for ICP-MS analysis. Three different dilutions were prepared, and analyzed in duplicate (i.e., total of 6 samples). A 2 M nitric acid solution was used as a blank solution to correct for background. For the alpha spectrometry method, Cm solutions were mixed with known quantities of tracers in glass beakers, then evaporated to dryness. After drying, the solutions were re-dissolved in 10 mL of 3M nitric acid. Sodium nitrite ($NaNO_2$, 200 mg) was added to each beaker 30 minutes prior to chromatographic separation to adjust the oxidation state of Pu to +IV.

2.3 ICP-MS method

Triplicate samples were prepared for the unknown sample (Sample 1) and the informal standard (Sample 3). Each of the triplicate samples were measured twice by ICP-MS. Uncertainties represent contributions from analysis of multiple samples and dilution (pipetting and weighing).

A Thermo Finnigan Element 2 sector field ICP-MS (Thermo Electron Corp., Bremen, Germany) was used for ICP-MS. The solution was introduced to the system using a 100 µL / min PFA microflow nebulizer (Elemental Scientific, Inc.). The operating parameters are summarized in Table 1. The tubing was washed with 2 M nitric acid for 60 s between samples. Each isotope abundance was measured by monitoring m/z from 238 through 246; counts were monitored for 100 times and the average was recorded. To address the concern of hydride formation identified by Guorgiotis et al, 2010,7 a uranium standard solution was also analyzed at least once daily using identical instrumental conditions to calculate the rate of ^{238}U + ^{1}H hydride formation; the rate was determined to be 0.006% for U+H (m/z = 239), and 0.002% for U+H2 (m/z = 240). Counts in all samples or channels were corrected using this rate.

2.4 Alpha spectrometry method

For alpha spectrometry, all three samples were analyzed. Samples were prepared in duplicate and analyzed once. As with the ICP-MS measurements, reported uncertainties represent contributions from analysis of multiple samples and dilution (pipetting and weighing).

^{244}Cm and its daughter, ^{240}Pu, were separated by extraction chromatography (TRU resin, Eichrom) using a published procedure.[23] ^{241}Am and ^{238}Pu were used as tracers to monitor chemical yields of ^{244}Cm and ^{240}Pu, respectively. Both Am and Cm are trivalent in acidic solution, making ^{241}Am an appropriate yield monitor for ^{240}Cm. Sample solutions were loaded onto TRU columns preconditioned with 3 M nitric acid. Beakers were rinsed three times with 3 M nitric acid and transferred to the column once the previous solution drained, and columns were subsequently washed with 10 mL of 3 M nitric acid.

Am and Cm were eluted from the column with 20 mL of 4 M hydrochloric acid, and then Pu was eluted with 10 mL of 0.1 M ammonium bioxalate solution. Each fraction was then evaporated to dryness, wet ashed with nitric acid and perchloric acid, and re-dissolved in 1 M hydrochloric acid. Neodymium carrier (75 µg) was added to the solution, and actinides were precipitated as fluoride salts using hydrofluoric acid.[24] Precipitates were filtered through 0.1 um filters (Pall Corporation, Michigan) and activities were measured using an ORTEC OCTETE Plus alpha spectrometry system (ORTEC, Oak Ridge, TN). Most samples were counted for as long as 2 days, depending on the activity level. The alpha peaks used to determine activities are 5485 keV for ^{241}Am, 5805 keV for ^{244}Cm, 5499 keV for ^{238}Pu, 5168 keV for ^{240}Pu. Background activities were also determined by counting with the chamber empty over a period of several months; background activities were subtracted from each spectrum before calculating final activity values.

Since ^{241}Am and ^{238}Pu have similar peak alpha energies, they cannot be resolved with alpha spectrometry. Therefore, Am and Pu must be separated from each other before measuring alpha activities. However, when incomplete separation happens, bleeding of Am/Cm into the Pu fraction requires correction. In this experiment, correction was done by calculation in following way. First, the activity ratio of ^{241}Am to ^{244}Cm was determined from alpha spectrum of Am/Cm fraction. Second, using that activity ratio, ^{241}Am counts underneath the ^{238}Pu peak were calculated based on ^{244}Cm counts in Pu fraction spectrum. Then, the ^{241}Am contribution to ^{238}Pu peak was subtracted.

