Los Alamos National Laboratory

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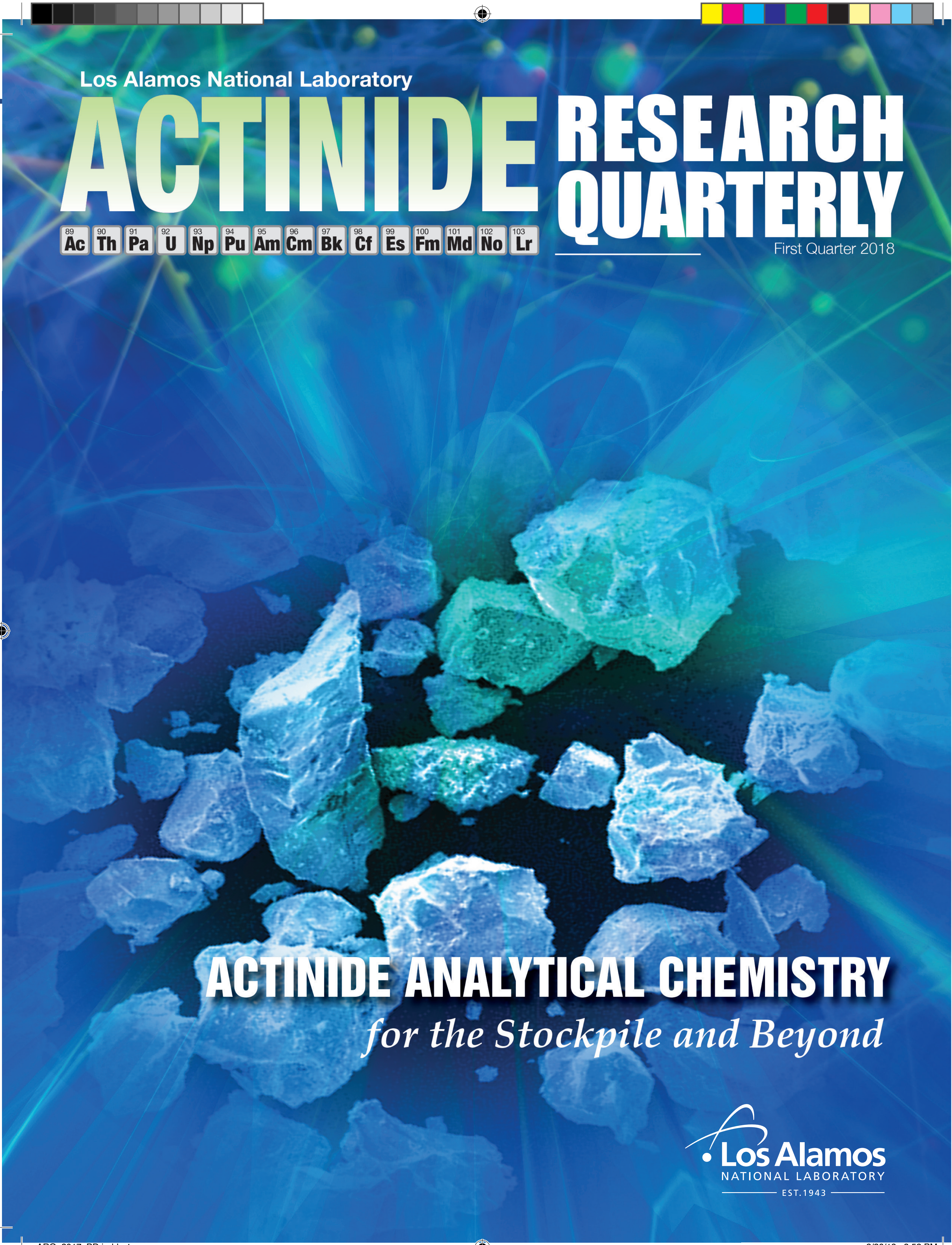


ACTINIDE ANALYTICAL CHEMISTRY

for the Stockpile and Beyond

Los Alamos
NATIONAL LABORATORY
EST. 1943

Rebecca Chamberlin

Preface

Actinide analytical chemistry—the comprehensive analysis of materials whose primary constituent is an actinide element such as plutonium or uranium—has been a core capability of Los Alamos National Laboratory since the Manhattan Project. Housed near Ashley Pond during World War II, analytical chemistry spent the next decade at DP Site and then settled into its permanent home in the Chemistry and Metallurgy Research (CMR) facility in 1953.

Over the next 60 years, the capability expanded, transformed, contracted, and diversified in response to the evolving programmatic demands of the eras of nuclear weapons testing, science-based stockpile stewardship, and pit manufacturing at Los Alamos. Always, we have partnered closely with chemical engineers and plutonium metallurgists to ensure that plutonium materials meet the specifications for their intended use. When process upsets occur, we provide chemical forensic investigation to help identify and correct production issues. We also prepare and certify plutonium reference materials that are distributed worldwide by our partner, the Department of Energy's New Brunswick Laboratory.

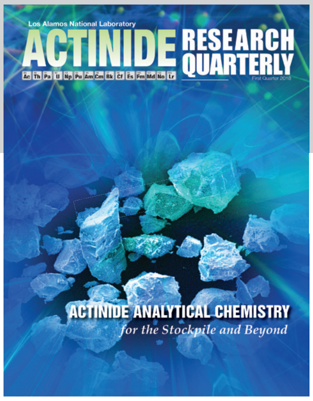
In recent years, the capability has expanded to applications in global security. Forensic analysis of bulk nuclear materials, detection of clandestine nuclear processing, disposition of surplus plutonium, and development of new instrumentation and methods for identifying nuclear materials in the field are just a few of these contributions.

At the other end of the spectrum, chemists perform low-level measurements of actinide elements and isotopes to ensure the radiological protection of plutonium workers throughout Los Alamos. And characterization of environmental plutonium at historic processing sites lends insight into mechanisms of deposition and transport, supporting both environmental protection and national security programs. The methods and instrumentation for analyses at microgram-to-femtogram levels in these natural matrices are remarkably similar to those used to analyze gram quantities of nuclear material, though specialized clean chemistry facilities are needed to handle the very tiniest amounts.

The CMR facility will soon be closing to programmatic work, with bulk actinide measurement capability moving to Technical Area 55 (TA-55). Construction and equipment installation in the Radiological Laboratory/Utility/Office Building (RLUOB) brings both opportunity and challenge. Because RLUOB was designed and authorized for much smaller quantities of plutonium than the CMR, we are reconsidering our entire workflow from the standpoint of minimizing the amount of material that we use.

This issue of *Actinide Research Quarterly* is titled "Actinide Analytical Chemistry for the Stockpile and Beyond" to reflect both our enduring commitment to the nuclear weapons program and the many other ways that the capability impacts the Laboratory and the nation.

In this issue



About the cover

Particles of plutonium-beryllium alloy ($PuBe_{13}$) recovered from sealed neutron sources, such as those once used in industrial applications, such as nuclear reactors and oil exploration, as well as in medical and university science laboratories. Los Alamos analytical chemists have the expertise and facilities to comprehensively analyze the chemical and radiological makeup of such materials, supporting U.S. government efforts to detect and prevent illegal possession and trafficking of Pu-Be sources and other radiological materials.

Plutonium-238 Analytical Chemistry Transition for Hazard Reduction

Nell Carver and Ning Xu

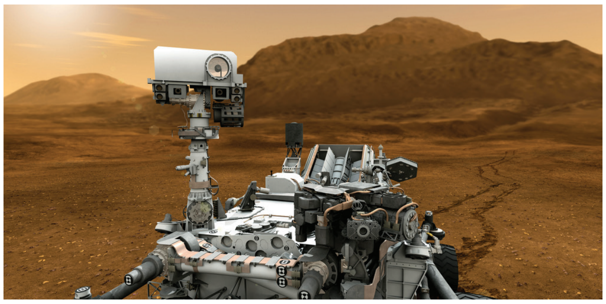
Introduction

The ^{238}Pu analytical chemistry process in the Chemistry and Metallurgy Research (CMR) facility was identified many years ago as significantly contributing to operational risk at the facility. This, in conjunction with CMR's aging condition, finally facilitated the 2013 transfer of ^{238}Pu analytical chemistry capabilities to TA-55 and consolidation of them in the PF-4 Plutonium Facility.

Transitioning these operations from CMR to TA-55 has greatly benefited the nationally important ^{238}Pu analytical chemistry program, which supports national security programs at Los Alamos National Laboratory and supplies heat source material to fuel NASA deep space missions. In addition to enabling improved service, the transition of $^{238}PuO_2$ analytical chemistry to TA-55 has addressed the longstanding operational risks associated with the CMR facility.

The ^{238}Pu Analytical Chemistry Transition Team received a Los Alamos National Laboratory Distinguished Performance Award for moving the ^{238}Pu analytical chemistry capabilities from CMR to TA-55's Plutonium Facility, PF-4. Shown here are team members (back row, left to right) Dennis Montoya, John Matonic, and Robert Jump and (front, left to right) Nell Carver, Julie Trujillo, and Ning Xu.

Plutonium-238 is a man-made isotope, produced by bombarding ^{237}Np with neutrons in a nuclear reactor. The oxide form, $^{238}PuO_2$, is purified, pressed into pellets, and welded into iridium cladding at Los Alamos for assembly into radioisotope thermoelectric generators (RTGs). Generally referred to as heat sources, RTGs provide power for spacecraft and rovers, such as the Mars Space Laboratory's Curiosity rover, and keep the scientific instruments warm on that desolate planet. The $^{238}PuO_2$ analytical chemistry operations are critical for the nation's current and future space exploratory missions. The operations support process control and product certification of nuclear fuel by determining its chemical composition. The chemical analyses required include direct current (DC) arc spectrometry for quantifying cationic



The RTG-powered Mars Curiosity rover.

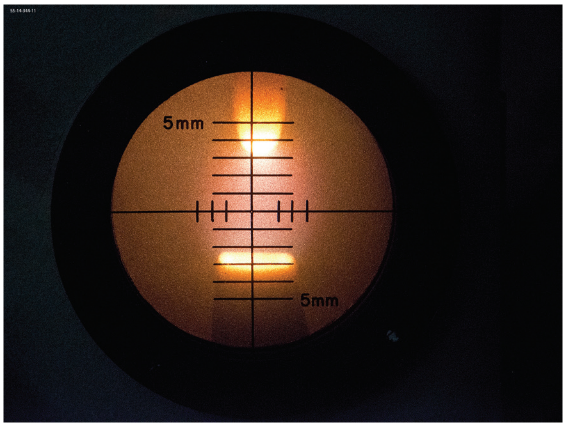
impurities, Pu assay measurement by UV-Visible spectrophotometry, radiochemistry for determining actinide impurities, and Pu isotopic determination by gamma spectrometry.

DC Arc Spectrometry

Transitioning the $^{238}PuO_2$ analytical chemistry capability from CMR to TA-55 was a critical milestone for Los Alamos National Laboratory’s Actinide Analytical Chemistry group (C-AAC) because the aging CMR facility will soon be decommissioned. The apex of the challenge was relocating the instrument used for cationic trace impurity analysis—the DC arc spectrometer. For decades, C-AAC chemists have used DC arc technology to determine trace elemental impurities in solid-form nuclear materials, especially those that are difficult or impossible to dissolve/digest into liquid form. Because portions of the $^{238}PuO_2$ fuel are high-fired at above 1600°C, that fuel is hard to dissolve with common solvents. As a result, DC arc spectrometry is the most practical and direct way to quantify the trace impurities in the $^{238}PuO_2$ solid.

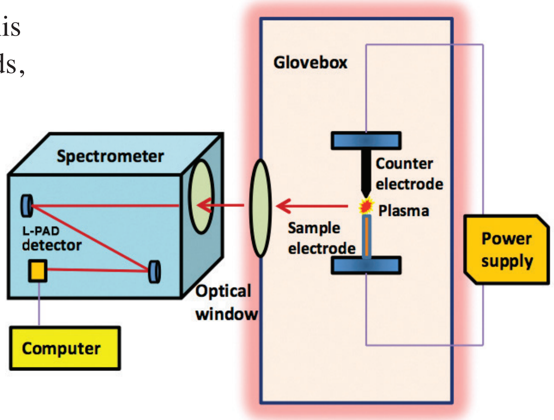
To perform a DC arc analysis, chemists load $^{238}PuO_2$ powder into a graphite sample electrode. The sample electrode and a counter electrode are then inserted into an arc stand (inside a glovebox) connected to a power source. An instant alternating-current spark between the electrodes initiates a plasma, in which trace impurities from the heated sample are vaporized. Within the high-temperature region of the plasma, sample atoms are excited and ionized, emitting light at characteristic wavelengths. The light is subsequently dispersed by a grating and detected by the optical detector, which is located outside the glovebox. The detector does not need to be radiologically contained because only transmitted light is collected. To minimize the spectral interference, chemists mix a small percentage of gallium oxide powder with the sample to suppress Pu matrix effects during sample analysis. This technique is called the carrier distillation method.

