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Analytical Chemistry Developmental Work Using a ^{243}Am Solution

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Introduction

Certified and working reference materials (CRMs and WRMs) of americium are needed to provide support to the LANL project for the production of $^{241}AmO_2$ for industrial use. Two recent reports (1,2), describe the plans for production; the first one provides the AmO_2 product material specifications and the second one describes the requirements for NIST traceable reference materials needed for certifying the product.

This project seeks to reestablish our analytical capability to characterize Am bulk material and develop a reference material suitable to characterizing the purity and assay of ^{241}Am oxide for industrial use. The tasks associated with this phase of the project included conducting initial separations experiments, developing thermal ionization mass spectrometry capability using the ^{243}Am isotope as an isotope dilution spike, optimizing the spike for the determination of ^{241}Pu-^{241}Am radiochemistry, and, additionally, developing and testing a methodology which can detect trace to ultra-trace levels of Pu (both assay and isotopics) in bulk Am samples.

Presently, there is no NIST traceable bulk Am mass spectrometry standard suitable for isotopic distribution determinations or assay by isotope dilution. The same applies to ultra-trace Pu in bulk Am samples. Unless there is a method that is developed, tested, validated and qualified, it cannot be applied to characterization of reference materials. Independently, methods such as radiochemistry will be used to validate the results for reference material characterization efforts.

To assist in developing the aforementioned analytical capability, an ^{243}Americium oxide powder was procured from the National Isotope Development Center (NIDC) at Oak Ridge National Laboratory (ORNL) to evaluate our ability to determine isotopic compositions and assay values within that matrix, for both Am and Pu (Pu is present both as an impurity and as a decay product of ^{243}Am). The material was received, dissolved, transferred to a dilution bottle, and experiments were performed to obtain Pu assay and isotopic compositions, separation factors using ion exchange columns between Pu and Am, Am isotopic distributions, and isotopic minimum detection limits for Pu in an Am matrix.

Experiments

The sample vial was received from ORNL containing nominally 10 mg of nearly pure ^{243}Am oxide. Gamma spectrometry of the as received ^{243}Am oxide material was performed using an Ortec model GMX40P high-purity germanium (HPGe) detector with a 45% relative efficiency, cooled by a Ortec X-Cooler, contained within an Ortec HPLBSF1 shield, and signal collected by an Ortec DSpec Pro multi-channel analyzer. Based on the nominal 10 mg of ^{243}Am the expected activity would be approximately 74 MBq and the same would be additionally present from its short-lived ^{239}Np decay progeny in secular equilibrium. Since both those isotopes have fairly abundant and in the case of ^{239}Np reasonably well penetrating gamma –ray photons is was necessary to limit the photon flux seen by the HPGe detector by counting the material within the steel pipe nipple in which it was received, using two sets of thin metal copper and cadmium low-energy photon attenuators, and managing the distance from the HPGe end cap. Even so the acquired gamma-ray spectra on July 30, 2014 had a 92% dead time and analysis of the spectra had to consider several random sum peaks due to coincident gamma-ray photons arriving simultaneously in the HPGe detector. Review of the acquired spectra didn't indicate the presence of any gamma emitting radioactive impurities beyond the trace amounts reported by NIDC at the time of receipt.

The outer packaging layers were subsequently and carefully removed to access the inner vial. The vial was heavily contaminated on its external surface, so a significant effort was devoted to cleaning that outer surface of the vial to the point where it could be safely handled in an open front hood. Since some material apparently escaped the inner vial, it is possible that the estimate of 10 mg of material being inside is an upper limit.

The Americium oxide was dissolved in situ in gently heated 16M HNO_3 to which a few drops of 1M HF was added to aid the dissolution. The dissolved material was transferred to a pre-weighed 125ml narrow mouth Teflon (FEP) bottle. The received vial was rinsed several times in 16M HNO_3 to ensure complete removal of the oxide powder. The solution in the receiving FEP bottle was then diluted with 2M nitric acid to bring the final acid molarity to approximately 4M.