3.0 Results and Discussions

ICP-MS results for Samples 1 and 3 are shown in Tables 2a and 2b. No chemical separation was done on the solution prior to ICP-MS analysis as initial alpha spectrometry screening indicated that no activity other than ^{244}Cm and ^{240}Pu was present in the sample solution. Therefore, we assume that all counts at mass 244 are due to ^{244}Cm, and counts observed in the 240 mass window are due to its daughter, ^{240}Pu. Table 3 shows the ratio of mass 240 to mass 244 determined by ICP-MS for Samples 1 and 3; Table 4 shows the activity ratio of ^{240}Pu/^{244}Cm for all three samples as determined by alpha spectrometry.

Alpha spectra for the Am/Cm and Pu fractions in this work are available in the ESI accompanying this manuscript (Figures ESI-2a and ESI-2b). Because ^{241}Am was added as a tracer and its activity is known, the activity of ^{244}Cm can be calculated using equation 1 below, where A is the activity, S is the area of the peak, subscript T is tracer.

$$A = \frac{S}{S_T} A_T \qquad (1)$$

Similarly, the activity of ^{240}Pu can be calculated using the areas of the ^{240}Pu and ^{238}Pu peaks in the alpha spectra and the known activity of the ^{238}Pu tracer. From the activity ratio of ^{240}Pu and ^{244}Cm determined in this way, the time after separation can be calculated based on radioactive decay equations (e.g., 2 and 3, below):

Parent: $$A_{Cm} = A^0_{Cm} \exp(-\lambda_{Cm} t) \qquad (2)$$

Progenitor: $$A_{Pu} = A^0_{Cm} \frac{\lambda_{Pu}}{\lambda_{Pu} - \lambda_{Cm}} \{\exp(-\lambda_{Cm} t) - \exp(-\lambda_{Pu} t)\} + A^0_{Pu} \exp(-\lambda_{Pu} t) \qquad (3)$$

where A_{Cm} and A_{Pu} are the activities of atoms of Cm and Pu respectively, λ_{Cm} and λ_{Pu} are the relevant decay constants, and t is the time after the last parent/daughter separation. Combining these two equations, the time after separation, t, can be calculated by equation 4:

$$t = \frac{\ln\left(1 - \frac{\lambda_{Pu} - \lambda_{Cm}}{\lambda_{Pu}} \frac{A_{Pu}}{A_{Cm}}\right)}{\lambda_{Cm} - \lambda_{Pu}} \qquad (4)$$

Estimated elapsed time since separation for each sample is shown in Table 4. In each case, the reported uncertainty in the time estimates represents the propagation of error as recommended by Pomme at al., 2014.[25] The uncertainties use for the half-lives of ^{240}Pu and ^{244}Cm were taken from the certificate for Sample 2, NIST SRM 4320A; they were 0.4% for ^{240}Pu and 1.2% for ^{244}Cm.

Confidence in our chronometric method is gained by examining the results for the second sample, e.g. NIST SRM 4320A. The activities reported in the NIST certificate were 37.06 ± 0.25 Bq/g for ^{244}Cm and 0.22 ± 0.11 Bq/g for ^{240}Pu. Using these values, the time after separation can be calculated to be 36 ± 8 years, with the reference date of February 15, 2002. The value we obtain using our alpha spectrometry results is 28 ± 16 years, which is consistent with the information provided by NIST. The large uncertainties for age estimates using our measurements are attributed primarily to the large RSD for ^{240}Pu measured by alpha spectrometry.

For the third sample in which the isotopic composition was known (e.g. our informal reference sample), the calculated time after separation matches well with the information provided by the supplier, regardless of the analytical method used, providing additional confidence in our method. Results by both ICP-MS and alpha spectrometry methods were within uncertainty of each other, and the RSD for each method is less than 10%. This low RSD, and agreement between two independent methods provides confidence in using this sample as an informal reference material for corroboration of our method. We are reluctant to consider the method fully validated until after testing with a standard reference material (which is currently unavailable) is completed.

Using this approach and propagating all associated uncertainties, the time after separation for the unknown sample (Sample 1) was estimated to be 33 ± 3 years by ICP-MS and 35 ± 2 years by alpha spectrometry. Both alpha spectrometry and ICP-MS provide the same result, although a smaller estimate of uncertainty was obtained for isotopic quantification via alpha spectrometry compared to isotopic ratios obtained by ICP-MS. Although the estimated uncertainty was slightly greater using atomic spectrometry, it was sufficient for our purposes and the isotope ratio method by ICP-MS is less laborious than using alpha spectrometry.