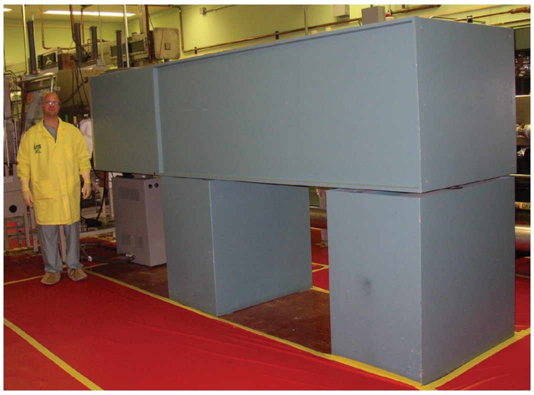
For decades, DC arc analysis at CMR was performed with a 40-year-old Jarrell Ash Ebert DC arc instrument. The extremely high resolution of this detector was supported by a 3.4-meter optical focal length; in other words, the detector was over 9 feet long. The instrument recorded elemental emission images onto a series of photographic glass plates, which chemists developed in a darkroom. The image’s position represented the wavelength of emission, informing scientists which elements were present, and its darkness showed the elements’ quantity. Chemists had to use a microdensitometer (similar to a library’s microfiche reader) to manually interpret the images. It took them a week to determine the impurity concentrations for a batch of 20 samples. Obviously, the outdated Jarrell Ash Ebert DC arc instrument was too large and its operating conditions too cumbersome to be desirable in PF-4.



DC arc plasma and the sample electrode. The sample electrode (bottom) is cupped to hold sample material. The plasma (bright light, top) forms between the sample electrode and the counter electrode above it (see schematic below).

Schematic of a DC arc emission spectrometer. As shown by the red arrows and line, light from the plasma passes through a quartz optical window mounted on a glovebox’s service panel, enters the spectrometer, is dispersed as a function of wavelength, and is detected by a large-format programmable array detector (L-PAD).





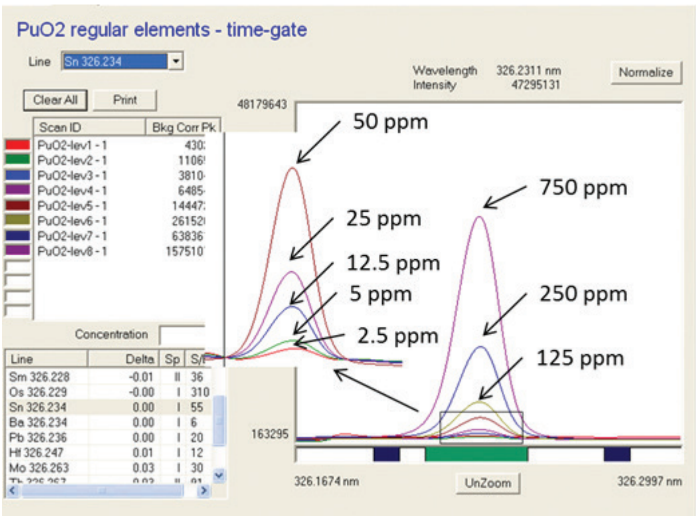
The Jarrell Ash Ebert DC arc instrument, with its 3.4-m focal length, at CMR. Chemist Jeff Miller was one of the instrument operators.

The new Prodigy DC arc instrument installed in PF-4 is just over a meter long. The sample chamber is radiologically contained in the glovebox, while the optics and computer controls are on the stand outside the glovebox.

Realizing the need for a modern DC arc instrument, C-AAC scientists collaborated with Teledyne Leeman Labs (Hudson, NH) to develop the Prodigy DC arc spectrometry system. The prototype of this instrument represented the newest generation in DC arc technology. A 1-meter-long spectrometer replaced the old 9-foot-long detector, and its 1-in.^{2} semiconductor chip replaced the old photographic glass plates.

The Prodigy DC arc spectrometer features computer software that allows chemists to choose emission lines for various elements and manipulate operational parameters. The new instrument acquires data much faster than the old DC arc instrument, significantly shortening analysis time. Chemists can measure the concentrations of more than 20 elements in a $^{238}PuO_2$ sample in less than 1 min. A typical elemental concentration is shown below. Furthermore, by eliminating the need for solvents to develop and fix images on photographic plates, the new instrumentation also eliminates a Resource Conservation and Recovery Act (RCRA) mixed liquid waste stream—a tremendous success for Los Alamos' pollution prevention efforts.

The prototype Prodigy instrument was installed at CMR, where it was used to develop and validate analytical methods for trace impurity determination in $^{238}PuO_2$. Now, a new Prodigy has been installed in PF-4 in the ^{238}Pu processing area and has recently been qualified for trace impurity analysis. The Prodigy instruments are a technological advance contributing to the resurgence of lost but needed instrumentation for analytical chemistry. More than 50 Prodigy units have been sold by Teledyne Leeman Labs throughout the world to measure trace elements in glass and high-purity metals,



PuO2 regular elements - time-gate

Line: Sn 326.234

Wavelength 326.2311 nm
Intensity 47295131

Scan ID	Bkg Corr Pk
🟥 PuO2-lev1 - 1	430
🟩 PuO2-lev2 - 1	1106
🟦 PuO2-lev3 - 1	3810
🟪 PuO2-lev4 - 1	6485
🟥 PuO2-lev5 - 1	14447
🟨 PuO2-lev6 - 1	26152
🟦 PuO2-lev7 - 1	63836
🟪 PuO2-lev8 - 1	157510

Concentration

Line	Delta	Sp	S/
Sm 326.228	-0.01	II	36
Os 326.229	-0.00	I	310
Sn 326.234	0.00	I	55
Ba 326.234	0.00	I	6
Pb 326.236	0.00	I	20
Hf 326.247	0.01	I	12
Mo 326.263	0.03	I	30

Typical elemental concentrations determined using the Prodigy instrument.

including the tungsten used inside light bulbs. The technological development of Prodigy is a proud Los Alamos contribution to the world.

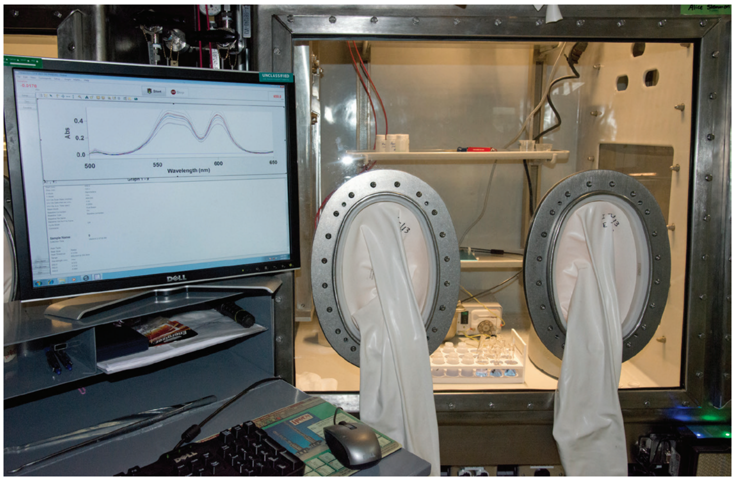
Plutonium Assay

The total Pu content (^{238}Pu through ^{242}Pu) of an oxide sample, or Pu assay, is measured by a scanning UV-visible spectrophotometer.

For the process, $^{238}PuO_2$ samples are dissolved with mineral acids in sealed Parr vessels. The high pressure in a Parr vessel, similar to that of a pressure cooker, facilitates the oxide dissolution. Chemists carefully adjust the Pu concentration to 4 mg/mL and HCl to 2 molar, while adding zirconium to complex the fluoride ion, which would otherwise cause interference. Ascorbic acid—vitamin C—is used to reduce Pu from Pu(IV) to Pu(III), which allows the spectrum to be measured.

The Pu absorbance at five wavelengths—516, 560, 586, 600, and 640 nm—is measured using a UV-Vis scanning photodiode array spectrophotometer controlled by a computer. The absorbance at each of these wavelengths is labeled A, B, C, D, and E, respectively. The method software uses four peak-minus-baseline or peak-minus-valley net absorbance points, designated as B-A, B-C, D-C, and D-E, to calculate the Pu concentration.

Scientists in C-AAC have improved this process significantly by using a fiber-optic immersion, or dip, probe. The dip probe eliminates the use of a peristaltic pump and pump tubing, where air bubbles can cause significant interference. The improved procedure shortens the time operators spend manipulating equipment in the glovebox, thereby reducing the workers' dose exposure while increasing the sample throughput. In addition, this improved process reduces sample consumption by more than half, thus reducing the amount of waste generated.



UV-Vis measurements from Pu analysis appear on a computer screen (left). Here, a graph shows wavelength versus Pu absorbance at five wavelengths—516, 560, 586, 600, and 640 nm. On the right is the glovebox where the measurements are taken. A vial of blue Pu solution can be seen in a sample rack inside the glovebox.

Radiochemistry

The actinide impurities (^{241}Am, ^{234}U, and ^{236}Pu) in ^{238}Pu materials are determined by radiochemical methods. Recently, C-AAC chemists developed new separation methods to eliminate the use of hazardous chemicals such as HBr, HIO_4, and TTA-methylbenzoate and have streamlined the counting techniques.

Plutonium-238 has a half-life of 87.7 years and decays to ^{234}U by releasing an alpha particle, as expressed by the following equation:

$$^{238}\mathrm{Pu} \rightarrow \alpha + {}^{234}\mathrm{U}\ .$$

Nell Carver and Bob Jump of C-AAC performing ^{238}Pu radiochemical analyses in the new PF-4 lab space.

Due to the relatively short half-life of ^{238}Pu, the ^{234}U progeny can grow to significant levels in just one year. At Los Alamos, we use aqueous processing to remove the U and other impurities before further material processing and chemical analyses.

Chemists load the dissolved Pu(III) onto a UTEVA® chromatography column to retain U(VI) while allowing Pu(III) to pass through the resin. They then elute the U with a very dilute mixture of nitric and hydrofluoric acids and dry microliter volumes of the U raffinate on a glass plate for alpha spectrometry counting.

Microliter volumes of the dissolved and diluted sample solutions are counted for ^{241}Am and ^{236}Pu using gamma and alpha spectrometry, respectively. Typically, the concentration of ^{241}Am in a heat source Pu (HS-Pu) oxide sample increases over time as the ^{241}Pu in the sample undergoes β^- decay to yield ^{241}Am, as expressed in the following equation:

$$^{241}\mathrm{Pu} \rightarrow \beta^- + {}^{241}\mathrm{Am}\,.$$

Since ^{241}Pu has a fairly short half-life, 14.4 years, and the half-life of ^{241}Am is much longer (432 years), the amount of ^{241}Am in a gram of HS-Pu oxide sample can increase by several hundred micrograms in a few years. Because ^{238}Pu is produced according to the following reaction:

$$^{237}\mathrm{Np} + \mathrm{n} \rightarrow {}^{238}\mathrm{Np} \rightarrow \beta^- + {}^{238}\mathrm{Pu}\,,$$

it is valuable to know how much ^{237}Np is present in the final fuel product. A small amount of ^{236}Pu is also formed by the following reaction:

$$^{237}\mathrm{Np}\,(\mathrm{n},2\mathrm{n})\,{}^{236}\mathrm{Np}$$

$$^{236}\mathrm{Np} \rightarrow \beta^- + {}^{236}\mathrm{Pu}\,.$$

Plutonium-236 is a byproduct of this process and an important impurity to quantify. One of the daughter products of ^{236}Pu, thallium-208 gives out strong gamma radiation, which is detrimental to equipment on a Mars rover. The ^{236}Pu is counted directly by alpha spectrometry in the diluted sample with the ^{238}Pu because the two cannot be separated by chromatography.

Plutonium Isotopics

To support the transition of ^{238}Pu analytical chemistry to PF-4, C-AAC chemists have also successfully developed a nondestructive analysis (NDA) method for Pu isotopic (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu) determination. This effort was completed through collaboration with the Nuclear Engineering and Nonproliferation Division's Advanced Nuclear Technology group. This newly developed NDA method uses high-purity germanium (HPGe) detectors in conjunction with Los Alamos–developed FRAM software.