To obtain separation factors and the isotopic composition of any Pu isotopic impurity, two, nominally 100 microgram (of the Am oxide) splits of the master Am solution were aliquotted, weighed, and taken to dryness in Wheaton vials. To these solutions were added a few drops of aqua regia to ensure as much conversion of Pu to the tetravalent (IV) state as possible, as conversion of Pu to the IV state is necessary in order to separate Pu from the trivalent Am on our ion exchange resin. These were dried and the solutions were then nitrated (in 16 M HNO_3) and dried twice per ANC130 ("Preparing Plutonium and Uranium Samples for Isotopic Analysis and Isotope Dilution Analysis"). Separations were carried out on Lewatit anion exchange resin to purify the Am from the Pu. In the re-established separation chemistry, Am has no retention on the column in HCl while Pu (IV) is retained quantitatively in 7-12M HCl. Pu is then chemically reduced and eluted in a mixture of HCl and HI (12M HCl: 0.2M HI). In this procedure, the sample is loaded onto the column and Am is immediately collected in the loading wash and an additional 4 column volumes of 12M HCl. Pu is then reduced by adding 1 c.v. of HCl:HI and allowing the Pu to reduce for a nominal 10 minutes. Pu is then quantitatively eluted from the column in 2 to 4 cv of HCl:HI.

Approximately 1/1000th of each of the two Am cuts was separated from the remainder to establish the isotopic composition of Am. The remainder of the two Am cuts were spiked with a nominally 44 ng ^{244}Pu spike solution to establish the amount of Pu that eluted in the Am cut.

The Pu fractions were each gravimetrically split. The smaller split was added to a 44ng ^{244}Pu spike to establish the Pu recovered in the Pu fraction. The larger split was dried down unspiked to determine the Pu isotopic composition of the Pu present in the material. From these experiments, the ratio of Am in the Am fraction to Pu in the Am fraction gave us the Pu decontamination factor in the Am and the percent recovery of Pu in the Pu fraction. To determine the total Pu in the material unambiguously, a separate weighed Am aliquot was spiked into a nominally 44 ng ^{244}Pu spike prior to column separation. We assumed that the Am was recovered quantitatively in the Am fraction due to the lack of obvious isobaric interferences on mass 241 in the Pu isotopic distribution determination.

Following the separations described above, the same Am fractions were spiked with 20 ng, 200 ng, and 2000 ng of NBL (New Brunswick Laboratory) CRM 126a (see Appendix for the Certificate of Analysis) to test for our ability to measure a well characterized Pu standard in the Am matrix. After "spiking" with the 126a solution, these solutions were dried, reacted with aqua regia and nitric acid, and re-separated on the Lewatit columns using the protocols described above so the Pu isotopic distributions of the Pu standard could be measured in the respective Pu fractions.

Mass spectrometry determinations were carried out on a Sector-54 thermal ionization mass spectrometer from VG Instruments (Now Isotopx Ltd). All but two of the analyses (the 200 ng and 2000 ng CRM 126a experiments) were analyzed on single Rhenium filaments using a carbon ionization enhancer. For single filament analyses, detection was done by an ion-counting Daly detector using a scintillation counter/photomultiplier tube and a peak hopping algorithm. Separate splits of CRM 126a were used as external QC standards. For the 200 ng CRM 126a experiments, total evaporation and ion counting techniques were both used. The 2000 ng CRM 126a measurement was made exclusively by total evaporation methods employing Faraday-based detection.

Results & Discussion

1, Effectiveness of Separations. The ion exchange separations (Table 1) showed that the Am was highly purified following single column separation, with the estimated ratio of Am/Pu in the Am cut being greater than 100,000 in both experiments equating to an effective decontamination factor was $>10^5$. The ratio of Pu in the Pu cut to Pu in the Am cut was measured at 303 and 375. The total recovery of Pu in the purified Pu fraction, measured as the ratio of Pu recovered in the Pu fraction to total Pu independently determined was 84%. We attribute the small amount of Pu in the Am cut to result from incomplete oxidation of Pu to the 4+ state, since any trivalent Pu would be eluted along with Am. For the actual reference material production and characterization effort this might require a confirmation of the oxidation state through spectrophotometry and an oxidation step to convert to Pu 4+ state. Improvements in separations incorporating these ideas are planned for the future.

