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Analytical chemistry of nuclear material: case studies from Los Alamos National Laboratory

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Abstract

AQ1 Presented here are three case studies that demonstrate the breadth of bulk actinide analytical chemistry at Los Alamos National Laboratory (LANL). This laboratory was established during the Manhattan Project and is still considered one of the premier analytical laboratories for special nuclear materials characterization around the globe. First, the analytical chemistry of ^{238}Pu is presented, showcasing the unique challenges of this high activity isotope. Next, the analysis of ^{241}AmO$_2$ is discussed from the perspective of supporting nascent production at LANL. Finally, the analytical chemistry support of the production of plutonium non-destructive assay standards is discussed. These examples paint a picture of the analytical capabilities needed to meet the dynamic challenges of LANL's nuclear programs.

Keywords Analytical chemistry · Actinide · Americium oxide · Plutonium

Introduction

Techniques for characterization of special nuclear material (SNM) have evolved since the inception of the nuclear era. Los Alamos National Laboratory (LANL) has the distinction of establishing one of the first nuclear analytical characterization laboratories in the world. The Analytical Chemistry group now called Actinide Analytical Chemistry (C-AAC) started under Project Y, the Manhattan Project, during World War II. The original laboratory buildings during the Manhattan Project are shown in Fig. 1. Both Analytical Chemistry and Plutonium Production activities occupied "D" Building across Trinity drive from "Ashley Pond" (Fig. 1). Today, the Richard P. Feynman Center for Innovation now stands at the approximate location of "D" building (Fig. 2).

The Analytical Chemistry group was established to support the increasing plutonium work going on at LANL towards the end of World War II. The same group has continued to exist and has evolved over the last 75 years to support changing national security missions. The current group has evolved to support numerous programs such as nuclear energy, defense programs, fundamental science, deep space missions, national and international safeguards and security, environmental management, and threat reduction.

The chemical and physical measurement requirements to support a wide range of programs and characterize nuclear materials have not fundamentally changed over the past 75 years. These characterization requirements include isotopic abundance and concentration measurements of the primary actinides, progeny radionuclides, and trace metallic and non-metallic impurities. At Los Alamos, a tremendous amount of work was done during the 1940s, 1950s, and 1960s to perform these analyses using, almost exclusively, the classical chemical methods of titration and spectroscopy. However, the analytical tools and techniques for these analyses have evolved with modern instrumentation such as mass spectrometry, high resolution radiometric spectrometry, and X-ray techniques [2, 3]. The advancement in techniques and improved instruments are necessary to meet enhanced requirements for measurement accuracy, precision, uncertainty, as well as sample size restrictions. Los Alamos National Laboratory has been a pioneer in the development and application of state of the art technologies for actinide analysis. Many improvements have emerged from the areas of thermal ionization mass spectrometry (TIMS),

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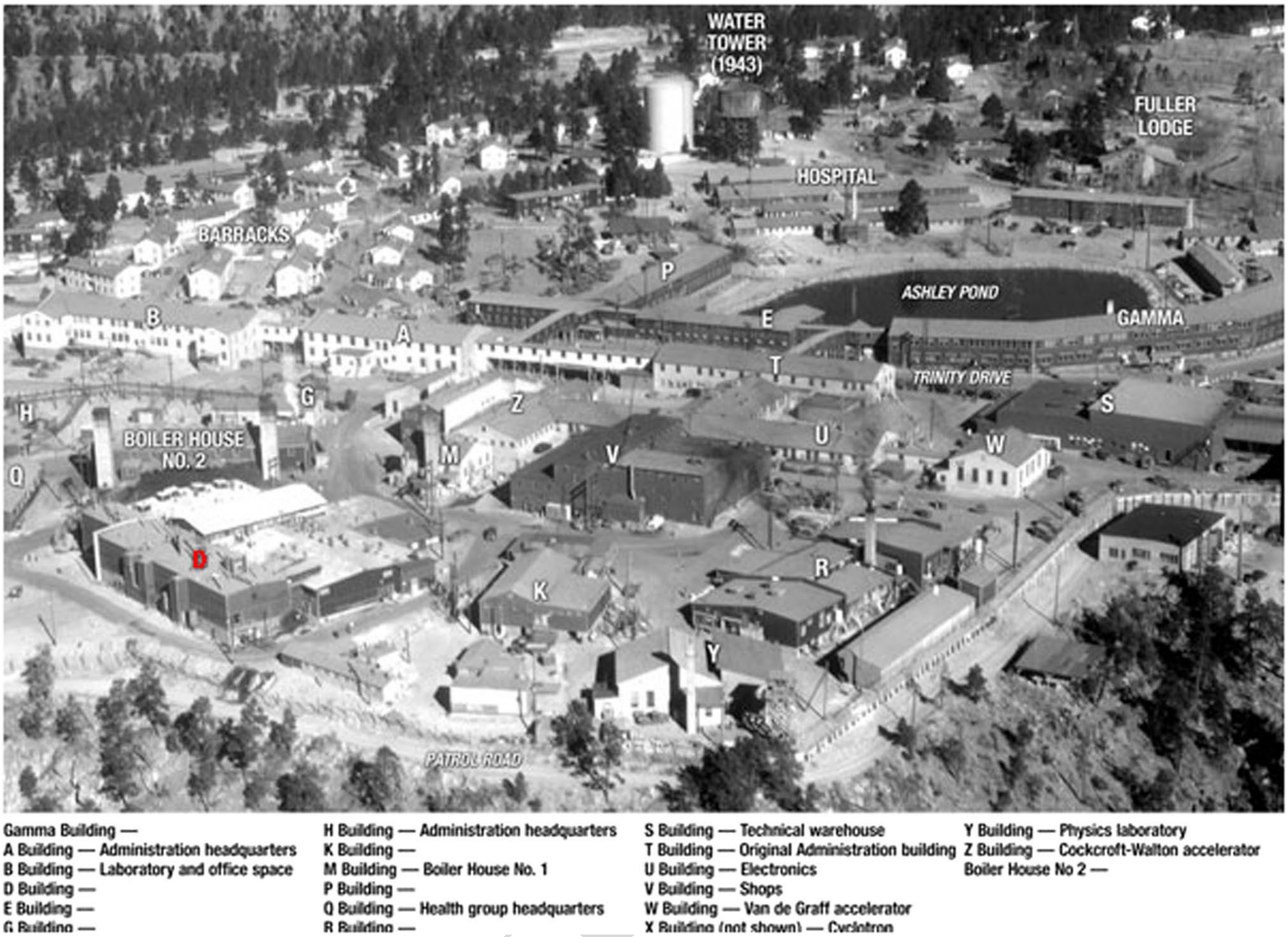


Fig. 1 Los Alamos during the wartime years (photo courtesy of the Los Alamos National Laboratory)

destructive actinide assay techniques, inductively coupled plasma atomic emission spectroscopy (ICP-AES), and X-ray fluorescence (XRF) in actinide analysis [4–8]. Table 1 lists currently available analytical techniques in C-AAC to support material characterization. Developing a new method or applying existing, non-actinide analytical technique to radioactive samples has many challenges. The most constraining aspect of actinide chemistry is the safe handling of radioactive materials. Methods may require significant modification to meet safety and security requirements. Additionally, a highly trained workforce with unique skill sets, and procedures with formal conduct of operations are needed to process the toxic and radioactive materials safely. All these constraints, in addition to meeting current environmental compliance requirements, makes simple analytical tasks related to chemistry, method development, processing, or installation of modern instrumentation a very challenging task.

Utilization of well developed, validated, and qualified methods under stringent quality assurance and quality control guidelines is required to support the missions mentioned above. One of the main tenets of these guidelines is the use of calibration standards traceable to international metrology laboratories, matrix-matched standards, and blank samples to ensure the quality of each sample analysis. This leads to one of the main concerns in this field, the lack of available matrix-matched reference materials (RMs) for key analytes of interest [9, 10]. Scientists at LANL, including the C-AAC group, have worked with international metrology laboratories (such as National Institute of Standards and Technology (NIST) and New Brunswick Laboratory (NBL)) for the last 50+ years in the development and preliminary characterization of plutonium matrix-matched RMs for various attributes. Technical competence by the analytical group has also been demonstrated over the last 60 years through participation in national and international performance tests or interlaboratory comparison programs for various national and international safeguards and security programs [11–15].