The compact gamma-counting instrument replaces the thermal ionization mass spectrometry (TIMS) system at CMR, eliminating the need to install large analytical equipment in PF-4. The NDA method requires very minimal manipulation in a glovebox, which promotes "as low as reasonably achievable" (ALARA) radiation protection principles and improves sample turnaround time. In addition to Pu isotopic measurement, chemists have also developed methods for determining ^{237}Np and ^{241}Am, using the same technique and generating extra cost benefits. The specific advantages of the NDA method are these:

- Nondestructive test (no dissolution or chemical separation)
- HPGe detectors in PF-4 (no shipment required)
- Faster and easier method development
- Ability to measure ^{241}Am and ^{237}Np in addition to Pu isotopics
- No waste generation
- Improved ALARA through reduced ^{238}Pu handling

In addition to the advanced instrumentation and methodologies, the chemical analysis will be performed in PF-4 in an infrastructure that is safer and more modern and efficient. PF-4's new Pu assay and radiochemistry gloveboxes provide added operational safety and improved ergonomics because of features such as oval glove ports, large viewing windows, fire suppression technology, fire skirting, larger zone 1 piping, corrosion coating (powder-coated halar), pneumatically actuated airlock doors, and compartment gloveboxes.

C-AAC has accomplished the complete transition of the ^{238}Pu analytical chemistry capabilities to PF-4, ensuring strong support for Los Alamos' national security mission.

New radiochemistry and Pu assay gloveboxes at PF-4.

Modernization and Infrastructure Investment in Actinide Analytical Chemistry and Materials Characterization Capabilities

Amy Wong, John Matonic, Jeremy Mitchell, and Tim Nelson

Introduction

Analytical chemistry (AC) and materials characterization (MC) capabilities provide critical measurements and characterizations essential to determine the chemical, material, radiological, and nuclear signatures of actinide-containing materials. These capabilities are important for certifying the U.S. nuclear stockpile, thereby ensuring it is safe, secure, and effective. AC and MC capabilities also support other national security missions, such as the characterization of recovered illicit nuclear material to protect against nuclear threats. (See "The Power of Nuclear Forensic Analysis in Determining a Sample's History" in this issue.)

The majority of AC laboratories at Los Alamos National Laboratory are currently located in the Chemistry and Metallurgy Research (CMR) facility, which was constructed more than 65 years ago. The CMR facility has been in use long past its planned lifetime, and programmatic operations in the facility will be soon be terminated. Before that happens though, the operations that had been performed there must be relocated to other facilities, and that transition must be done in a way that does not jeopardize essential AC and MC capabilities.

Planning for CMR Replacement (CMRR) facilities has been under way for more than 15 years [see sidebar at left]. Completing the transition to CMRR will improve overall operational efficiency and reduce the costs and risks of maintaining an aging infrastructure. Work essential to National Nuclear Security Administration (NNSA) missions will be performed in newer facilities and laboratory space that meet today's standards for operations and infrastructure, which are vital for reducing risks to workers and the public. The opportunity to work in upgraded and new facilities, with modern instrumentation for AC/MC operations, may also help attract the next generation of actinide chemists to join the Los Alamos workforce.

The CMRR project comprises the design and construction of modern laboratory facilities, as well as the transfer of operations from the old

In 2002, the Department of Energy (DOE) approved the start of the CMR Replacement (CMRR) project, to design and build new facilities to replace the aging CMR facility. The initial plan, approved in 2005, was to build two new buildings, the Radiological Laboratory/Utility/Office Building (RLUOB) and the Nuclear Facility (NF). The first two phases—construction of the RLUOB and RLUOB Equipment Installation (REI)—were completed in 2010 and 2013, respectively, and RLUOB started radiological operations in 2014. However, the third phase of the CMRR project, the Nuclear Facility, was deferred in 2012 and subsequently cancelled in 2015.

The Radiological Laboratory/Utility/Office Building (RLUOB) started radiological operations in 2014.

In late 2011, the NNSA released guidance requiring the use of updated dosimetry information for calculations to determine the maximum quantities of radionuclides permitted in its facilities. Based on the updated dosimetry information, the radioactive materials inventory permitted in RLUOB was increased from 8.4 grams of ^{239}Pu equivalent to 38.6 grams, which in turn freed up lab space in PF-4 for other programmatic work.

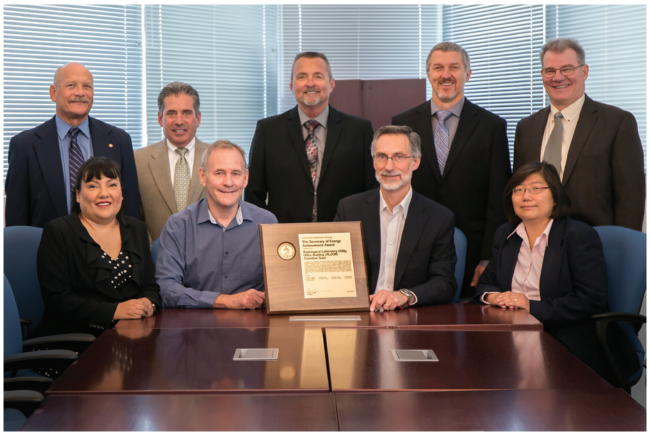
Consequently, in 2014, NNSA revised the Plutonium Infrastructure Strategy for maintaining continuity in AC and MC operations—a strategy that did not hinge on the status of the NF—using existing facilities at TA-55. This proposal outlined a strategy for maximizing the use of existing laboratory space in RLUOB and PF-4 to meet programmatic needs.

In August 2014, the new phases of the CMRR project were approved, authorizing the project to move forward with outfitting new and existing laboratory space in RLUOB and PF-4, installing additional new laboratory equipment, and consolidating remaining AC and MC capabilities from CMR at TA-55.

CMR facility into the new space. The first two phases of CMRR—the construction of the Radiological Laboratory/Utility/Office Building (RLUOB) and the initial outfitting of RLUOB laboratory space (RLUOB Equipment Installation, or REI) were completed in 2013.

Four phases of the CMRR project are still to be completed:

- RLUOB Equipment Installation, Phase 2 (REI2): Outfit lab space (~10,000 ft^2) with new enclosures and AC/MC instrumentation, start up radiological operations, and complete equipment testing and validation.
- PF-4 Equipment Installation, Phase 1 (PEI1): Expand AC/MC activities in PF-4 (~2,800 ft^2) by modifying existing gloveboxes, installing new gloveboxes and introduction hoods, and completing equipment testing and validation.
- PF-4 Equipment Installation, Phase 2 (PEI2): Consolidate and expand MC activities in PF-4 (~5,550 ft^2) by replacing outdated instruments, installing new gloveboxes and equipment, and decontaminating and decommissioning outdated equipment and laboratory space.
- Recategorization of RLUOB to Hazard Category 3 (RC3): Outfit laboratory space (~3,000 ft^2) with new enclosures and instruments, start up radiological operations, upgrade the facility as needed, and prepare and implement the safety and operations requirements to upgrade RLUOB from a radiological facility to a Hazard Category 3 (HC-3) nuclear facility with a material-at-risk limit of 400 grams of ^{239}Pu equivalent.

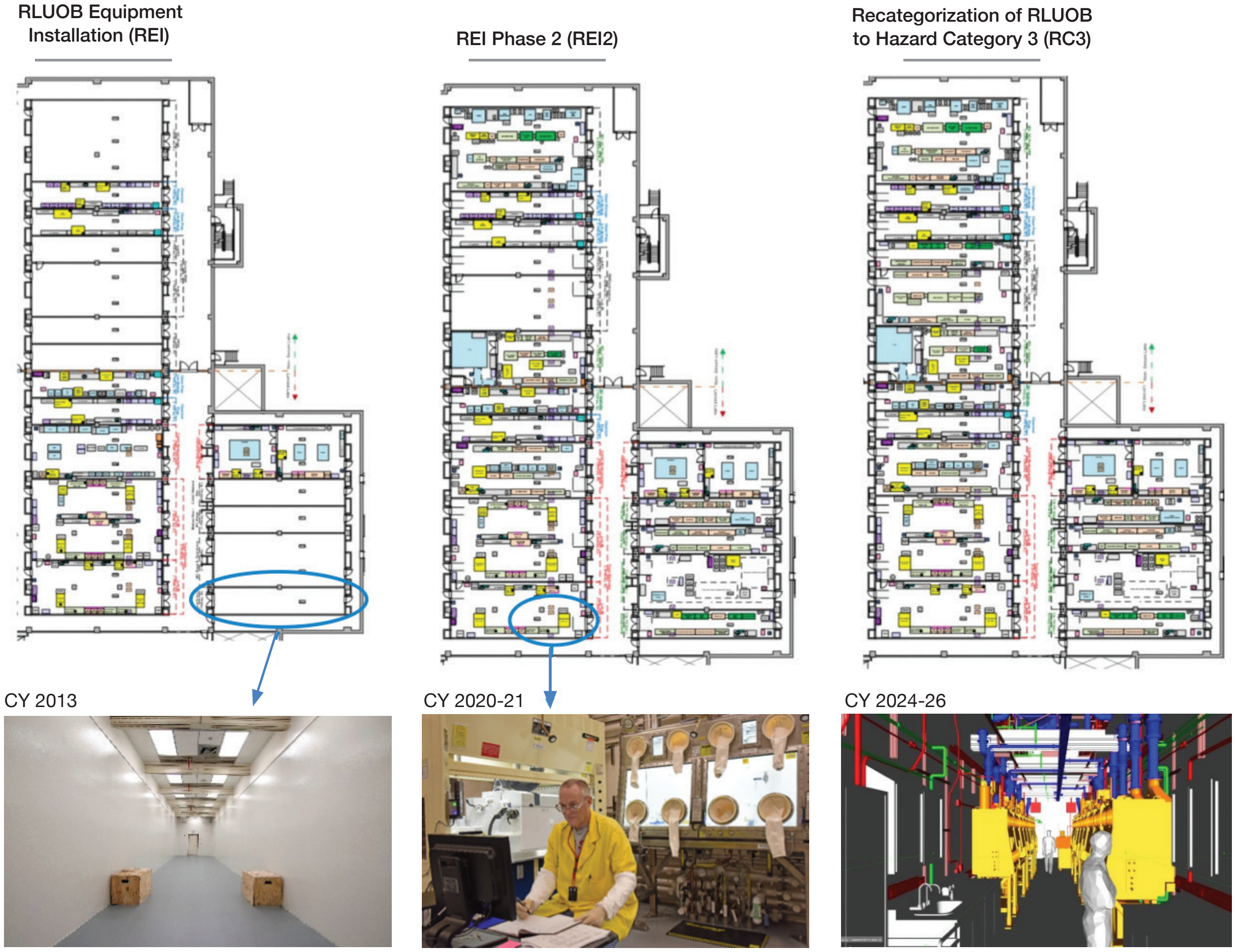


In 2014 the RLUOB Transition Team received the DOE Secretary's Achievement Award for the successful startup of RLUOB laboratory operations. The team, as shown here, is (top, from left) David Gallimore, Brett Cederdahl, Mike Parkes, Tim Leckbee, and Tim Nelson and (bottom, from left) Denise Thronas, acting Deputy Laboratory Director Paul Henry, Laboratory Director Charles McMillan, and Amy Wong. Team members Mark Myatt and Scott Warnock are not shown.

The completion of REI2 and PEI1 will enable the relocation and transition of AC/MC capabilities from the CMR facility to TA-55 and the termination of programmatic operations at CMR. The final two phases, PEI2 and RC3, will consolidate and outfit existing and new laboratory space in RLUOB and PF-4 to establish enduring AC/MC capabilities. The fiscal year 2017 appropriation bill determined that PEI2 and RC3 would be executed as separate line item projects: the PF-4 Reconfiguration Project and the RLUOB Reconfiguration Project.

Materials characterization comprises multidisciplinary expertise in actinide materials science for characterizing new and aged stockpile materials and the development of new technologies for actinide materials analysis to investigate actinide performance.

MC examines the structure and properties of a material to answer questions about why certain materials behave as they do and how they



RLUOB Equipment Installation (REI)

REI Phase 2 (REI2)

Recategorization of RLUOB to Hazard Category 3 (RC3)

CY 2013

CY 2020-21

CY 2024-26

Empty lab module

Outfitted lab module

Lab module with gloveboxes

differ from other materials. Examples of MC techniques include optical microscopy, hardness testing, transmission electron microscopy (TEM), scanning electron microscopy (SEM), Auger electron microscopy, x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), secondary ion mass spectrometry (SIMS), optical profilometry, and ellipsometry.