Table1. Pu-Am separations	Experiment 1	Experiment 2
Pu in Am cut, ug	0.00059	0.00073
Pu in Pu cut, ug	0.220	0.221
Ratio	375	303
Am/Pu in Am fractions, estimates*	146000	118000
Pu recovery (spk after/spk before)	83.6%	84.1%

* Since the 243Am in the parent bottle has not been assayed, this is an estimate.

2. Am Isotopic Analysis. The Am fractions were analyzed by ion counting and monitoring mass 239 for a potential Pu spectral interference on mass 241, using the measured Pu isotopic distributions to determine isobaric correction factors. The results of this analysis (Table 2) showed very low levels of ^{241}Am and that ^{242}Am below our current detection limits. Since we do not currently have a mixed Am isotopic standard, we cannot certify these measurements against an inter-laboratory or NIST-traceable standard.

Table 2. Am isotopic compositions (not “certified” as there is no mixed isotope standard) All analyses were performed on 17 Sept., 2014

^{241}Am	0.0097 atom %
^{242}Am	<0.0005 atom %
^{243}Am	99.99 atom %

3. Pu Isotopic Analysis. In measuring Pu isotopic distributions in ^{241}Am, a complete separation of Am from Pu is typically required to avoid isobaric interferences on the minor mass ^{241}Pu and to ensure optimal ionization efficiency in the Pu when Pu is present at trace or ultratrace-element levels in Am. Since we were measuring Pu in a ^{243}Am matrix, this was a relatively minor problem. The decay product of ^{243}Am is ^{239}Pu after the short lived ^{239}Np intermediate. We monitored for Am while tuning on Pu but found negligible 243Am during preliminary mass scans. The ^{243}Am/^{239}Pu ratio was monitored during the analysis in case an isobaric correction factor should be needed. However, when measuring Pu isotopic distributions in a purely ^{241}Am matrix, there is no independent monitor with which to make an isobaric correction, so high degrees of purification are needed if one is to determine the correct ^{241}Pu signal and from it, accurate Pu isotopic distributions. But there are other (radiochemical) indicators of separation factors between Pu and Am that will assure that the results are accurate. Also, more tracer experiments are planned to insure that the chemistry is robust, reproducible and provides excellent separation factors.

Pu isotopic results are shown in Tables 3-5. Since the same starting material was re-used to preserve valuable material, we observed small elevations in the ^{244}Pu/^{239}Pu of the CRM 126a that was “spiked” into to the Am solutions. These elevated ^{244}Pu/^{239}Pu ratios were consistent with the previously measured separation factors, and the elevated ^{244}Pu/^{239}Pu were used to make small corrections to the isotopic distributions (primarily of the ^{242}Pu and ^{240}Pu isotopes) by “unmixing” the minor isotopic contaminants in our ^{244}Pu spike from the samples. These final corrected values have been reported here and the distinction between CRM 126a and the intrinsic Pu in the sample shown in Figure 1.

Table 3. Intrinsic Pu isotopic composition. All analyses were performed on 17 and 18 Sept. 2014

Ratio	Run 1	Run 2	Run 3	ave	RSD, % 1 sd
238/239	0.00087	0.00090	0.00090	0.00089	1.95%
240/239	0.109199	0.109186	0.109436	0.109274	0.13%
241/239	0.000642	0.000646	0.000657	0.000648	1.2%
242/239	0.109533	0.109795	0.110081	0.109803	0.25%
244/239	0.000036	0.000036	0.000036	0.000036	0.00%

Table 4. ^{244}Pu/^{239}Pu in CRM 126a indicating residual Pu from yield experiments. "TE" indicates the total evaporation technique was used (Callis and Abernathy, 1991). "Ion" indicates the analysis was performed by ion counting.