This publication seeks to highlight LANL's unique bulk actinide analytical capabilities that showcase the work chemists in nuclear facilities engage in on a regular basis to characterize: (1) ^{238}Pu heat source production

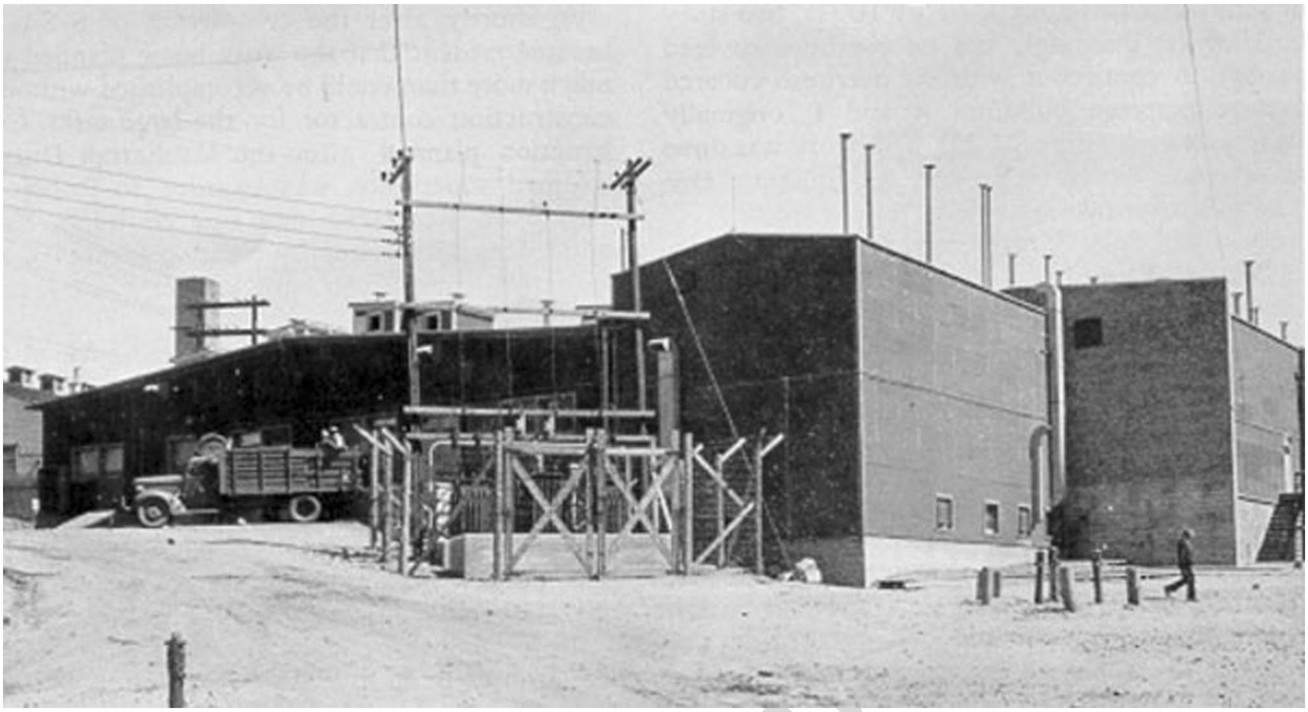


Fig. 2 "D" building at the original Los Alamos Technical Area [1]

Table 1 Formalized, operational analysis capabilities for chemical characterization of nuclear materials

Analytical Techniques	Implementation
High resolution gamma-ray spectrometry (*Radiochemistry*)	Isotopic analysis, assay
Alpha/beta spectrometry (*Radiochemistry*)	Assay
Titration	Pu assay
Coulometry	Pu, Np assay
Spectrophotometry	Pu, Fe, Si assay
DC-Arc emission spectroscopy	Trace element analysis
Plasma methods (ICP-AES, ICP-MS)	Trace element analysis
Mass spectrometry (TIMS, IDMS)	Isotopic analysis, U, Am, Np assay
Confocal X-ray fluorescence (XRF/WDXRF/EDXRF)	Ga assay, identification of unknown elements
Ion chromatography	F^-, Cl^-, Br^- analysis
Gas mass spectrometry	Various gas analyses
Interstitial gas analysis (TC/IR)	C, S, H, N, O analysis

ICP-AES inductively coupled plasma atomic emission spectroscopy, *ICP-MS* inductively coupled plasma mass spectrometry, *TIMS* thermal ionization mass spectrometry, *IDMS* isotope dilution mass spectrometry, *WDXRF* wavelength dispersive X-ray fluorescence, *EDXRF* energy dispersive X-ray fluorescence, *TC* thermal conductivity, *IR* infra-red spectroscopy

samples used as Radioisotope Thermoelectric Generators (RTGs) by National Aeronautics and Space Administration (NASA) to support deep space exploration missions; (2) analysis of $^{241}AmO_2$ to provide americium for use in smoke detectors and neutron generators by commercial vendors; and finally, (3) production of plutonium non-destructive assay (NDA) standards for use in various portal monitoring applications. All materials used in these projects are highly radioactive and require a specialized skill set, well-engineered safety controls, and radiological facilities to process and characterize them. These examples were chosen to illustrate the nature of actinide analytical chemists' work, demonstrate interesting global applications, show the diversity of applied analytical tools and challenges, and present the unique science and chemistry associated with production and subsequent analysis. Each of these examples are presented as separate sections in this paper.

Plutonium-238 Analytical Chemistry

The unique properties of plutonium-238 (heat source plutonium) has enabled significant scientific discoveries over the last half century. Interplanetary missions that included the Pioneer (10 & 11), Voyager (1 & 2), Galileo, Ulysses, Cassini, and New Horizons spacecraft all utilized electricity generated from the heat given off by the decay of heat source plutonium [16–18].

The unique properties of heat source plutonium stem from a combination of factors:

- Relatively short half-life (~ 87 years); the decay from the isotope produces heat that can be converted into electricity
- Easily shielded radiation; ^{238}Pu is primarily an alpha emitter
- Stable fuel form; plutonium oxide is a stable, inert fuel form
- Availability; ^{238}Pu historically has been made from a ^{237}Np target material, a byproduct separated from cold war activities [19]

The properties of ^{238}Pu that make it useful as a heat source also complicate the chemistry. Radiolysis from the high alpha activity change the solution chemistry compared to weapons grade Pu, and the heat generated from the isotope can self-heat solutions to ~ 80 °C. While the ^{238}Pu isotope is primarily an alpha emitter, in its fuel form (PuO_2) the material poses more of a neutron flux hazard than an alpha radiation hazard because of the (α, n) interactions with light elements. Most of the gamma radiation from heat source plutonium is easily shielded. However, two sources of gamma radiation within the material can become significant if they are in high enough concentration—^{241}Am and ^{236}Pu. The radiation from these isotopes is a concern as it can cause damage to parts of the spacecraft, putting the mission in jeopardy. The americium grows in from decay of ^{241}Pu, and the ^{236}Pu is an unwanted byproduct from the irradiation of ^{237}Np when making ^{238}Pu [20]. The ^{236}Pu is especially important to keep at low concentrations when making the ^{238}Pu, because the daughter products ^{212}Pb, ^{212}Bi, and ^{208}Tl are high-energy gamma emitters and not easily shielded. Most heat source plutonium has ^{236}Pu concentrations well below 2 ppm. However, the lower ^{236}Pu content in the heat source plutonium comes at the cost of lower ^{238}Pu enrichments during the ^{237}Np target irradiation process. A typical heat source plutonium composition is shown in Table 2.