4.0 Conclusions

In this paper, two analytical methods have been used to measure parent-progenitor isotopes for ^{244}Cm decay that enabled estimation of the time elapsed since last chemical separation, e.g. the age of the solutions. Calculated ages from both methods match with the known age for two reference solutions, providing confidence in our analytical methods. The age of an unknown sample was determined using the same approach. The estimated date of separation for the unknown sample (mid 1970's) corresponds to historical Savannah River Site records documenting a time period for an exploratory curium production campaign. While both alpha spectrometry and atomic spectrometry yielded similar results, the ICP-MS method involves no chemical separation and does not require a chemical yield monitor. This is a significant advantage over the traditional radiochemical method.

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Table 1. ICP-MS operating parameters. Instrument used was a Thermo Finnigan Element 2.

Plasma power	1250 W
Nebulizer gas flow rate	1.05 L / min
Auxiliary gas flow	1 L / min
Plasma gas flow	16 L / min
Interface cones	Ni
Monitored Masses	238, 239, 240, 241, 242, 243, 244, 245, 246
Dwell time	0.01
Number of points per peak	10
Detector dead time	19 ns
Number of passes	10
Number of runs	10
Resolution setting	Low (resolution ~ 300)

Table 2. Isotopic composition of curium containing solutions analyzed by ICP-MS. *Table 2a* corresponds to Sample 1, which was a legacy solution of unknown provenance and storage time. *Table 2b* corresponds to Sample 3, which is the well characterized solution provided by the supplier, Eckert & Ziegler Analytics. This sample served as an informal standard.

2a

Sample 1, Unknown	^{243}Cm	^{244}Cm	^{245}Cm	^{246}Cm
Atom %	5.6	77.5	2.7	14.2
RSD (k=1)	5.9	1.0	11	1.9
Activity %	4.3	95.6	0.01	0.07

2b

Sample 3, Informal Standard	^{243}Cm	^{244}Cm	^{245}Cm	^{246}Cm
Atom %	3.1	79.8	2.7	14.4
RSD (k=1)	4.4	3.2	4.1	2.1
Activity % determined in this study	2.3	96.1	0.007	0.07
Activity % provided by the supplier	N/P	N/P	0.00697	0.06720

N/P: Not Provided

Table 3. Ratios of masses 240 and 244, as determined by ICP-MS, based on data reported in Table 2. Sample 1 is the legacy solution of unknown provenance and storage time; Sample 3 is the well characterized solution provided by the supplier, Eckert & Ziegler Analytics. This sample served as an informal standard.

	Sample 1, Unknown	Sample 3, Informal Standard
^{240}Pu/^{244}Cm Atom Ratio	2.582	0.584
^{240}Pu/^{244}Cm Activity Ratio	0.0071	0.0016
RSD (k=1)	16	7.3
Time after separation (years) determined in this study	33 ± 3	12.5 ± 1.8
Actual time after separation provided by the supplier	Unknown	12 years 1 month

Table 4. Isotopic ratios of ^{240}Pu/^{244}Cm for all three samples, as determined by alpha spectrometry. Sample 1 is the legacy solution of unknown provenance and storage time. Sample 2 is NIST SRM 4320A. Sample 3 is the well characterized solution provided by Eckert & Ziegler Analytics that served as an informal standard.

	Sample 1 Unknown	Sample 2 NIST SRM 4320A[1]	Sample 3 Informal Standard
^{240}Pu/^{244}Cm Activity Ratio	0.0077 ± 0.0005	0.0052 ± 0.0030	0.0017 ± 0.0001
RSD	6.9	7.4	8.6
Estimated time after separation (years)	35 ± 2	28 ± 16	12.5 ± 1.8
^{240}Pu/^{244}Cm Activity Ratio	0.0071	0.006 ± 0.003 [2]	0.0016
Actual time after separation (years)		36±8 [2]	12.1 [3]

1 Reference date provided by NIST: 2/15/2002

2 Calculated based on provided ^{244}Cm and ^{240}Pu activities.

3 Information provided by the supplier, Eckert & Ziegler Analytics.

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