	TE-2 ug	TE-200 ng	Ion-200 ng	Ion -20 ng
Mix ^{244}Pu/^{239}Pu	0.000041	0.000347	0.000317	0.002706

Table 5. Final, corrected results on CRM 126a "spiking". The CRM 126a "control" is the current, average value of the standard as measured in the mass spec laboratory on the same instrument. TE=total evaporation analysis, Ion=ion counting analysis. All analyses were performed between 26 and 29 Sept 2014

Atom %	CRM126a "control"	TE-2 ug	TE-200 ng	Ion-200 ng	Ion -20 ng	ave	rsd, 1 sd
^{238}Pu	0.011	0.0123	0.0135	0.0092	0.0098	0.0112	18%
^{239}Pu	93.973	93.973	93.971	93.980	93.992	93.979	0.01%
^{240}Pu	5.892	5.891	5.890	5.893	5.881	5.889	0.09%
^{241}Pu	0.087	0.0872	0.0878	0.0841	0.0828	0.0855	2.8%
^{242}Pu	0.037	0.0367	0.0375	0.0334	0.0344	0.0355	5.4%

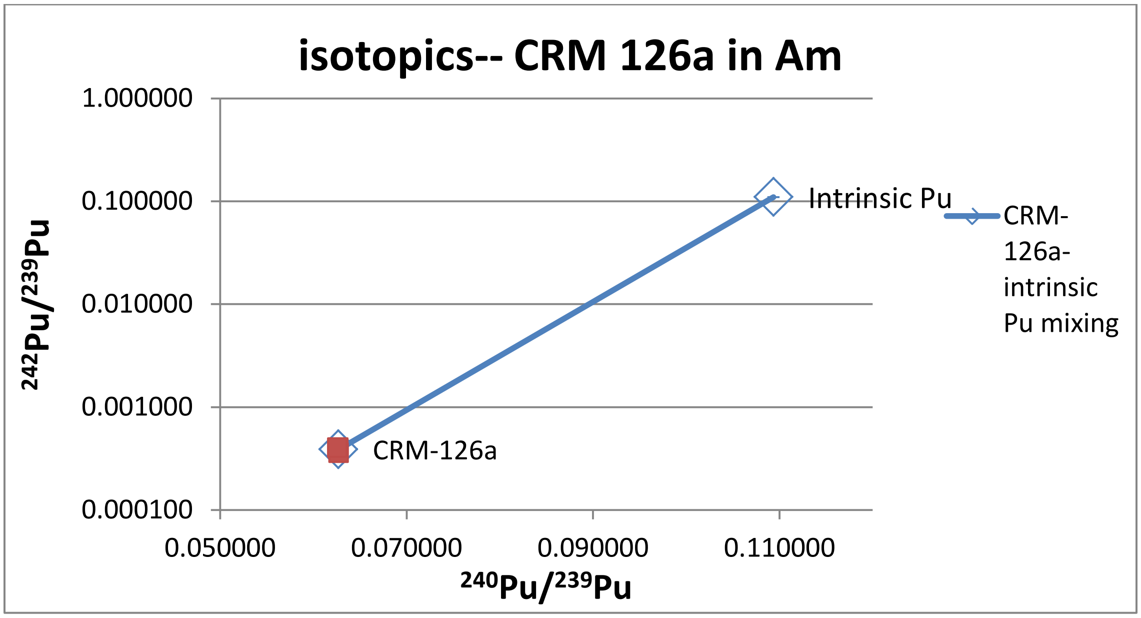

Figure 1. ^{242}Pu/^{239}Pu vs. ^{240}Pu/^{239}Pu of CRM 126a (red closed square, lower left) that was added to the ^{243}Am aliquots vs. intrinsic Pu in the sample (open blue diamond, upper right). Data from tables 3 and 5. If large and variable quantities of the Pu intrinsic to the Am material had been left in the material following separations, the subsequent analyses of CRM126a added to the Am would have been dispersed along a mixing line between the CRM126a (lower left) and intrinsic Pu (upper right) end members. Such mixing was not seen in the analyses.

Limits of Detection of Pu in ^{243}Am.