Table 2 Typical composition of heat source fuel [21]

Isotope	Mass fraction (%)
^{236}Pu	< 1 ppm
^{238}Pu	82–86%
^{239}Pu	12–15%
^{240}Pu	1–3%
^{241}Pu	0.2%
^{242}Pu	0.05%

Table 3 Specific neutron yields from light element impurities in heat source plutonium

Element	^{a}n/s g^{-1} ^{238}Pu (per ppm of impurity)	Typical concentrations (ppm)
Li	5.7	< 1
Be	162	< 1
B	51	< 5
C	0.2	< 50
^{17}O	23.9	< 100
^{18}O	52.4	< 100
F	22	< 10
Na	2.7	< 50
Mg	2.6	< 20
Al	1.2	< 100
Si	0.2	< 50

^{a}Neutrons per second per gram

Given these radiation characteristics, the daily handling of heat source plutonium is largely similar to handling ^{239}Pu materials with the added concern of thermal radiation produced from ^{238}Pu. Laboratories outfitted with gloveboxes are required in handling heat source plutonium materials. If the material contains large amounts of light elements and the neutron flux is severe, the glovebox may be outfitted with neutron absorbing material such as poly(methyl-methacrylate) (PMMA) or water-filled windows. Table 3 shows the contribution of particular isotopes of several light elements to the neutron dose.

For analytical chemistry operations, a few grams of heat source material are handled routinely. The dose from this amount is relatively small and as a result, the glovebox design does not generally include the types of shielding mentioned above. An example of a typical glovebox used for ^{238}Pu analytical chemistry operations is shown in Fig. 3.

The analytical chemistry associated with heat source materials has always been directly related to the production requirements which relate specifically to the characteristics that are important to the function as a power supply. The following analysis techniques have been developed over a number of years at LANL to support the heat source plutonium production needs [22].

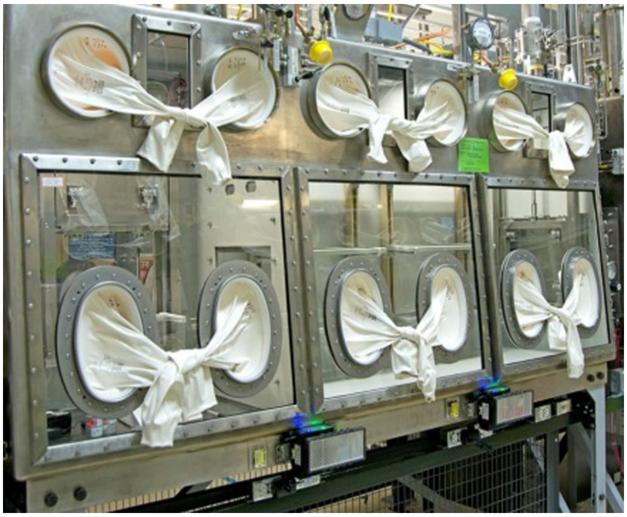


Fig. 3 A typical glovebox used to handle heat source plutonium analytical chemistry samples

Fig. 4 Vessel used to dissolve heat source samples, commercially available vessel from Parr Instrument Co

Methods

Sample dissolution

AQ2 A rigorous dissolution treatment is needed for the dissolution of PuO_2 as it is typically calcined at 1600 °C, giving PuO_2 refractory properties. Various approaches have been attempted in the past to solubilize heat source PuO_2 with limited success [23, 24]. Current dissolution schemes utilize elevated temperature and pressure. Typically, ~ 300 mg of plutonium oxide is dissolved for analysis using an acid digestion vessel consisting of an outer jacket made of stainless steel and an inner cup made of Teflon (Fig. 4). The solid samples are dissolved by adding a few milliliters of concentrated hydrochloric acid with a few drops of hydrofluoric acid to the solid which is then sealed in the digestion vessel and heated at ~ 150 °C for ~ 8 h or overnight using a block heater. Once the samples are dissolved, they are transferred quantitatively and aliquoted for different analyses. These include total Pu assay; radiochemical assay of ^{241}Am, ^{234}U, and ^{236}Pu; Pu isotopic analysis; and trace element analysis.

Plutonium assay

The dissolved sample solution (~ 80 to 100 mg of $^{238}PuO_2$) is concentration-adjusted to ~ 2 M HCl and zirconium is added to complex any residual F^- ions. The plutonium is then reduced to Pu(III) with ascorbic acid. The plutonium assay is determined by the Pu(III) spectrophotometric method which uses the well characterized *f–f* transitions of the Pu(III) ion to calculate concentration. A set of known concentration ^{239}Pu-secondary standards (traceable to NBL CRM 126a, Pu metal) are used to generate calibration curves based on the absorbance differences, as seen in Fig. 5. The concentration of Pu in a sample is determined from the calibration curve. Figure 5 shows a UV–Vis dip probe that is used for measuring absorbance and a typical spectrum from Pu(III) in 2 M HCl. With gravimetric preparation, an estimated precision of 0.2% relative standard deviation and a mean recovery of 99.9% have been reported [25].

Radiochemical Analysis of ^{241}Am, ^{234}U, and ^{236}Pu

Approximately 30 mg $^{238}PuO_2$ in solution (1 mL of ~ 30 mg/mL solution) is used for ^{241}Am, ^{234}U, and ^{236}Pu radiochemical analysis. From this solution, a 100µL parent aliquot (~ 240 µg of ^{238}Pu) is removed and evaporated in a glass scintillation vial for ^{241}Am analysis by gamma spectroscopy on a high-purity germanium detector (HPGe). For ^{236}Pu analysis, ^{244}Cm is removed by an anion exchange column, then the resulting solution is diluted twice, stippled and dried on a glass plate, and analyzed by alpha spectrometry. The ^{244}Cm separation is carried out as the energy of the two alpha particles emitted by ^{244}Cm at 5.762 MeV and 5.805 MeV respectively are close in energy to the two alpha particles emitted 5.721 MeV and 5.768 MeV by ^{236}Pu. For ^{234}U analysis, an aliquot of the parent dissolution sample is heated to near dryness on a hotplate and the residue is reconstituted in 3 M HNO_3-0.1 M ferrous sulfamate-0.1 M ascorbic acid. Ferrous sulfamate and ascorbic acid are used to reduce plutonium to Pu(III). The sample is loaded onto a TEVA/UTEVA® column (Eichrom Technologies, Inc. USA), where U(VI) is retained while Pu(III) and Am(III) pass through the resin. U is then eluted with a dilute mixture of HNO_3 and HF. Microliter volumes of the U eluate are stippled and dried on a glass plate for alpha spectrometry [26].