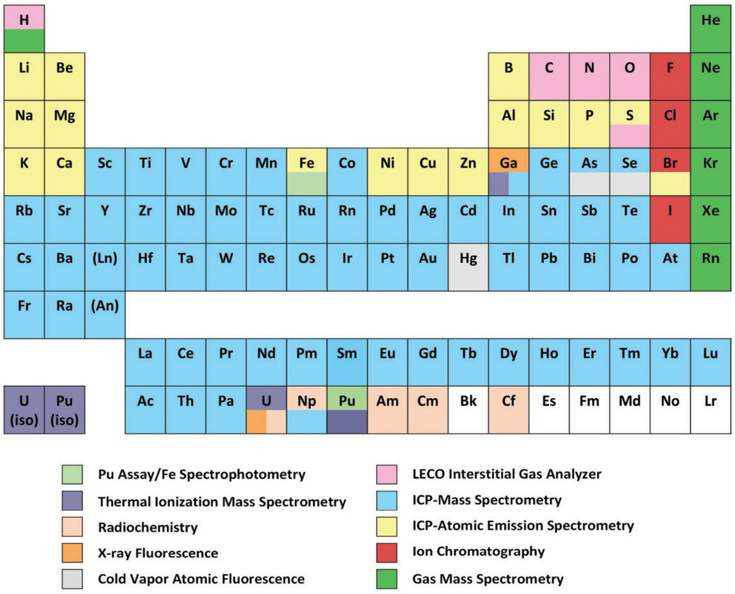
CMRR will provide laboratory space equipped for the following:

- **Measuring the physical and mechanical properties of materials.** Examples include single-crystal x-ray diffraction (XRD), powder XRD, dilatometry, thermogravimetric analysis, differential scanning calorimetry, Sievert's apparatus, physical property measurement system (PPMS), precision density measurements, tensile testing, and Taylor-Anvil impact testing.

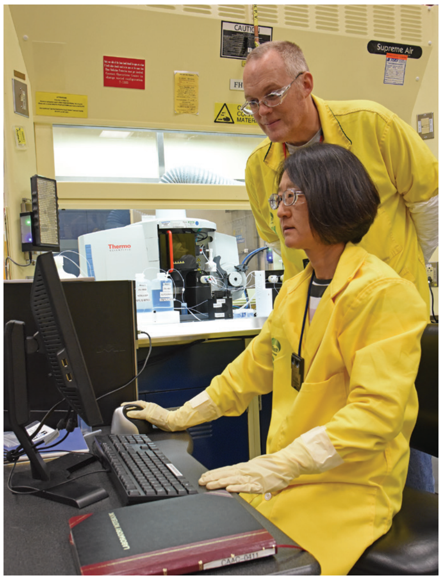
- **Materials synthesis and sample preparation.** Synthesis and preparation of actinide-containing materials is not trivial. Most work is performed in specialized gloveboxes modified to integrate with the equipment. Examples of the techniques will include a heat treatment furnace, an environmental chamber, arc melting, sample encapsulation, induction casting, a rolling mill, and a lathe.

Actinide analytical chemistry comprises chemical and radiochemical analyses of materials in which actinide elements are present. These analyses identify and quantify components, ranging from major components to trace impurities, producing results that span more than seven orders of magnitude. CMRR will provide laboratory space for consolidating AC capabilities, including the following:

- **Mass spectrometry,** to provide isotopic composition of samples with the highest precision available today. The RLUOB laboratory has two thermal ionization mass spectrometers (TIMS) and a high-resolution gas mass spectrometer in operation. In addition, it has a dedicated sample preparation laboratory for preparing and segregating various types of materials.
- **Radiochemical analysis,** a powerful forensic tool with the ability to provide a survey of radioactive materials in a sample. In addition, with the use of radiochemical standards, these capabilities are able to provide quantities of the radioactive actinides in the samples to very low concentrations. Capabilities will include high-purity germanium gamma detectors, alpha spectrometers, gas proportional counters, sodium iodide detectors, neutron counters, and liquid scintillation counters.
- **Actinide assay,** to determine the amount of an actinide in a sample at percent-level concentration, providing a critical indication of the sample’s purity. These capabilities can determine the amount of actinide in the sample with very high precision. Instruments will include coulometers, ceric titrators, Davies-Gray titrators, UV-visible spectrophotometers, and loss on ignition (LOI) furnaces.
- **Trace element analysis, x-ray fluorescence (XRF), and combustion techniques,** to accurately measure the small amounts of impurities that can have a large impact on a material’s performance or have other detrimental effects. Measuring these impurities requires very sensitive instruments and specially trained personnel. Instruments will include inductively coupled plasma (ICP) mass spectrometers (ICP-MS), ICP optical emission spectrometers (ICP-OES), laser ablation ICP-MS, high-performance liquid chromatography, fluorimeters, a variety of



Los Alamos maintains a suite of AC techniques that can be used to determine essentially any element on the periodic table.



Ning Xu and Michael Schappert develop and test analytical procedures using new inductively coupled plasma optical emission spectrometry (ICP-OES) instruments in a RLUOB laboratory.

XRF instruments (wavelength-dispersive, energy-dispersive, total reflectance, and micro-XRF), carbon-sulfur (C/S) and oxygen-nitrogen-hydrogen (O/N/H) combustion furnaces and analyzers, and a pyrohydrolysis ion chromatography system.

- **Diagnostic tools,** for troubleshooting, process development, and ensuring that production processes remain within process control. They provide a characterization of sample unknowns. Diagnostic tools include FTIR, Raman spectroscopy, particle-size analysis, density measurements, and an SEM.

The challenges of terminating program operations at CMR are not limited to the design and construction of new laboratory space. The challenges also include transferring capabilities from an old facility to a new facility, adapting processes as required, and meeting the necessary operational startup and equipment qualifications. Other articles in this issue of *ARQ* describe in more depth some of the progress made toward meeting these challenges.

Arrival of the last glovebox train for RLUOB on October 4, 2017, marked a major REI2 milestone: delivery of a total of 16 glovebox trains encompassing 66 enclosures (gloveboxes and open fronts). The glovebox procurements were initiated on June 30, 2015.

The glovebox trains awaiting installation into RLUOB laboratory space.

Contractors installing glovebox trains at RLUOB.

Thinking Small: Reducing Analytical Chemistry Sample Sizes to Support Future Program Needs

Ning Xu and Rebecca Chamberlin

Traditional analytical schemes for certifying plutonium were developed by chemists at Los Alamos during an era when virtually unlimited amounts of the metal could be handled in the analytical chemistry facilities. In the past, 5 g samples of Pu metal were prepared in Los Alamos' Plutonium Facility (PF-4) at Technical Area 55 (TA-55) and transferred to the Chemistry and Metallurgy Research (CMR) facility for partitioning into smaller "cuts" for different analytical tests. Today, we are preparing to relocate most analytical chemistry operations from the soon-to-be-decommissioned CMR facility to the new Radiological Laboratory/Utility/Office Building (RLUOB) at TA-55. Because the total amount of radioactive materials permitted in RLUOB is much lower than that permitted in the CMR facility, this move—or transition—of operations from CMR to TA-55 has significant implications for the entire analytical chemistry workflow supporting the nuclear weapons program.

The Department of Energy (DOE) sets limits on the total quantity of radioactive materials permitted in buildings at DOE facilities. This quantity, known as Material at Risk (MAR), is the hazard-weighted impact of all radioactive materials permitted in a specific building. The MAR allowance for RLUOB is currently just under 39 g of ^{239}Pu equivalent. Clearly, if production at PF-4 is to be supported at any meaningful rate, analytical chemistry processes requiring 5 g cuts of metal can rapidly consume the available operational MAR of the facility.

Relative sizes of the portions (cuts) of Pu metal used in analytical chemistry. The samples shown here (left to right) weigh approximately 5 g, 500 mg, 250 mg, 150 mg, and 100 mg.

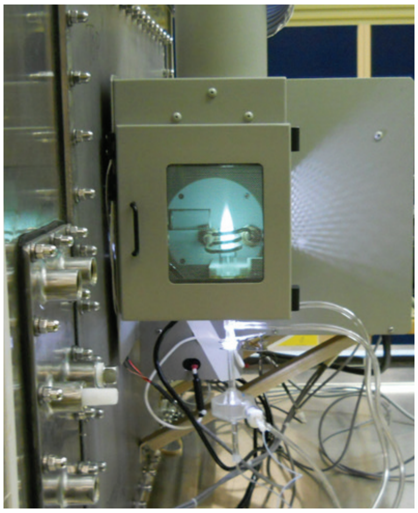
Fortunately, we have had an opportunity to examine ways to rework our processes to reduce the amount of material needed for our analyses. There are two avenues we can take to reduce our MAR requirements. First, we may be able to analyze smaller sample cuts. Second, we may be able to shorten the time the material used for our analyses resides in RLUOB, perhaps by automating some of the sample preparation steps so they can run unattended overnight and be ready for analysis in the morning. We are examining all such opportunities as part of our MAR reduction project. In this article, we describe how several recent advances in analytical instrumentation and greater collaboration between analytical teams can enable the use of smaller sample cuts.

To have the greatest impact, we need to integrate all processes in the life cycle of an analytical sample. One example of this integrated approach for our MAR reduction project concerns the analysis of trace elements in Pu. This analysis, which provides parts-per-million detection of approximately half the elements in the periodic table, is required for certifying production metal from PF-4. This analysis is also used in the Bulk Special Nuclear Material Analysis Program (BSAP) to identify impurities that could provide clues to a nuclear material's process history and intended use. (For more on BSAP, see "The Power of Nuclear Forensic Analysis in Determining a Sample's History" in this issue.)

A sample of Pu metal being prepared for analysis. Plutonium metal is first dissolved in hydrochloric acid, resulting in aqueous Pu(III) (the blue solution on the left). Next, the Pu is oxidized to its tetravalent state, Pu(IV), and the solution is poured into a column of anion exchange resin. The resin selectively adsorbs the Pu (right, the green bands in the columns), allowing trace contaminants to pass through. All the chemistry is carried out in a glovebox or in similar containment to protect the worker from exposure to the radioactive elements in the sample.

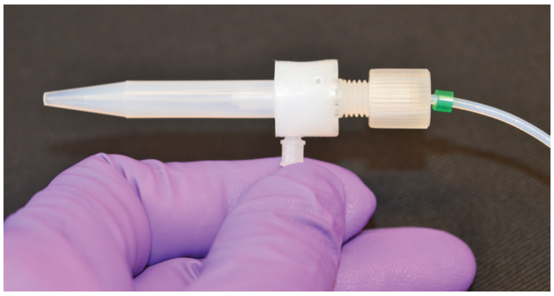
The analyses required for certifying Pu usually involve a sequence of three general processes: dissolution, separation or other processing, and instrumental analysis. Our operations are no exception. First, we divide the original 5 g sample into smaller cuts ranging from 50 to 500 mg and, if necessary, polish the metal's surface to remove any oxide layer. Next, we dissolve the metal in strong mineral acids, add specific reagents or reference standards to the solution, and pass the sample through separation steps to isolate the analytes of interest. Finally, we quantitatively analyze the sample.

Trace multi-element analysis is often performed using inductively coupled plasma–based methods, such as inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). These methods traditionally require a concentrated solution prepared by dissolving approximately 250 mg of Pu metal. Plutonium emits light across a wide range of wavelengths in the plasma, which can interfere with the identification and quantification of many trace elements. Consequently, to ensure that the emitted light from each trace element can be accurately measured at its characteristic wavelengths, all Pu must be removed from the samples before the solution containing the trace elements is aspirated into the ICP-OES. Although the new instruments in RLUOB are



The plasma torch in an inductively coupled plasma instrument moves electrons to a higher energy state or strips them off the atoms in a sample, creating unstable atoms or ions that can then be identified and measured by the light they emit (ICP-OES) or by their masses (ICP-MS). The sample is drawn into the torch as a fine mist from the spray chamber immediately beneath.

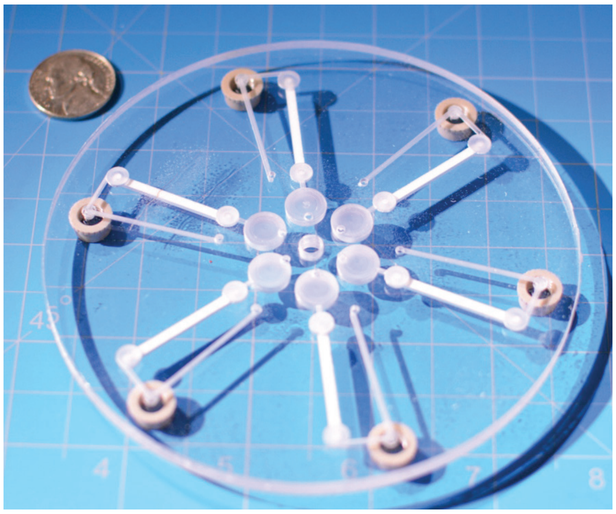
not significantly more sensitive than the old instruments in the CMR facility, the new instruments have several features that make it possible to reduce by as much as 90% the quantity of material required for analysis. First, the new instruments have been outfitted with low flow rate nebulizers, a modification that allows solutions containing trace elements to be introduced into the spray chamber at 10%–20% of the original rate—without compromising the measurement accuracy. Second, the flow of solution to the instrument can be controlled so that none of the solution is lost to holdup in the flow path. We have already demonstrated that these changes will allow us to use just 25 mg of Pu or U to produce measurements of the same or even higher quality than was previously achieved using 250 mg samples.