Given that this experiment was carried out using nearly isotopically pure ^{243}Am as a substrate, there was minimal interference between the Am and Pu isotopes, even with imperfect column separations. Furthermore, the very low ^{241}Am/^{243}Am in the matrix would allow a very good isobaric interference correction on the ^{241}Am-^{241}Pu isobar. The actual limits of detection will therefore be controlled by the amount of Pu recovered vs the amount of Pu required for a duplicate analysis, using either the total evaporation or ion counting methods. Presently, our analytical capabilities require us to collect nominally 2 ng of Pu to perform an ion counting analysis or 20 ng to perform a total evaporation analysis of sufficient quality to characterize the major and minor isotopes in weapons-grade Pu to our stated analytical objectives (0.1-0.01 % RSD major isotopes, 1-2% minor isotopes, ~10% trace isotopes). Using a conservative recovery factor of 80% of the Pu (Table 1) and assuming an ion counting analysis (in order to minimize the amount of material), we can calculate how much Am matrix would be required to perform a duplicate ion counting analysis. This ranges from approximately 5 grams of Am oxide at 1 ppb Pu to 5 micrograms of Am oxide for a sample with 1000 ppm Pu. This is shown in Figure 2. We add the caveat that this presumes blanks consistent with historic practice (a few picograms to a few tens of picograms blank) and a sample collection technique that enables us to completely recover the Pu, such as using cone bottomed collection vials.

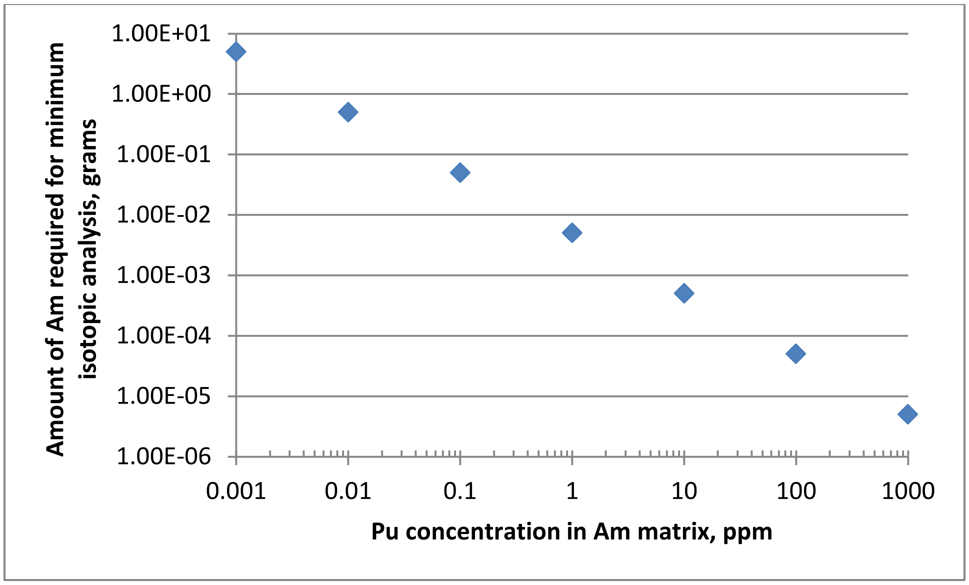

Figure 2. Graphical relationship between Pu concentration in Am matrix vs. amount of matrix required for minimal sample requirements.

Conclusions and remaining work

We were able to quantitatively separate Pu and Am such that it was possible to measure both the intrinsic Pu in the sample and the "spiked" CRM 126a Pu that we deliberately added to previously purified samples. The presence of ingrowth ^{239}Pu and initial "tramp" Pu would have resulted in mixing lines between the intrinsic Pu and the CRM 126a (Figure 1) had the samples not been previously separated. Indeed, the presence of the approximately 0.5% remaining Pu from previously performed separation factor experiments on the Am cuts was manifested in an elevated ^{244}Pu/^{239}Pu in the samples during the final CRM 126a spiking experiments. These minor amounts of mixing could be "unmixed" by using mixing line algorithms.

Remaining work includes performing reverse-isotope dilution on the ^{243}Am itself to constrain the concentration of Am in the solution. We also need to make further measurements of the ^{243}Am solution's isotopic composition to better define minor ^{241}Am and ^{242}Am constituents. Traceability of these results will be established through the production and characterization of reference materials. Method detection limits will be evaluated against sponsor requirements and if needed, improved.

Acknowledgements

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