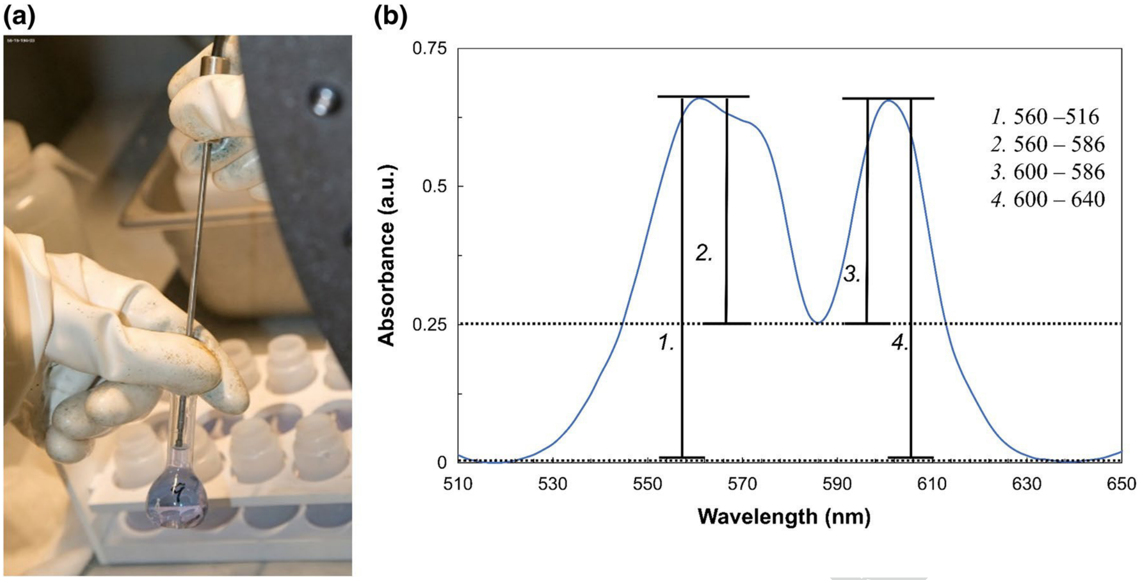


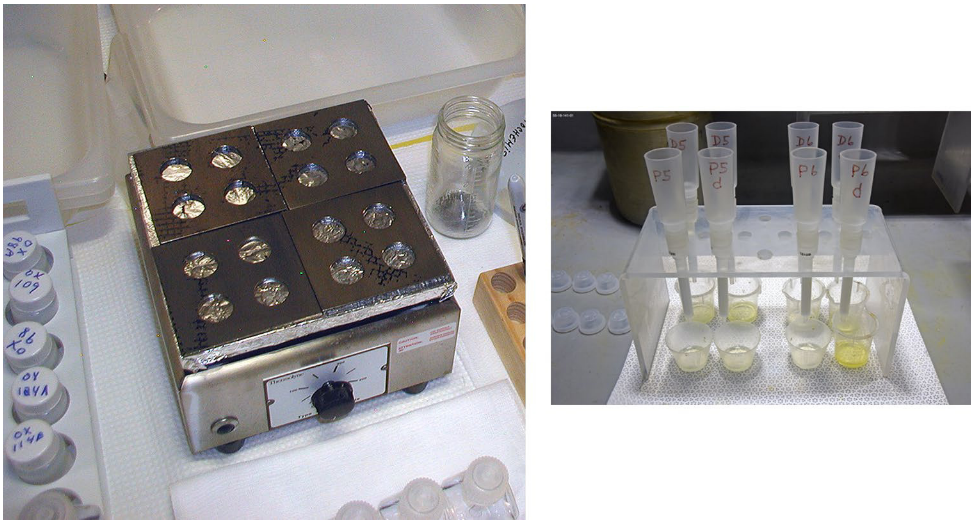
Fig. 5 Dip probe acquiring UV–Vis spectra and the Pu(III) visible spectrum from 500 to 650 nm

Other column resin material may be used for the removal of Pu and Am; however the use of the prepacked Eichrom columns allows for greater throughput and more consistent results (Fig. 6).

Th determination

Thorium can be up to a 0.5% by weight contaminant as a result from an impurity in the ^{237}Np target material and is undesirable because it detracts from the overall power density of the fuel. In the past, ICP-MS has been used to quantify Th concentration; however, spectrophotometric determination using Arsenazo III as a colorimetric reagent is now implemented as this method can easily be applied in a glovebox and uses the same instrumentation as Pu assay [27–30]. Approximately 7–30 mg $^{238}PuO_2$ in solution is taken to dryness on a hotplate. The residue is reconstituted in 3 M HNO_3-0.1 M ferrous sulfamate-0.1 M ascorbic acid and loaded onto a TEVA® column, where Th(IV) is retained and Pu(III) passes through the resin. The Th is then eluted from the column with 9 M HCl. Arsenazo III is added as a coloring reagent and the concentration of the Thorium is measured by UV–Vis and quantified by comparison to a calibration curve constructed from NIST-traceable Th standard solutions. Representative samples, colored the characteristic pink/purple, and resulting spectra are shown in Fig. 7.

Fig. 6 Hot plate used for plating alpha samples and columns used for separation



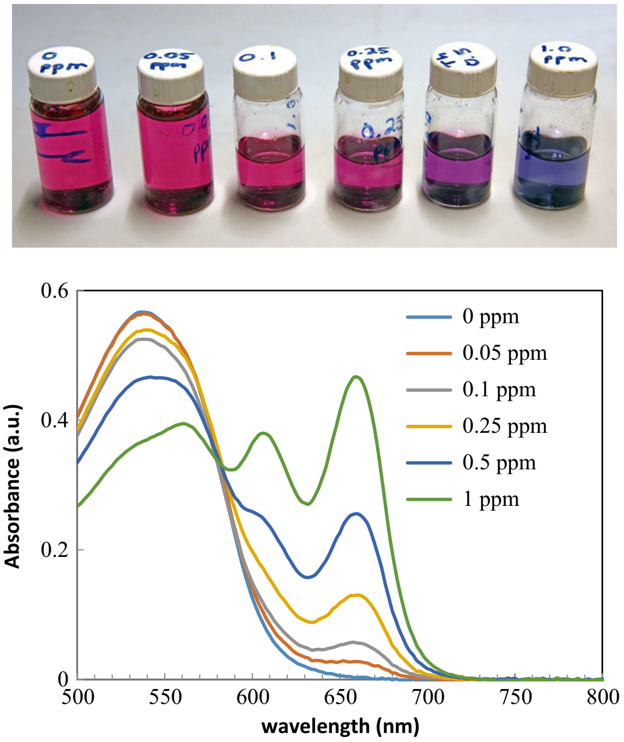


Fig. 7 Colorimetric technique showing various concentrations of thorium in HCl with Arsenazo III

Pu isotopic determination

The routine method for the determination of plutonium isotopic abundances in heat source plutonium uses high-purity germanium (HPGe) detectors to acquire gamma-ray spectra. Sealed containers are used to greatly simplify sample movement and loading. The obtained spectra are then analyzed using the LANL-developed FRAM (Fixed-energy Response-function Analysis with Multiple efficiency) software package [31, 32]. This method provides a non-destructive analysis (NDA) approach to determine plutonium isotopic abundances in heat source plutonium. The method was optimized specifically for the analysis of ^{238}Pu gamma spectra. For example, samples sizes, configuration in a tantalum vial, distance from the detector, and software parameters were adjusted to provide the best results. Table 4 provides results from a representative set of samples, showing the ratio of gamma-FRAM to TIMS data [33, 34].

Table 4 Sample data showing the difference between gamma-FRAM and TIMS data, given as a ratio

Sample	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu
S1	1.0024	1.0264	0.6528	0.9966
S2	0.9967	1.0282	0.9098	1.0263
S3	1.0012	1.0036	0.8997	0.9851
S4	1.0007	1.0096	0.8871	1.0155
S5	1.0019	1.0117	0.8556	1.0313
S6	0.9886	1.0762	0.9097	1.0098
S7	1.0013	1.0031	0.9045	0.9998
S8	1.0041	0.9974	0.8180	1.0300
S9	0.9995	0.9984	1.0236	1.0117
S10	1.0041	0.9766	0.9747	1.0238
S11	1.0066	0.9925	0.7830	0.9843
S12	1.0070	0.9989	0.8186	1.0098

Non-actinide cationic impurities by DC Arc—Al, B, Be, Cd, Cr, Ca, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, and Zn

The routine measurement of trace element impurities in heat source materials has historically been performed by DC-arc emission spectrochemical analysis. It provides fast, quantitative analysis of the difficult-to-solubilize, high temperature-fired PuO_2 fuel with a sensitivity that meets the requirements for NASA. The technique requires limited sample and is a well proven method of analysis. The DC-arc technique involves placing sample material in a graphite cup electrode, striking an arc between the sample electrode and a counter electrode separated by 4 mm [35–37]. The arc vaporizes the material in the cup to the plasma where it is excited to higher energy levels. As the atoms relax to lower energy levels, visible and ultraviolet light is emitted and collected by a spectrometer [37]. Each element emits its own unique spectrum which can lead to thousands of emission lines, each corresponding to a specific atomic energy level of each element. Plutonium is a large contributor to these emission lines, for that reason a carrier is added to the sample mixture to help suppress the valorization of plutonium and help selectively distill the impurity elements into the plasma for analysis. For a typical analysis of PuO_2, ~ 240 mg of solid oxide sample is prepared with 10 mg of carrier internal standard mixture (Ga_2O_3 and Co_3O_4). Two cuts (~ 100 mg each) of samples are loaded into graphite electrodes and transferred to the arc chamber for analysis (Teledyne Leeman Lab's Prodigy DC Arc Hudson, NH, USA). A series of known concentration multi-element $^{239}PuO_2$ standards are used to determine the concentration of samples.