The low flow rate nebulizer injects a very precise, very fine mist into the spray chamber of an inductively coupled plasma instrument. Technological improvements such as this nebulizer make it possible to dramatically reduce sample sizes for analyzing bulk U and Pu without compromising the quality of the results.

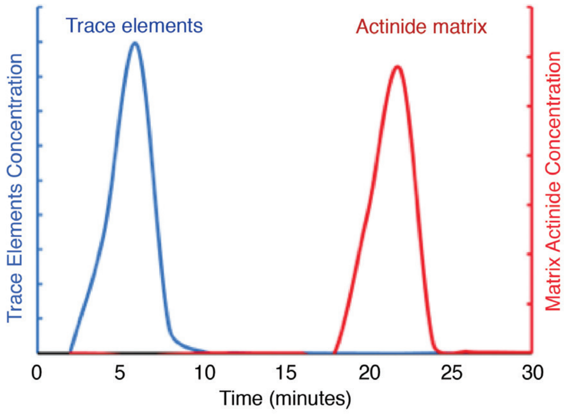
But what needs to happen further upstream for the improved instrumentation to have an impact? We now must carefully tailor the chemical separation steps to the small volumes of sample solution needed. Traditionally, the analyst would dissolve a 250 mg sample into 3 mL of strong acid, load it into a gravity-driven column containing ion exchange resin, and adsorb the Pu selectively onto the resin while the other elements passed through quantitatively. These columns work best when the analyst is available to feed as much as 13 mL of solution continuously to the column, ensuring that the resin bed never runs dry.

Looking to the future, we are looking into using microfluidic chips that contain microcolumns designed for small volumes of liquid, as well as automated solution-transfer systems to manage the separation steps. We have been working with our Los Alamos colleague Jun Gao to design and test microfluidic chips that can handle small liquid samples. One of the advantages of these chips is that they make it possible for samples to be processed in a closed system, which reduces the risk of introducing background contamination from ubiquitous environmental elements such as silicon, calcium, and iron. We can also build several separation columns into a single spinning disc, such as the unit shown at right.



Microscale solid-phase ion exchange extraction columns (white segments) are built into a spinning disc for preparing analytical chemistry samples. The translucent segments are chambers and flow channels for the liquid samples.

We have tested microcolumns with working volumes of 25 and 100 µL using the chemistry processes already described, but on a much smaller scale. We have been able to achieve the desired separation by using a low-speed pump to deliver very small volumes of liquid through the chip. The chromatogram on p. 16 shows the separation achieved using microcolumns. In strong nitric acid, the 26 trace elements for ICP-OES analysis pass through the column without adsorbing to the resin. Then, after the system is changed over to dilute acid, the actinide matrix is recovered from the column. No actinide is pulled into the trace element sample, which ensures the sensitivity of



A chromatogram showing the highly efficient separation achieved using a microcolumn to extract trace elements (blue curve) in a sample from the actinide matrix (red curve). The time axis shows the time elapsed as different acid solutions are passed through the column.

the ICP-OES measurements, and no trace elements remain in the actinide sample. These results demonstrate that we have quantitatively recovered all the trace elements, which is essential for an accurate measurement. In addition to the microfluidic chips, we are evaluating other automated systems for their reliability and accuracy under the harsh operating conditions they will be exposed to during their lifetimes.

Finally, we are looking even further upstream to the metal cutting and dissolution steps. The improvements made so far have allowed us to reduce the amount of metal needed for ICP-OES trace element analyses to as little as 25 mg. However, such a small amount of material is difficult to cut and handle precisely. Furthermore, such small samples are subject to bias from heterogeneity in the composition of the bulk sample. That is, slight variations in the distribution of elements in a 25 mg cut of Pu metal may not reflect the composition of the bulk sample.

To prevent this potential problem, we are now working on a combined dissolution approach, in which one sample is dissolved and then divided into smaller samples for different analyses. While this sounds like a simple task, it becomes considerably more difficult once we recognize that every analytical method in our toolbox was optimized for accuracy, precision, efficiency, and reliability. Even seemingly simple questions, such as what type of container the metal should be dissolved in and how the container should be cleaned, can affect all the processes downstream from this step.

In the meantime, we are continuing to pursue additional ways to shorten the time required to complete an analysis or to reduce the amount of material that is needed. Our Los Alamos colleague Christopher Worley has been experimenting with a spot deposition technique for x-ray fluorescence analysis of percent-level alloying agents in Pu metal. His initial results suggest that he may be able to greatly reduce the required sample size, compared with what is required using traditional techniques. However, additional development is needed to ensure that the new method is reproducible. In another article in this issue (see “Postdoctoral Fellows Advance Measurement Capabilities for Actinide Analytical Chemistry”), several former postdoctoral researchers describe their efforts to support MAR reduction and the transition to operating in RLUOB. As we begin the process of leaving the CMR facility, Los Alamos’ analytical chemists look forward to the ongoing challenge of reinventing our processes for a new building and a new era.

Postdoctoral Fellows Advance Measurement Capabilities for Actinide Analytical Chemistry

Benjamin T. Manard, Jung Rim, Jamie L. Doyle, and Benjamin Byerly

The Actinide Analytical Chemistry group at Los Alamos National Laboratory is known for its ability to characterize the elemental and radiological composition of nuclear material samples. Currently housed in the Chemistry and Metallurgy Research (CMR) facility, the group typically processes analytical sample sizes ranging from milligrams to tens of grams, and it has the instrumentation and expertise to provide a variety of analyses in support of Los Alamos' nuclear security missions.

The transition to the new Radiological Laboratory/Utility/Office Building (RLUOB) offers a few challenges for the group's nuclear material handling and analysis. Considering that the nuclear material limits for RLUOB are significantly lower than for the CMR facility, we have begun revising current procedures and investigating new methods for reducing the number of material analyses required while improving operational efficiency. At the forefront of this effort are four early-career scientists, all of whom were postdoctoral fellows with the Department of Homeland Security's National Technical Nuclear Forensics program or the Seaborg Institute at Los Alamos. Bridging a generational transition of actinide analytical chemistry capabilities over the next several years, postdocs can provide fresh perspectives on traditional analytical procedures and work with current scientific staff on improvements and adjustments. The postdocs also developed new measurement capabilities for the analysis of bulk nuclear materials. This article describes some of those efforts.

Nondestructive analysis

Nondestructive analysis (NDA) using gamma-ray spectroscopy is a well-established method for characterizing the overall content of nuclear material in a sample or container. NDA measures the energy and intensity of photons being emitted by gamma radiation from a radioactive sample. These photons are emitted at different energies, depending on which radioactive elements and isotopes are present, and the photons' intensity is proportional to the quantity of material present.

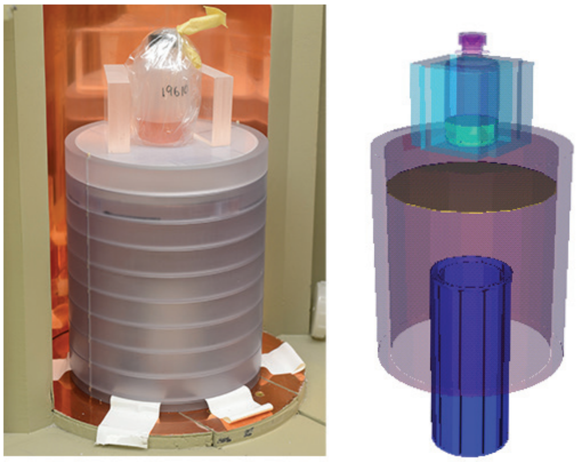
Gamma-ray photons are usually energetic enough to pass through container walls, which means gamma-ray spectroscopy can be performed on a packaged sample to obtain a good estimate of what is inside. Because of this, a survey measurement by gamma spectroscopy is usually the first method applied to an unknown nuclear forensics sample. Once the nuclear material is identified and the approximate quantity is known, all subsequent analyses can be planned and performed more efficiently, and initial descriptions can be provided to law enforcement. For operations in RLUOB, the ability to quantify small packaged samples of plutonium will also help ensure adherence to administrative limits on nuclear materials.

Measuring a sample accurately without opening its container can present a few challenges, considering that samples can vary significantly in their shape, size, and containment. Photons are attenuated to varying degrees by the layers of containment and by the nuclear material itself, and reference standards are not always available in the matrix or configuration to match the sample. The greater the amount of material or the more layers of containment, the more difficult it can be to obtain an accurate measurement because of an increase in signal attenuation. For high-precision radiometric assays, we process the sample into a defined, consistent geometry, but for the greatest flexibility in our NDA measurements, we need a tool that quickly and accurately models the effects of geometry and self-attenuation on the nuclear material in its as-received form.

The Monte Carlo N-Particle (MCNP) code is one software tool that we are evaluating for use in improving the gamma NDA measurements. This code allows for a large amount of flexibility in simulating the sample to match the geometry and calibrate the spectrometric data accordingly. We have developed MCNP models for several of the gamma spectrometers and sample

Examples of the various sample geometries encountered during NDA by gamma-ray spectroscopy.

geometries we use in NDA analysis. These models were developed from manufacturer specification sheets and physical measurements of containers and shielding. We evaluated the accuracy of these models using National Institute of Standards and Technology (NIST) traceable standards. To date, a few simulations have been performed on various Pu and U samples, including oxide powders, metals, and solutions, which provide a great deal of variety in their geometry. An example of a geometry simulated using the MCNP code is shown at right. The simulated container is a typical laboratory sample bottle containing a certified Pu reference material; application of the MCNP model predicted its contents to within 90%–95% accuracy.



(left) Simulation setup with a 125 mL Nalgene bottle containing a solution of a certified Pu reference material positioned on the sample platform. (right) Schematic simulation of the HPGe detector (blue cylinder) surrounded by the plastic sample platform (grey) and the sample geometry of the material in the bottle (yellow-green disk). The light blue around the sample in the simulation represents the plastic dividers used to stabilize the sample on the platform, while the gold disk within the platform represents the copper-cadmium shielding used to improve detector efficiency.

Trace elements

The nuclear forensics and stockpile stewardship missions of actinide analytical chemistry require detection and quantification of various contaminants: trace elements and actinides. Production of Pu metal must meet specific limits on these contaminants if the Pu is to be used in the nuclear stockpile. Minor actinides such as the neptunium isotope ^{237}Np in nuclear forensics samples can be used to determine the approximate date that a sample was last processed, while fission product signatures can indicate the reactor operating conditions that an irradiated sample was exposed to. Nonradioactive contaminants may also indicate nuclear material processing methods or recent uses.

Neptunium, a primarily alpha-emitting actinide that is of increasing interest to the forensics community, is currently measured by alpha spectrometry, which measures the energy and intensity of alpha radiation from a material. Although alpha spectrometry is a highly effective way to measure Np in environmental and biological samples, our application is unusual because we are looking for microgram-to-nanogram levels of Np in grams of Pu or U. In order to achieve accurate Np measurements in these bulk samples, highly efficient processes must be developed to separate these one-in-a-million Np atoms from their actinide matrix.

Current methods for separating Np involve lengthy processing with flammable solvents and generate mixed hazardous and radioactive wastes. In order to reduce or remove these undesirable properties while improving Np recoveries, we are investigating several solid-phase chromatographic methods. Scientific literature is readily available regarding Np separations from Pu and U, but nearly all of these reports are intended for significantly higher Np concentrations than we would experience in forensics and stockpile samples.

For our separation studies, three promising resins were selected, and although each resin requires different materials and solutions for the separation, all require the Np to be in the 4+ oxidation state. Reduction of Np, which prefers the 5+ state, can be difficult and had to be mastered before the separation studies with the resins began. Comparisons of several oxidation-state adjustment methods have been completed in order to identify possible alternatives to ferrous sulfamate, a commonly used oxidation adjustment reagent that is highly disfavored by the analytical community because of its inconsistent performance with identical samples. We have completed the separation studies and have achieved success using one of the resins selected. Thus far, the method has proven successful at Np concentrations down to 60 ppm; however, we believe this method can perform at much lower concentrations than this. We are currently completing final validation studies with significantly lower concentrations of Np (< 30 ppm) using real samples with well-characterized Np concentrations. Collaborations with chemists in the medical radioisotope program at Los Alamos and at the UK's Atomic Weapons Establishment and National Physical Laboratory are ongoing, with the goal of finding a Np separation scheme that will benefit not only nuclear forensic applications but also isotope production projects.

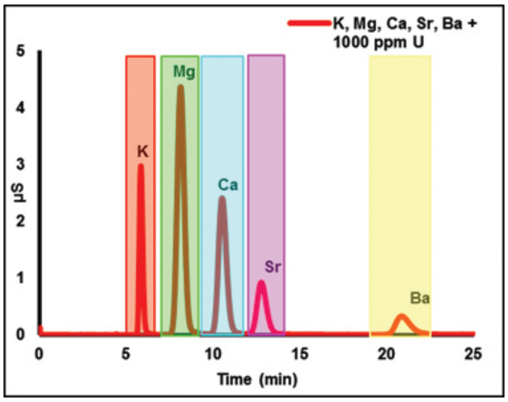
Another project supporting trace-level detection and measurement is trace element determination in bulk U by inductively coupled plasma mass spectrometry (ICP-MS). This ppm-level elemental measurement extends beyond the actinides to nearly all other elements of the periodic table.