Discussion

In summary, the analytical chemistry of heat source Pu is complicated by the intense radiation and heat associated with the isotope. As mentioned previously, radiolysis from the high activity isotopes in heat source Pu can cause solution effects such as gas production and bubbles in solution, decomposition of materials and reagents, colorimetric and electrochemical instabilities that will affect overall accuracy and precision in the determination being made. In addition, constant vigilance must be taken to minimize the dose to the workers, contributing to the difficulties in handling this material. Current methods used at Los Alamos take advantage of longstanding analytical approaches from decades of experience handling this material, as well as new analytical chemistry techniques available to modern chemists and are readily adaptable to glovebox work, yielding a suite of analytical tools that meet the demands of ^{238}Pu production.

Analytical method testing for AmO_2 production support

The beta decay of ^{241}Pu (half-life of 14.4 years) to ^{241}Am produces high isotopic purity americium material in a Pu matrix. This decay path provides a synergistic tie between Pu reprocessing operations and ^{241}Am separation/isolation campaigns. Historical information on separation efforts to produce $^{241}AmO_2$ can be obtained from other sources [38–40]. Kilogram quantities of $^{241}AmO_2$ were produced at various DOE sites across the U.S., including the Rocky Flats Plant (~ 1960 to 1980), Savannah River Site (1978–1981), and the Hanford Site (~ 1960 to 1970). From 1979 to 1984, 6.5 kg was purified at Los Alamos [41]. Domestic production of $^{241}AmO_2$ tapered off towards the end of the 1980s due to declining demand and the closure of the Rocky Flats Plant. Since the early 1990s the major global suppliers of bulk $^{241}AmO_2$ have been non-domestic.

LANL has recently re-started an effort to produce a purified americium oxide product for external vendors. These $^{241}AmO_2$ production operations rely on analytical chemistry measurements to guide processing decisions and certify product materials with quality isotopic and elemental results [41]. Outside of this particular application, purified americium materials are seldom encountered as samples for destructive chemical analysis. However, the recent demand for $^{241}AmO_2$ sample characterization initiated an accelerated effort to adapt existing, well-tested methods for Pu sample analysis to the dissolution, preparation, and analysis of $^{241}AmO_2$ samples. The goal of this study was to develop, test and validate NIST traceable analytical techniques on matrix matched AmO_2 materials for key production specifications that include Am assay, Am isotopics, Pu content, Pu isotopics and trace element quantification. In each of these analyses, the challenge of handling high-dose ^{241}Am demanded reduced sample sizes for worker safety and instrument stability. The experimental plan developed and discussed in this section was designed to test overall analytical method uncertainty, encompassing sample dissolution, sample preparation, and instrumental analysis.

Development work required a suitable mass of well-characterized Am material to validate the analytical techniques. To date, there are no commercially available NIST-traceable americium isotopic or assay standards suitable for this type of validation work. Instead, ^{241}Am oxide produced during a previous ^{241}Am recovery campaign at Los Alamos National Laboratory was acquired as a parent material for testing. This material was available in quantity required for the developmental work and historic chemical analyses suggested this material would be comparable to current ^{241}Am oxide production material. This material was chosen as the primary test material, and the composition of this material after re-analysis is provided in Table 5.

Am isotopic abundances determined by thermal ionization mass spectrometry (TIMS) identified the parent as isotopically pure ^{241}Am. No other Am isotope was detected. A stoichiometric $^{241}AmO_2$ material would produce a theoretical assay value of 88.28 wt%. The measured ^{241}Am concentration using the ID TIMS method was nominally 76 wt%, well below the theoretical. Additional elemental constituents accounted for only about 4.6 wt% of the parent material matrix. The obvious inconsistency in stoichiometry with respect to $^{241}AmO_2$ was not a particular concern in using this parent material to evaluate analytical methods since the material itself was homogeneous, easily dissolved, and straightforward to isolate.

Am isotopic determination

For use in isotopic measurements, a small mass of $^{243}AmO_2$ material from the National Isotope Development Center at Oak Ridge National Laboratory (ORNL) was obtained. The ^{241}AmO2 test material did not contain any ^{243}Am and it was necessary to add a trace amount of ^{243}AmO2 to the ^{241}Am material to be able to validate TIMS technique for Am isotopic measurements. The $^{243}AmO_2$ parent was selected based on quoted Am isotopic abundance values provided by the vendor. These isotopic abundances were given without uncertainties or a reference date (Table 6).

Table 5 Chemistry results of $^{241}AmO_2$

Analyte	Average results (wt%)	Analytical method
^{241}Am isotopic abundance	99.999 ± 0.005	TIMS
^{241}Am concentration	75.97 ± 0.18	IDMS (TIMS)
^{237}Np concentration	4.3 ± 0.7	ICP-MS
Pu concentration	0.1362 ± 0.0003	IDMS (TIMS)
Pb concentration	0.110 ± 0.010	ICP-AES
Fe concentration	0.024 ± 0.002	ICP-AES
Cr concentration	0.0049 ± 0.0007	ICP-MS
Al concentration	0.0040 ± 0.0013	ICP-MS

Table 6 ORNL $^{243}AmO_2$ parent material isotopic composition

	Isotopic abundance (atom%)
^{241}Am	0.012
^{242}Am	< 0.001
^{243}Am	99.987

^{243}Am is a key analyte listed in the specification requirement for the $^{241}AmO_2$ products being produced at LANL. Both of the americium oxide samples were dissolved with concentrated HNO_3 and 1.3 M HF in a Savillex® digestion vessel. The vessel was closed tightly and heated to 130 °C in a heating block for approximately 12 h until the material dissolved completely. Parent ^{241}Am and ^{243}Am solutions were mixed gravimetrically to prepare a ^{241}Am–^{243}Am mixture solution suitable for testing and refining analytical methods (Fig. 8, 9).

Radiological dose considerations reduced the total amount of AmO_2 material that could be handled and used for analysis. This offered a significant challenge since the accuracy, precision, and uncertainty requirements were near the levels typically attained with larger amounts of sample, and any modification to existing techniques required a demonstration of proof of the concept prior to analyzing actual product samples. Existing actinide analytical methods are optimized for larger mass samples and some concessions were made for the smaller sample size. About 300 mg total was dissolved for method testing compared to the usual 2500 mg used for trace element and TIMS measurements for Pu samples. For ICP-AES and ICP-MS measurements, sample masses were reduced from 225 and 25 mg to 9 and 1 mg, respectively. Although sample size reduction lowered precision for ICP measurements. The Am sample mass had no impact on TIMS and IDMS measurements as these methods typically prepare and run with less than 5 mg sample masses.

Trace element techniques

For ICP-MS measurements, an aliquot of the dissolved Am sample discussed above was further diluted and analyzed directly by an Agilent 7700 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrument (Agilent Scientific Instruments USA). For ICP-AES, a separation was

Fig. 8 Graphite cup electrodes used for sample analysis and an Arc chamber used for striking an arc in sample analysis

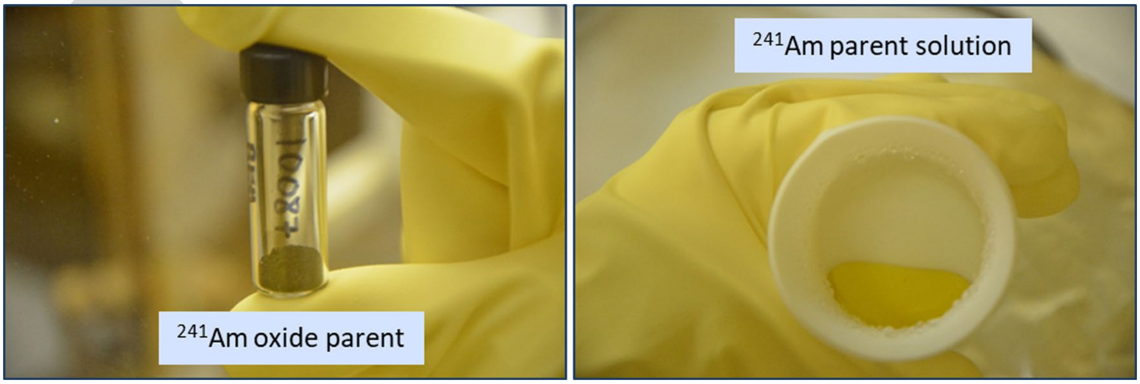


Fig. 9 $^{241}AmO_2$ parent sample (left), and ^{241}Am solubilized in nitric acid (right)

performed using TRU columns obtained from Eichrom Technologies, Inc. Solutions containing high concentrations of emission-line rich *f*-block elements such as Am and Pu interfere with the detection of trace elements necessitating removal of the actinide elements for successful ICP-AES analysis [42]. To remove Am from these samples, 2 mL (~ 10 mg Am) aliquot of solution in 2 M HNO_3 was passed through a column of TRU resin using 2 M HNO_3. Radiochemical measurements suggested that this process resulted in Am decontamination factors (DF) > 1000. The eluent was analyzed with a Horiba Jobin–Yvon Ultima 2 ICP-AES (Horiba Scientific, USA). The schematic of the separation for ICP analysis is shown in Fig. 10.

All standards for ICP-MS and ICP-AES calibration and verification were traceable to NIST. To ensure measurement robustness blank and QA/QC samples were run in parallel with the samples. Multi-element calibration standards (10 µg/mL) procured from Inorganic Ventures were used for instrument calibration. Multi-element calibration verification standards were procured from a different vendor (Spex Certiprep, USA) at a concentration of 10 µg/mL. For both the ICP-MS and the ICP-AES analyses, calibration checks were performed prior to, during, and after each batch of analyses. Multiple QCs including matrix spike solutions were analyzed with each batch of samples. A sample preparation blank was also included and analyzed with each batch of samples and used to calculate MDLs listed in Table 7.

Ion exchange separation recoveries were evaluated by spiking with an internal standard. Table 8 shows the calculated recovery percentages of the elements analyzed by ICP-AES.

Am, Pu assay and isotopic analyses

Isotope Dilution can be coupled with TIMS to provide a high precision assay measurement of elements with multiple available isotopes which is particularly useful for actinide analysis. In this method, a “spike” of known concentration is added to the sample during the chemical dissolution and separation steps of isotopic analysis. NIST traceable spikes of ^{243}Am and ^{244}Pu were used to measure elemental assay of Am and Pu respectively as shown in Table 5 for the parent $^{241}AmO_2$. The precision of the isotope dilution method is limited by the quality of the spike calibration, sample weighing, and the quality of the chemical processing, as TIMS provides high accuracy with low uncertainty in isotopic measurements.

The isotope dilution technique was used for measurement of trace Pu in the presence of Am. The sample contained 0.1379 ± 0.0010 (wt%) of Pu as shown in Table 9. The technique is capable of measuring Pu in Am matrix down to parts per million levels indicated in Table 7. Chemical separation was necessary prior to remove isobaric interference for Pu, Am and U respectively. Isotopic and assay analysis

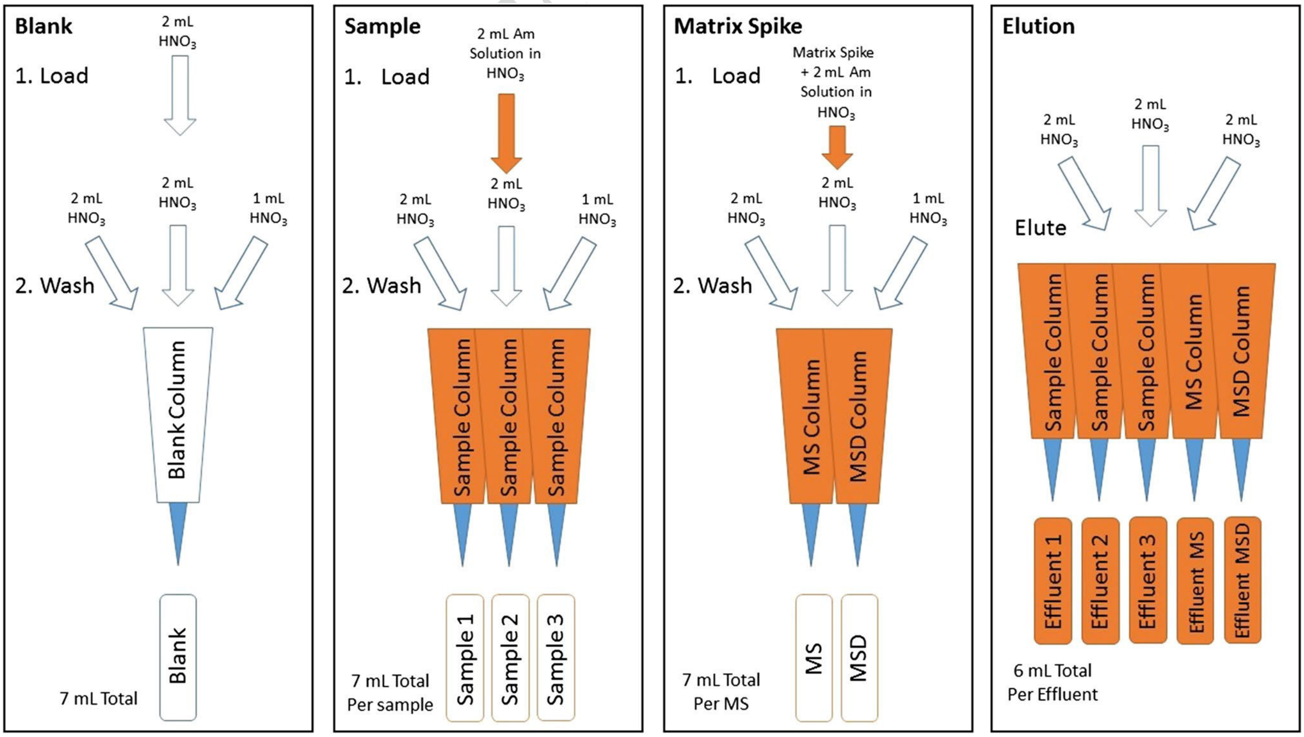


Fig. 10 Schematic for the separation experiments for ICP-AES analysis

Table 7 Minimum detection limits for analyte measurements in AmO_2 mixture solutions

Analyte	Minimum detection limit	Method
Am isotopic abundance (wt%)	0.00005	TIMS
Am concentration (pg)	3.0	IDMS (TIMS)
Pu concentration (pg)	8.0	IDMS (TIMS)
Al concentration (ppm)	<1.3	ICP-MS
Be concentration (ppm)	<0.1	ICP-MS
Bi concentration (ppm)	<0.27	ICP-MS
B concentration (ppm)	<7.0	ICP-MS
Cd concentration (ppm)	<0.1	ICP-MS
Ca concentration (ppm)	<9	ICP-AES
Cr concentration (ppm)	<0.97	ICP-MS
Co concentration (ppm)	<0.1	ICP-MS
Fe concentration (ppm)	<130	ICP-AES
Pb concentration (ppm)	<16	ICP-AES
Mg concentration (ppm)	<8.0	ICP-MS
Mn concentration (ppm)	<0.30	ICP-MS
Mo concentration (ppm)	<15	ICP-MS
Na concentration (ppm)	<170	ICP-AES
Np concentration (ppm)	<0.06	ICP-MS
Ni concentration (ppm)	<0.2	ICP-MS
K concentration (ppm)	<370	ICP-AES
Si concentration (ppm)	<80	ICP-AES
Sn concentration (ppm)	<0.14	ICP-MS
Zn concentration (ppm)	<1.6	ICP-MS
Zr concentration (ppm)	<0.84	ICP-MS

Table 8 Empirical ion-exchange separation recoveries for select elements

Analyte	Ion exchange recovery (%)	Method
Ca concentration	107 ± 6	ICP-AES
Fe concentration	102 ± 19	ICP-AES
Pb concentration	112 ± 7	ICP-AES
Na concentration	100 ± 7	ICP-AES
K concentration	101 ± 7	ICP-AES
Si concentration	116 ± 2	ICP-AES

Table 9 Americium isotopic by TIMS and plutonium concentration by TIMS-IDMS

Analyte	Results
^{241}Am (At%)	99.9087 ± 0.0017
^{243}Am (At%)	0.0916 ± 0.0020
Pu (wt%)	0.1379 ± 0.0010

are the most critical measurement listed in requirements document for the $^{241}AmO_2$ product.