Sample
(solid)
+
Stable
Isotopes

Dissolution →

Ion Chromatography for Separation

→



Collection of Individual Fraction(s)

↓

Schematic of the ID-HPLC-ICP-MS methodology. The solid sample is dissolved and spiked with stable isotopes before undergoing ion chromatography to provide inline separation of the elements. The separated fractions containing specific elements are then fed to a high-resolution ICP-MS for detection and quantification of the elements.

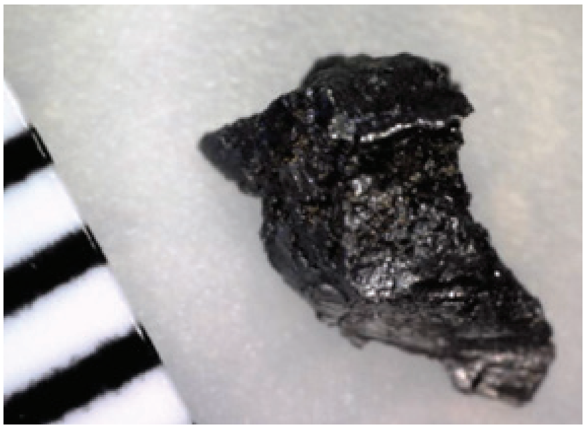
HR-ICP-MS for Analysis

We are developing a new technique to reduce the measurement uncertainty (imprecision) in trace element analysis by improving the accuracy and precision of ICP-MS measurements. We are developing this capability by coupling isotope dilution (ID) and high-performance liquid chromatography (HPLC) to our conventional ICP-MS measurements.

The resulting ID-HPLC-ICP-MS process, shown at left, involves dissolving the sample, "spiking" it with known quantities of stable isotopes for the elements of interest, chromatographically separating and collecting individual elements, and finally, analyzing the elements with high-resolution instruments. The addition of isotope dilution spikes enhances the measurement precision by internally calibrating the instrument response for each element, while the addition of the HPLC separation allows for faster, in-line separation of the trace elements from the U matrix and from each other. Without the HPLC separation step, isobaric (same-mass) interferences between neighboring elements cannot be fully resolved.

The ID-HPLC-ICP-MS system has been set up at RLUOB, and in collaboration with two other national laboratories, we are completing developmental studies on the Group I (e.g., sodium and potassium) and Group II (e.g., calcium and magnesium) elements, as well as the rare earth elements (lanthanum, cerium, neodymium, etc.). Successful separation and quantification of the Group I and Group II elements from a U matrix was achieved with 99.5% accuracy, with a 2.5% relative standard deviation. Although the analysis is significantly more time intensive, the accuracy and precision of the results are 5–10 times better than with the traditional method. Long-term reliability of the method was evaluated over three months using similar samples, and the results stayed consistent with this initial separation accuracy.

Ratios of fission products, the elements that grow into fuels during irradiation, can be used as signatures of the reactor conditions that the nuclear fuel was exposed to. One project we have pursued in collaboration with modelers at Los Alamos involves the measurement of volatile fission product ratios to estimate the reactor operating conditions using a set of archived U samples. The comparison of experimental results thus far has shown a wealth of information can be gleaned from these ratios, especially when paired with Pu and U isotopic data. Some examples of the information that can be determined are initial fuel state, neutron flux, and the number of reactor shutdowns. Reactor modeling to verify the use of these volatile fission product ratios in determining the reactor conditions is the next step in this work.



Piece of polished U metal from a reactor irradiation experiment. This sample would be dissolved and separated into the actinide and elemental constituents for analysis. The experimental results of this sample could be compared with models of the fission product ingrowth so conclusions could be drawn about the conditions the sample experienced during irradiation.

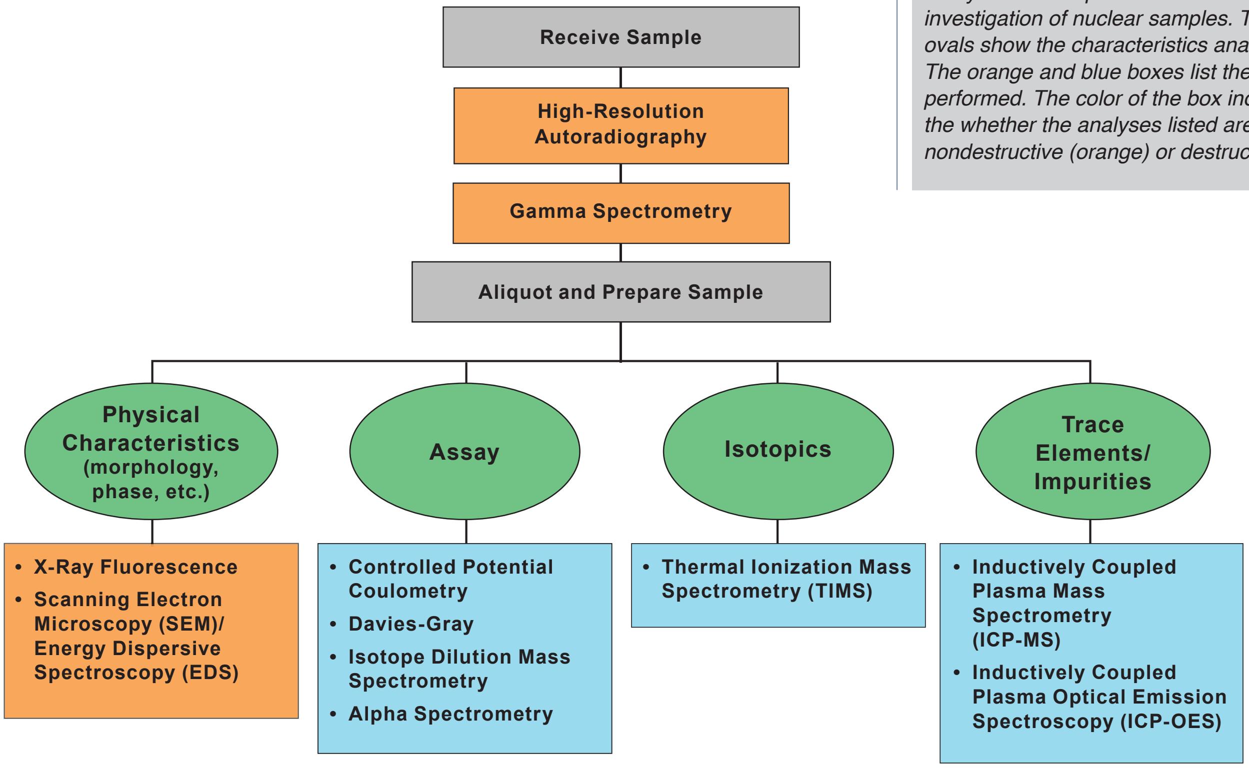
Modifications to the current analytical methods are necessary in order to accommodate the lowering of nuclear material limits in RLUOB, but these adjustments cannot sacrifice the ability of the methods to provide legally defensible results. Advances in the Np separations and measurements are currently being studied on the macroscale, but we anticipate their incorporation into microfluidic devices down the road to further reduce the amount of material used. The use of ID-HPLC-ICP-MS has already reduced the nuclear material sample size necessary for measurement while improving accuracy and precision. Although the NDA methods are limited in their ability to reduce the sample size, improvements in applying the MCNP code to small-scale nuclear material samples will help us manage our work processes and sample inventories within the nuclear material limits for RLUOB. The various methods and instruments developed by the postdoctoral fellows—new staff scientists at Los Alamos or other laboratories—relate directly to Los Alamos' nuclear forensics and stockpile stewardship missions and to the transition of capabilities from the CMR facility to RLUOB.

The Power of Nuclear Forensic Analysis in Determining a Sample's History

Jamie L. Doyle, Kevin Kuhn, Dan Schwartz,
and Lav Tandon

In 1995, the International Atomic Energy Agency (IAEA) established the Incident and Trafficking Database to manage information reported by participating states on potential trafficking and other illicit activities involving nuclear or radioactive materials. By the beginning of 2015, participating states had reported more than 2700 incidents, ranging from unauthorized possession, use, transport, or disposal of material to outright theft or loss. Although any of these incidents can pose a security risk, cases involving the theft or loss of nuclear material cause the most concern. When nuclear material is recovered from outside of regulatory control, it becomes the subject of a nuclear forensics case.

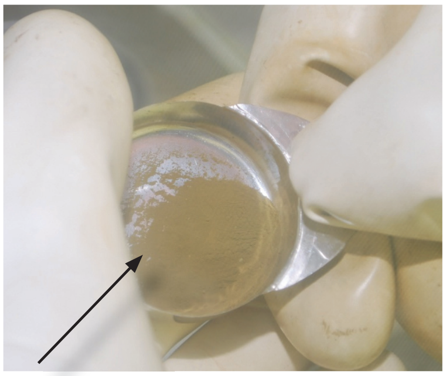
For more than a decade, Los Alamos National Laboratory has been part of multi-agency efforts to analyze nuclear forensic samples. As a designated operational laboratory for the Bulk Special Nuclear Material Analysis Program (BSAP), we are responsible for pre-detonation characterization of nuclear



Analytical techniques used in the forensic investigation of nuclear samples. The green ovals show the characteristics analyzed. The orange and blue boxes list the analyses performed. The color of the box indicates the whether the analyses listed are nondestructive (orange) or destructive (blue).

forensics samples. Forensics samples must be handled according to strict chain-of-custody requirements, and analytical methods must be validated and qualified. Consequently, the receipt and analysis of a forensics sample requires extensive communication and coordination among experts in analytical and radiochemistry, materials science and technology, nuclear physics, nuclear fuel and weapons production, reactor and weapons modeling, statistics, material control and accountability, shipping, radiation protection, and quality assurance.

Nuclear forensics applies a suite of analytical tools and techniques to answer questions about a sample's intended use, history, age, and origin. The techniques include nondestructive methods, which preserve the material in its original form, and destructive methods, which require the sample to be treated in some way that permanently changes its form, for example, through dissolution or heating. Nondestructive methods generally yield results more quickly than destructive analyses. However, although nondestructive methods provide a great deal of information, destructive methods can provide many more details, often with higher accuracy and precision. Forensics analyses often begin with nondestructive methods because the results of those initial tests can help investigators determine which follow-up (destructive) analyses are needed to answer the essential questions about a sample.



Photograph of the bulk sample we received for analysis. The light green-brown powder appeared to be a Np oxide.

This article highlights the analysis of one material we recently studied for the BSAP mission. The material, reported to contain neptunium, was received and transferred to our team for analysis. Our first step was to use gamma spectrometry to inspect the sample while it was still in its original shipping container. The results confirmed the material was relatively pure ^{237}Np, containing only a few actinide impurities. After this initial characterization, the shipping container was opened, and the material inside was inspected and its physical characteristics documented. The material was a fine, free-flowing, light green-brown powder, suggesting the material was a Np oxide.

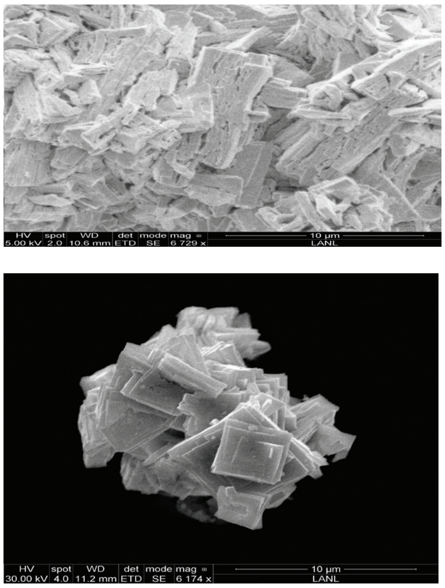
The sample was then divided, with one portion set aside for additional nondestructive analyses and another portion dissolved for destructive analyses. We used scanning electron microscopy (SEM) and x-ray diffraction (XRD)—which provides molecular composition and crystalline form—to inspect the bare oxide material. These techniques can reveal important information on the material's morphology, composition, and process history. The XRD pattern showed the material was relatively pure NpO_2.

Assay of the sample's Np content was required to confirm its chemical form and determine its purity. Certified measurement standards are available for Pu and U. (These standards are used to verify analytical measurements.) However, such standards do not exist for assays of bulk Np samples. Fortunately, Los Alamos maintains multiple independent, validated methods and techniques for analyzing unconventional or unusual samples, such as the Np sample, enabling us to corroborate our results. These techniques include controlled potential coulometry (CPC)—the electrochemical standard, which provides the highest precision available. CPC determined an assay value of 88.14 ± 0.5% Np per gram of sample, consistent with the assay value expected for NpO_2 (88.10%) and the relatively high purity observed during the initial nondestructive analyses. We verified the accuracy of the CPC-determined value by using two other assay methods, corroborating our initial results.

Characterization of low-level contaminants can be crucial to answering forensics questions about a material's process history and the expertise of the workers who produced it. Consequently, even though our sample was found to be highly pure, our next steps were to measure the levels of trace actinide impurities and any other trace elements present in the sample.

Neptunium is produced through the irradiation of U targets, and Pu is a byproduct of the production. In order to produce relatively pure Np, the U and Pu and other irradiation byproducts need to be removed. Although there are several effective methods for removing or reducing these contaminants, traces of them usually remain. We used thermal ionization mass spectrometry (TIMS) to measure the trace actinide impurities in our sample, finding elevated levels of ^{238}Pu and ^{235}U. Most U targets or fuels are enriched with some percentage of ^{235}U, which could explain the presence of ^{235}U in our sample: because the Np was likely originally produced through irradiation of a U target or fuel, the ^{235}U would be an expected impurity. The ^{238}Pu contaminant, however, suggests the ^{237}Np sample itself had been irradiated as a target and reprocessed. Pure ^{237}Np has few applications—its primary application has been production of ^{238}Pu, also referred to as heat-source Pu, which is used in radioisotope thermoelectric generators (RTGs) for space missions. The elevated ^{238}Pu level suggests the Np sample had been used for heat-source production or processed in a facility where heat-source Pu was produced.

We then used inductively coupled plasma mass spectrometry (ICP-MS) to measure the low-level trace elements. The ICP-MS analysis showed elevated levels of cerium, thorium, and phosphorous, which could be signatures of the reagents or tools used in processing. For example, Th could be a signature of the chemical purification scheme, as Th and Np have similar affinities in chemical purification steps. Likewise, Ce can also follow Np through the purification since Ce and Np can exist in a similar oxidation state. The presence of Ce can also be an indication of the separation scheme used, in that $Ce(SO_4)_2$ is frequently used in chromatographic elution solutions for separating out Np. Overall, minimal trace element impurities were measured, as nearly all elements were found in the low- to sub-ppm levels. Thus, the separation scheme used to purify the Np was most likely an advanced scheme with which the production personnel had significant experience.



SEM images of our sample, taken during the initial nondestructive analyses, showing the sample's rigid crystalline structure (10 µm scale).

Once the elemental and isotopic information for the Np sample had been collected, we used the measured isotopic ratios to estimate the time elapsed since the last chemical separation (see the table below). This method for determining the "model age" is based on the following assumptions: (1) the separation process successfully removed all progeny, (2) there has been no contamination into the system or preferential loss of analytes from the system, and (3) the physical constants for the radioactive decay are accurately known.

The measureable quantity of ^{233}U in the sample allowed us to use the relative amounts of ^{233}U and ^{237}Np to estimate the time since last separation to be 7.5 to 8.0 months. Often in chronometry, chronometers will be reset or altered if the material is manipulated after its initial production. In order to verify the model age of the Np sample, we used a second chronometer (^{234}U–^{238}Pu), which determined the age to be 7.7 to 8.2 months, validating our initial results. The agreement between the two independent chronometers provides an increased degree of confidence about the model age of the material.

Isotopic Composition of Pu and U, as Measured by TIMS

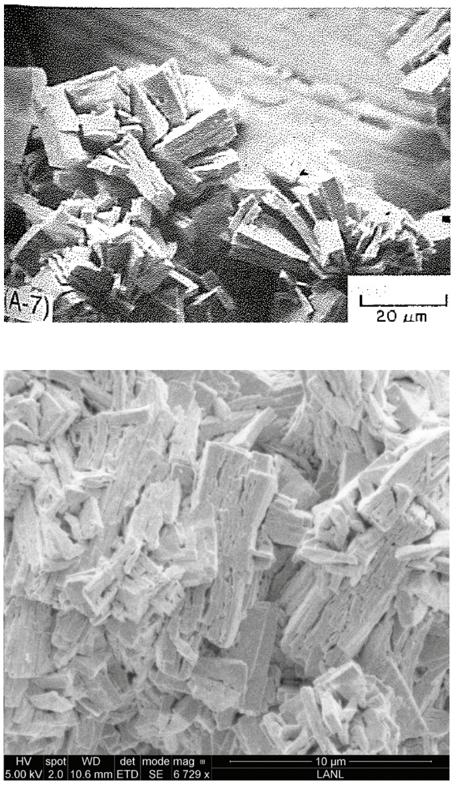
Isotope	Percent	Isotope	Percent
^{238}Pu	68.887	^{233}U	94
^{239}Pu	24.896	^{234}U	19.862
^{240}Pu	3.435	^{235}U	29.854
^{241}Pu	0.224	^{236}U	10.641
^{242}Pu	2.614	^{238}U	20.309

Red indicates progeny from ^{237}Np; Blue indicates progeny from ^{238}Pu.

Relatively pure Np oxide is an uncommon material, which narrows the list of possible points of origin. One known Np oxide production facility was the Savannah River Site (SRS). SRS produced highly refined Np oxide targets for heat-source ^{238}Pu production until production at the facility ceased in 1988, ending U.S. production of ^{238}Pu. During the production years, many reports and publications on the Np material produced at SRS were released, and a few of the reports contained morphology information. We performed a second SEM analysis of our sample—this time coating the sample in gold so we could zoom in to see the details more clearly—in order to compare the morphology of our sample with that reported in the historical literature. The figure on p.27 shows SEM images of an SRS material (top) and the forensics sample we received (bottom).

Although details in the SRS image are somewhat difficult to discern, descriptions of the material's morphology from reports agree with the terminology used by our experts to describe the morphology of the forensics sample. Both materials show a highly crystalline, layered square-plate-like structure. Additionally, a quantitative analysis of the SEM images using specialized Morphological Analysis of Materials (MAMA) software developed at Los Alamos showed morphological and microstructural parameters comparable with those reported in SRS literature. The number of similarities between the samples' morphology and chemical composition, including impurities, does support SRS as a possible point of origin for the material in our sample.

Nuclear forensics provides a means of identifying recovered nuclear material so that safety and security risks can be appropriately addressed. Nuclear forensics is a relatively young field of study, and extensive collaborations are imperative for advancing the field in order to tackle evolving challenges. The collaborations extend beyond pure analytical chemistry, as the results from analytical methods can be modeled to help provide useful correlations or predictions about materials. For example, specific elemental signatures measured by analytical methods can be modeled in relation to irradiation times or exposure to specific conditions. Los Alamos' nuclear forensics team is collaborating with other Department of Energy national laboratories, including Lawrence Livermore, Argonne, Pacific Northwest, Oak Ridge, and Savannah River, as well as internationally with the Atomic Weapons Establishment (UK), the Japan Atomic Energy Agency, and the Institute for Transuranium Elements (Germany) to advance the science and application of nuclear forensics.



SEM images of NpO_2. (top) A historical SEM image of the NpO_2 produced at SRS (20 µm scale). (bottom) An SEM image of our forensics sample, coated in gold to show the morphological details (10 µm scale). Both samples have a highly crystalline, layered square-plate-like structure.

Commemorating the Discovery of Plutonium-239

P.R. Vasudeva Rao and David L. Clark

Preamble

Plutonium, besides being an element with unique properties and applications, has a special significance for India, as it presents a unique route for efficient and sustainable exploitation of the nation’s uranium and thorium resources. Plutonium is at the heart of the second stage of the Indian nuclear power program envisioned by Dr. Homi Bhabha. Thus, 2016, marking 75 years of the isolation and identification of ^{239}Pu by Glenn T. Seaborg and Arthur C. Wahl, was indeed a special year for the Indian nuclear community.

The Indian Department of Atomic Energy (DAE) commemorated the discovery of Pu by holding the three-day theme meeting “Plutonium 75 Years (Pu75)” at the Indira Gandhi Centre for Atomic Research (IGCAR), which is responsible for establishing the fast-reactor program that would enable India to reap the benefits of Pu utilization in the form of abundant nuclear energy. IGCAR, along with the Bhabha Atomic Research Centre (BARC) and other units of DAE, in association with the Southern Regional Chapter of the Indian Association of Nuclear Chemists and Allied Scientists (IANCAS-SRC), organized the meeting, which was held May 23–25, 2016, at Kalpakkam.

The meeting had more than 200 participants from different units of DAE, as well as lecturers, professors, and doctoral students from selected academic institutions. Dr. David Clark from Los Alamos National Laboratory; Dr. Ken Czerwinski from the University of Nevada, Las Vegas; and Dr. Philippe Moisy from the French Alternative Energies and Atomic Energy Commission (CEA) were among the invited participants. Invited talks were delivered by a number of specialists, showcasing the strength of the Indian program in various facets of the nuclear fuel cycle, and particularly with respect to fuel fabrication, fuel reprocessing, safety in Pu handling, and instrumentation.

The highlight of the meeting was a special session in which DAE veterans who had participated in the pioneering development of Pu science and technology in India shared their reminiscences about the early years of the program. The participation of Dr. Sekhar Basu, chairman of the Indian Atomic Energy Commission and secretary of DAE; Dr. R. Chidambaram, prinicipal scientific advisor to the government of India; Mr. K.N. Vyas, director of the Bhabha Atomic Research Centre in Mumbai; Dr. Baldev Raj, director of the National Institute of Advanced Studies in Bengaluru and the former director of IGCAR; and Dr. P.R. Vasudeva Rao, former director of IGCAR underscored the importance accorded to the event by DAE.

As part of the meeting's technical program, a special session was held wherein the Seaborg Memorial Lecture was delivered by Dr. Clark of Los Alamos. IANCAS-SRC has been holding this distinguished lecture series for the past several years in memory of Glenn T. Seaborg, the discoverer of ^{239}Pu. The program included a detailed presentation describing Seaborg's achievements, special qualities, and laurels and a video of him describing in his own words the discovery of Pu and development of the actinide concept.

Dr. Clark, in his Seaborg Memorial Lecture, titled "Plutonium Science for the 21st Century," spoke of the continuing excitement in studies on actinides. He illustrated the same by highlighting the results of recent investigations into actinide complexes by using ligand K-edge x-ray absorption spectroscopy, systematic studies on $PuO_{(2+x)}$ formation using EXAFS, and the first observation of NMR transition in ^{239}Pu compounds.

P.R. Vasudeva Rao is the former director of IGCAR.

Nontraditional Nuclear Forensics from Environmental Samples

Warren Oldham, Khalil Spencer, and Robert Roback

Our ability to characterize nuclear materials by their chemical purity and isotopic composition is critical to supporting Los Alamos National Laboratory's national security and strategic defense responsibilities. Modern actinide mass spectrometry, in combination with improved separation techniques and robust quality assurance, provides the most precise and reliable measurements. These capabilities, developed largely to support the nuclear weapons program, are well established at Los Alamos.

Mass spectrometry has evolved considerably over the past several decades, achieving ever better precision and accuracy with smaller and smaller sample sizes. An outgrowth of these efforts has been greatly improved measurement capabilities for use in nuclear forensics. Many environmental nuclear forensics samples have been exposed to natural environmental conditions. Exposure to rain, humidity, or soil biological and chemical processes can alter the chemical and isotopic signatures of sample components, interfering with efforts to determine apparent age. In addition, the ubiquitous and persistent background from fallout produced during the era of atmospheric nuclear testing complicates the reliable detection of local sources of contamination.

Understanding how environmental processes affect actinide signatures constitutes an important research area with significant national security implications. Two studies we recently conducted on material from remediated sites related to the Manhattan Project provide an instructive perspective on the role that environmental processes play in preserving and modifying isotopic signals, as well as on early plutonium operations at Los Alamos. The studies are also valuable for developing and testing methods for detecting proliferation because the conditions at former Manhattan Project sites are likely to resemble the technical conditions encountered during international monitoring efforts.

The red arrow points to the Pu-processing building, known as D Building, in the main wartime technical area. Ashley Pond, seen in the upper right of the photo, is still the centerpiece of downtown Los Alamos.

Our first study was of samples from the remediated site where Pu work was first conducted during the Manhattan Project: the site of D Building in the main technical area, at the center of the Los Alamos townsite. Constructed in December 1943, D Building held laboratory facilities for Pu chemistry, processing, and metallurgy; from December 1944 to September 1945, it was at the center of significant production-scale operations.

Even during the war, D Building was notorious as a source of local contamination, resulting from the facility's unfiltered exhaust stacks. A 2010 study by the Centers for Disease Control and Prevention (CDC) estimated that wartime operations in D Building released approximately 0.4 Ci (6.5 g) of Pu-containing aerosol particles onto the building's roof and surrounding landscape.