Certified Reference Material (CRM) 126a (Pu metal) and Standard Reference Material (SRM) 4332C (^{243}Am) were used for spike calibration of Pu and Am, respectively, for IDMS measurements. Plutonium Triple Atom Spike, in nitrate form, CRM 144,—^{240}Pu/^{242}Pu/^{244}Pu was used as used as quality control (QC) reference materials for Pu isotopic analyses. A series of QC NIST-traceable radiochemical isotopic standards were prepared gravimetrically from pure isotope solutions of ^{241}Am and ^{243}Am (Eckert & Ziegler) with varying ratios of ^{241}Am/^{243}Am (1:1, 20:1, 200:1). The primary standards were certified for assay and isotopics by the vendor using radiochemical methods, but overall uncertainties associated with certified radiochemical measurements were higher than ideal for TIMS measurements. However, no applicable TIMS RMs were available for the study.

Discussion

The combined results from this Am study were used to demonstrate that the restarted production of $^{241}AmO_2$ at LANL could be supported by existing analytical facilities and using modified analytical techniques. A challenging actinide to handle, this study demonstrated that small modifications in analytical techniques can be made to achieve a defined degree of confidence in the repeatability of analytical AmO_2 sample measurements and estimates for minimum detection limits, precision, and accuracy for future analyses. The success in analyzing bulk quantities of this high activity isotope demonstrates the versatility of the analytical chemistry group and how techniques can often be readily adapted to other actinides, provided the right skill sets, facilities and trained personnel are available.

Analysis and certification of Pu NDA standards

A series of non-destructive assay (NDA) plutonium standards were required to support remote monitoring of various items through public roads, ports, and other means of travel [43]. Portal monitors help to identify radioactive items that being moved clandestinely [44–48]. These standards would replicate the composition of nominally weapons grade plutonium. These were sealed in multiple layers of containment to ensure chemical stability [49]. These standards had to be very well defined dimensionally (in terms of diameter and thickness) and by mass. The various monitoring systems for which these standards were developed measure both absolute activity and acquire a gamma spectrum. These standards are designed to calibrate and test the detection system in the field. Globally, there is a lack of mulit-gram Pu metal standards available. NIST traceability was also achieved through

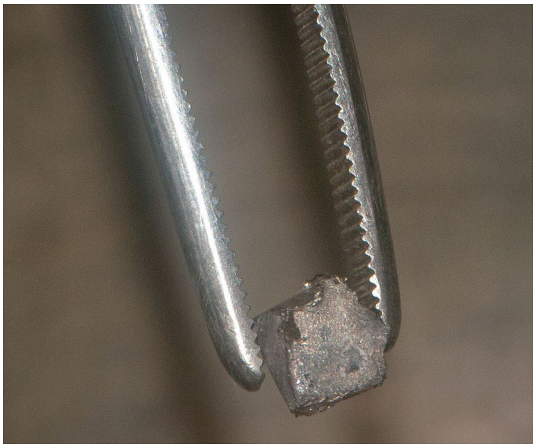


Fig. 11 Plutonium metal analytical samples

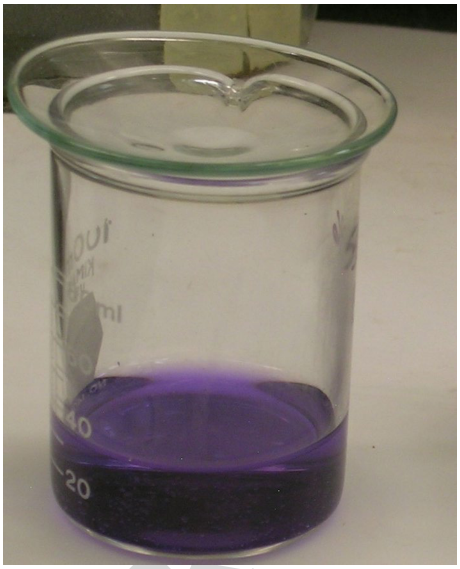


Fig. 12 Solution of Pu(III) in HCl media after metal dissolution

use of RMs for critical analytes. This effort required a significant amount of Pu, unusual casting, specific machining, and accurate actinide chemistry designating LANL as the ideal environment to accomplish the work. Ten standards were cast at once to ensure homogeneity and uniformity across all disks. A graphite mold was used to cast these standards as disks which were later machined to fixed dimensions.

First, samples were taken from the Pu rods that would eventually be used to cast the each disk. To best reflect the individual composition of each disk, 5 g samples were taken from the runner area adjacent to each disk in the casting mold (Fig. 11). For each sample, Pu assay, Pu isotopics, Am assay, trace element, U assay and isotopics, Am, Np, and Ga assay were performed. While samples were taken from each disk, only five of the disks were analyzed. The additional samples were taken in case of anomalous results. Material reporting specifications only required a suite of analytical methods to be applied to the samples to provide the necessary values for Pu assay, Pu isotopics, Am assay, and Ga assay.

Pu assay determination

Assay of Pu begins with metal dissolution by hydrochloric acid, as shown in Fig. 12. Plutonium metal reacts readily with HCl (typically 6 M is utilized), going into solution as Pu^{3+} while driving off H_2 as seen in Eq. 1. Pu assay was determined by controlled-potential coulometry (CPC), a well-developed method for Pu assay that provides an uncertainty of ± 0.08 wt% at a 95% confidence level for plutonium metals [50–52]. The CPC method involves taking a weighed aliquot of Pu in a sulfuric acid medium and electrochemically reducing it to the + 3 oxidation state, then oxidizing it to the + 4 oxidation state while monitoring the electric charge in coulombs over time. The amount of Pu is then calculated using Faraday's law. Iron directly interferes with Pu in this method and a correction based on the Fe assay must be applied. Iron assay is performed spectrophotometrically by coordinating 1,10-phenanthroline to Fe, creating the $Fe(phen)_3^{2+}$ complex, which has a high molar absorptivity in the visible region which can be quantified easily [53]. The method is calibrated against CRM 126A and a well characterized, homogeneous, stable PuO_2 was analyzed with each batch of samples using a Savannah River National Laboratories Coulometer, Model SRNL-Rev. 2.

$$Pu_{(m)} + HCl_{(aq)} \rightarrow H_{2(g)} + PuCl_{3(aq)} \tag{1}$$

Pu isotopic determination and Ga assay

Plutonium isotopics were measured by thermal ionization mass spectrometry (TIMS), incorporating total evaporation techniques [54, 55]. Thermal Ionization Mass Spectrometry (TIMS) measurements on these samples were completed using magnetic sector mass spectrometers (Model VG 354 or VG Sector-54, Thermo Corp, USA). Samples were dissolved in HCl. Chemical separations were performed using a macroporous anion-exchange (60–150 mesh, chloride form) resin with a variety of mineral acids (HCl, mixed HCl-HI, and HNO_3) to sequentially elute americium (Am), plutonium (Pu), and uranium (U). Americium and U elutions were collected, dried, loaded onto rhenium (Re) filaments, and analyzed in separate mass spectrometer batches to eliminate isobaric interferences between Pu (^{241}Pu, ^{242}Pu) and Am (^{241}Am, ^{242}Am) and Pu (^{238}Pu) and U (^{238}U). Additionally, Ga assay was accomplished by ^{71}Ga isotope dilution mass spectrometry (IDMS). The gallium assay specification was somewhat strict with a value between 1 and 2 wt%. The assay results

Table 10 Plutonium concentration and isotopic abundance results for Rod and Disk samples

Sample	Pu assay (wt%)	^{239}Pu (wt%)	^{240}Pu (wt%)	Fe assay (ppm)	^{241}Am (ppm)	Gallium (wt%)
Rod 1	98.23 ± 0.01	93.935 ± 0.001	5.906 ± 0.001	24 ± 4	279 ± 14	1.813 ± 0.002
Rod 2	98.27 ± 0.05	93.935 ± 0.001	5.907 ± 0.001	32 ± 6	279 ± 14	1.809 ± 0.003
Disk 1	98.09 ± 0.03	93.941 ± 0.001	5.906 ± 0.001	45 ± 5	287 ± 17	1.813 ± 0.009
Disk 2	98.09 ± 0.05	93.942 ± 0.001	5.906 ± 0.001	47 ± 5	285 ± 17	1.815 ± 0.008
Disk 6	98.20 ± 0.04	93.936 ± 0.001	5.906 ± 0.001	41 ± 6	279 ± 15	1.810 ± 0.008
Disk 7	98.27 ± 0.04	93.942 ± 0.001	5.906 ± 0.001	41 ± 5	285 ± 17	1.802 ± 0.007
Disk 8	98.18 ± 0.04	93.937 ± 0.001	5.907 ± 0.001	34 ± 4	283 ± 15	1.819 ± 0.005

Isotopic values are decay corrected

fall at the high end of that range, but within specifications. The results are fairly consistent throughout the samples.

Radiometric determination of ^{241}Am and ^{237}Np

A ^{241}Am assay was completed by radiochemical methods. To measure ^{241}Am, diluted samples stippled and dried on a glass plate were gross alpha-counted using a gas-proportional counter. A solution measurement of the dilute sample was also measured using a NaI(Tl) gross gamma counter. The ^{241}Am concentration was calculated based on the two measurements, and shown to be less than 300 ppm for all samples. ^{237}Np was measured by radiometric counting preceded by extraction from the bulk Pu by the TTA (2-thenoyltrifluoroacetone) extraction method [56]. ^{237}Np will grow in at a rate of a few ppm per year emits gamma rays that could be detected by the portal monitors, however concentrations were all below 30 ppm for disks.

Trace element analysis

Measurements of C as a trace element was accomplished by combustion coupled with IR spectroscopy. Trace metals: Al, B, Be, Ca, Cd, Cr, Cu, Mg, Mn, Mo, Ni, Np, Pb, Ni, Si, Ta, Th, and W were measured by ICP-MS and ICP-AES, as described in the previous sections. The total impurity concentrations summed to 190 ppm (excluding Fe). The only notable impurities present were C (~ 30 ppm), Np (~ 30 ppm), Si (~ 60 ppm) and W (~ 50 ppm); all other trace element impurities were below 5 ppm or at or below

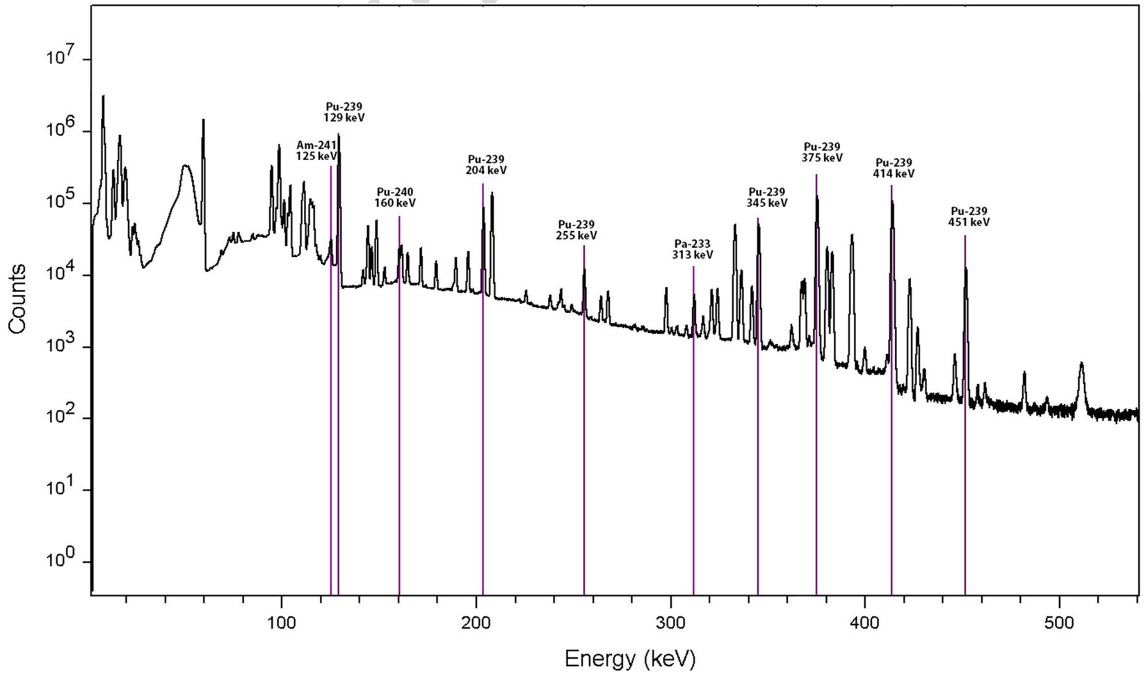


Fig. 13 Typical gamma spectrum of NDA standard disk. Key peaks are highlighted

minimum detection limits for the analytes. If these elements were present in high concentrations they could drastically affect the absorption and scattering of gamma rays, however all of these elements were at very low concentrations and will not be discussed further. All methods were calibrated with NIST-traceable standards or run with NIST-traceable controls where applicable.

Discussion

Overall, our chemical analyses revealed the disks were generally homogenous with minor variations. The results were well within the specifications needed for these NDA standards.

The primary elements of concern for this analysis are shown in Table 10. All the disks had a Pu content between 98.08 and 98.27% when decay corrected to the same date. Given the uncertainty of the CPC method described above, the variability seen in Table 10 are actual variations, but fall well within the range specified for the product. The ^{240}Pu content was consistent throughout all of the samples at just under 6% of the total Pu.

The combined results of the analytical measurements demonstrated homogeneity and the consistent chemistry between material rod and cast disk. Following final machining, the disks' density and dimensions were also measured and found to be consistent. Overall, the disks were able to act as NDA gamma standards for remote detection, as is evident in the representative gamma spectrum of the actual Pu metal sample from the project seen in Fig. 13. This spectra was acquired using gamma-spectrometry with a HPGe detector with a beryllium end window. This work represents one of the unique capabilities of LANL as the ability to produce and characterize this standard to address the needs of national security programs, with support from analytical chemistry.

Conclusions

It is the authors' hope that the three case studies presented here display the capabilities of the actinide analytical chemistry group at LANL, and how the capability has grown and adapted to meet the dynamic challenges of various programs over the course of several decades. The analytical chemistry of heat source Pu requires unique methods to overcome the radiolysis effects of the isotope and the heat generated from the analyte. Support of restarted $^{241}AmO_2$ production demonstrates the adaptability of Pu techniques to bulk ^{241}Am characterization, while maintaining high precision and accuracy. Finally, the production and analysis of Pu NDA standards exemplifies the classic analysis capabilities of the group with a specialized sample, and how production and analytical chemistry at LANL work closely with one another to ensure successful delivery of all program objectives.

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