After D Building was dismantled in 1954, the area was remediated for unrestricted public access. Decontamination took place in stages over the course of two decades as the significance of the building's environmental legacy became known. Today, the former site of D Building is an unremarkable parking lot adjacent to modern commercial and administrative buildings in downtown Los Alamos.

We recently characterized trace Pu contamination at this location using a nontraditional environmental sampling method, followed by inductively coupled plasma mass spectrometry (ICP-MS) for isotopic analysis. The sampling method was designed to differentiate local signatures from global fallout and was made possible by advances in the understanding of actinide geochemistry and environmental behavior.

Rusty bottle caps collected from a parking lot at the former site of the Manhattan Project's D Building were analyzed for trace Pu contamination. The samples were found to contain ^{240}Pu–^{239}Pu isotopic ratios characteristic of Pu from the earliest years of the U.S. nuclear weapons program.

Plutonium is known to be strongly associated with sediments and surface soils. However, when it is exposed to oxygenated surface waters, its favored thermodynamic form is the soluble and potentially mobile plutonyl species, $[PuO_2]^+$. We recognized that if natural solutions encountered rusty objects in the environment, even ultratrace levels of solubilized Pu or Pu-containing colloids would be strongly adsorbed to the surface of those objects and over time could build up to measurable Pu levels.

The samples for this study were rusty bottle caps littering the parking lot where D Building had been located. The bottle caps were collected and taken to a low-level analytical laboratory for Pu analysis. For each collection of four or five bottle caps, the surface oxide coating was dissolved, the oxide solution spiked with a ^{242}Pu tracer for quantification, and the sample purified using an anion exchange process. The samples were then analyzed using ICP-MS to determine their isotopic composition. Remarkably, the samples contained low levels of isotopically distinct Pu. For example, one sample from this location contained 1.6 pg of Pu, characterized by a ^{240}Pu–^{239}Pu isotopic ratio of 0.0032. This uniquely low ^{240}Pu–^{239}Pu ratio is a local signature characteristic of Pu dating from the earliest years of the U.S. nuclear weapons program. In comparison, rusty bottle caps and nails retrieved from remote locations in the area contained comparable total Pu levels but with isotopic signatures characteristic of Pu from fallout from atmospheric nuclear testing (^{240}Pu–^{239}Pu ratios of ~0.18). The results of this study suggest that our novel iron-oxide environmental sampling strategy can be used for selective identification of local nuclear signatures even when only trace-level contamination is present.

Our second study focused on what became known as DP Site, located at Technical Area 21 (TA-21), approximately two miles away from D Building. DP Site was constructed toward the end of the Manhattan Project so that the most-hazardous Pu operations could be relocated to a purpose-built laboratory away from the center of town. The laboratory and support facilities at TA-21 became the locus of research and development related to Pu and U processing for many years. Such efforts were central to processing Pu into weapons material for the earliest postwar nuclear devices. TA-21 was in use until the late 1970s. It has long since been decommissioned, although contamination at some legacy sites still needs to be remediated.

Technical Area 21 during decommissioning and decontamination.

The legacy TA-21 site we chose for our study was Material Disposal Area A (MDA A), known colloquially as the General's Tanks, for General Leslie Groves. The General's Tanks are two 50,000-gallon steel tanks used for the retrievable storage of low-level waste streams from Pu reprocessing and recovery operations carried out at Los Alamos from 1945 to 1947. The tanks were used to "temporarily" store alkaline solutions whose Pu levels made them too valuable to discard but from which no further Pu could be practically removed at the time. As industrial-scale production of Pu increased over the following years, large-scale recovery of Pu from the General's Tanks was deemed uneconomical. The tanks were sealed and left buried in place until 1974, when they were partially excavated and the water in the tanks removed. The tanks were resealed and reburied in 1985, remaining buried until 2010, when they were again partially excavated for sampling.

The material remaining in the tanks includes "sludge," a fine precipitate that formed when the original supernatant solutions were purposely neutralized. The sludge coats the bottoms of the tanks, to depths of up to several inches in places. The tanks also contain sand and soil that washed in when the tanks were open, as well as liquid layers that are a combination of rainwater and the neutralized supernatant solution originally placed in the tanks.

Plutonium, americium, and other actinides occur in all of these phases, but the highest concentrations are present in the sludge.The Pu and Am in the General's Tanks are some of the oldest and rarest samples of such materials in the world. (Significant quantities of Pu started to become available only in late 1944.) The actinides in the General's Tanks have reasonably well known production dates, and the material has been preserved in a sealed environment for most of the time since its production. As a result, samples from the tanks provided a unique opportunity to use high-precision isotopic dating techniques to evaluate how chemical processes that may have occurred in the tanks over approximately 65 years could affect the forensics measurements of their apparent isotopic ages.

Sample ages can be derived from the relative concentrations of parent and daughter radionuclides in three decay schemes: decay of ^{241}Pu to ^{241}Am, ^{239}Pu to ^{235}U, and ^{240}Pu to ^{236}U. Because the radiological half-lives of the parent nuclides are known, we can compare the concentration of the remaining parent to that of the daughter to estimate the time that has elapsed since the parent was last purified of decay products. While the decay of long- lived daughter elements such as ^{235}U and ^{236}U may be ignored in the present context, the decay of daughters with short half-lives, such as ^{241}Am, must be mathematically taken into account to avoid systematic errors.

In a potentially complex environment, it is important to be able to identify natural processes that may affect the ages indicated by radiological systems. These natural processes include gain or loss of elements because of the differential mobility of Pu, U, and Am in the natural environment. The indicated ages may also be affected by mixing, especially of natural U, from external sources. The isotopically paired Pu–U decay systems provide an additional means for discriminating between gain or loss of Pu and U and contamination from another source. Natural processes can add or remove parent or daughter elements but cannot alter the Pu or U isotopic ratios (^{235}U–^{238}U or ^{240}Pu–^{239}Pu) from what would be produced by radioactive decay. We can thereby discriminate U produced by the in situ decay of the Pu parent from potential U added from natural sources—and thus better constrain model ages that may be affected by an open system (i.e., the gain or loss of elements) and by mixing (contamination) processes.

Samples of sludge from the General's Tanks were analyzed for Pu, U, and Am isotopic compositions and concentrations using ion exchange chromatography

The inside of one of the General's Tanks before sampling. Most of the liquid was removed when the tanks were partially excavated in 1974, leaving only this thin layer over the sludge at the bottom of the tank. Some of the sludge is barely visible at the lower left, next to the pink rod.

A sample of rust-colored sludge dredged from one of the tanks. The scaffolding in the foreground supports a portable glovebox-like sampling apparatus designed to protect the researchers and samples from contamination.

Khal Spencer (left) and Russ Keller operating a TIMS instrument in the CMR facility.

for purification, followed by thermal ionization mass spectrometry (TIMS); both methods are well established in weapons and national security programs at Los Alamos.

The ^{241}Pu– ^{241}Am ages for the General's Tanks samples indicate production dates between 1940 and 1943, with a measurement uncertainty of >1 year. Even though these dates are slightly older than the known age of the material, the initial results were very encouraging. First, they indicate that the material in the two tanks was emplaced around the same time, which is consistent with historical records. Second, the results show that the Pu and Am in the tanks behaved like Pu and Am in other samples, even while entrained in sludge for 65 years. We conclude that there was little to no preferential separation of Pu and Am. That the ^{241}Pu–^{241}Am ages are slightly older than the known value (the "true age") from the historical record suggests that an excess of Am was present when the supernatant was originally transferred to the tank— which is to be expected, given that the tanks' contents were waste streams from Pu purification.

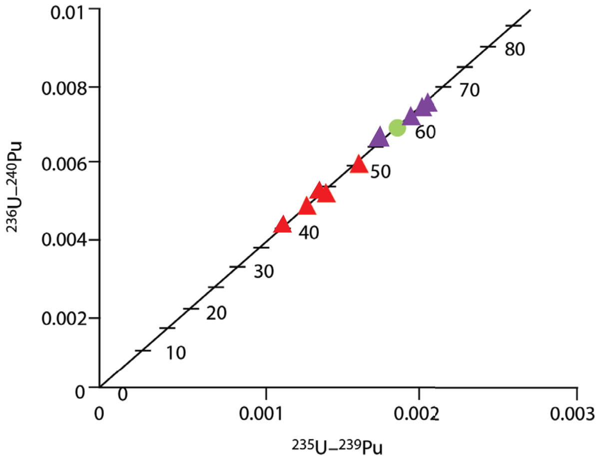
In contrast to the Pu–Am ages, the ages calculated from the Pu–U systems are considerably younger, with production dates between 1955 and 1966. They also show greater variability. The process for calculating these dates is more complex than for the Pu–Am system. By evaluating the U isotopic ratios, we conclude that the U in the General's Tanks is a mixture derived both from Pu decay and from naturally occurring U, perhaps introduced through runoff and soil that fell into the tanks when they were repeatedly opened and closed.

To correctly calculate the Pu–U ages, we first determined the "natural U" component based on our knowledge of the isotopic composition of U in nature and the isotopic composition of the U in the tanks. After mathematically subtracting the presumed natural U component, we then calculated the ^{240}Pu–^{236}U and ^{239}Pu–^{235}U ages. The results for the individual samples (the ^{240}Pu–^{236}Pu and ^{239}Pu–^{235}U ratios and the corrected ^{236}U–^{235}U ratio) are internally consistent with the isotopic and parent–daughter ratios expected for ingrowth of U from the Pu parent. In other words, the ratios lie on the Pu–U growth curve. Therefore, we see no reason to believe that our assumptions for these "unmixing" calculations are in error. We propose that the apparent discrepancies in the Pu–U ages are evidence of preferential loss of U (relative to the parent Pu) to the liquid layers and that the loss was variable from sample to sample. This interpretation is consistent with the relatively high solubility and environmental mobility of U relative to Pu. These results demonstrate the importance of using multiple isotopic systems to determine accurate ages and, at the same time, point out some of the pitfalls of the methods currently available for analyzing environmental and waste samples.

Our studies made use of two nontraditional means for obtaining nuclear forensics information from environmental remediation samples. Importantly, because these studies were conducted on samples from which we knew or could postulate a reasonable answer, we are able to evaluate the limitations inherent to the analysis of samples that have been affected by complex environmental processes. Studies such as these can help us interpret future nuclear forensics data and evaluate the meaning of data collected from samples with complex or unknown histories.

Model ages of radioactive materials can be determined from the relative amounts of parent and daughter nuclides present in the sample. With knowledge of the decay rate, or half-life, of parent and daughter nuclides, the age of the parent material—in this case, Pu in materials found in the General's Tanks—can be calculated, age being the time elapsed since the purified parent began to accumulate decay products.

Determining accurate ages from isotopic ratios requires that several conditions be met. First, we assume that there was no daughter present in the sample when the parent was first produced. Second, we assume that there has been no loss or gain of daughter or parent since their entrainment in the sample. Finally, we assume that the U used in these calculations is entirely the result of Pu decay (or that valid corrections can be made for "background" U from other sources). If any of these assumptions are not met, the calculated ages will reflect the interplay of multiple processes rather than a single event.



In the figure, the measured Pu–U isotopic ratios are shown as red triangles, which fall along the diagonal axis representing the time (in years) elapsed since the Pu began accumulating daughter product. The Pu–U isotopic ratios make the samples appear to be somewhat younger than what is documented in historical record (the "true age," represented by the green circle). We propose that some of the daughter U was lost from the system when liquids were transferred out of the tanks. That is, the Pu–U decay chain was an "open" system in the context of the General's Tanks: U is preferentially soluble in water compared with Pu, so when water was pumped out of the tanks in 1974, some U was also removed. This would result in samples plotting at younger ages than expected, that is, moving along the figure's diagonal axis line in the direction of the origin, at lower left.

Conversely, the measured age of the Pu–Am decay chain (purple triangles) is plotted along the diagonal axis line toward the top right, making the samples appear to be somewhat older than they actually are. The bias in the Pu–Am model is probably due to an overabundance of Am in the sample, the result of Pu being deliberately recovered from the waste stream by TA-21 process chemists.

Los Alamos National Laboratory Radiobioassay Program—Protecting Radiological Worker Health and Safety

Robert E. Steiner, Stephen P. LaMont, and Tom L. Waters

Los Alamos National Laboratory's national security mission includes ensuring that radiological work at the Laboratory is conducted in a way that minimizes workers' exposure to radiation, both external and internal. Dosimetry—measuring the amount of radiation a worker receives—is essential to evaluating the effectiveness of the controls in place to limit potential exposure. Radiobioassay, or bioassay for short, is used to detect and measure radionuclides inside a worker's body resulting from an intake, an event in which radionuclides are inadvertently inhaled, ingested, or absorbed through a wound or even intact skin. Federal regulations on occupational radiation protection require radiobioassay monitoring for individuals likely to receive a committed effective dose (CED) of 100 mrem or higher from radionuclide intakes in a year. Los Alamos monitors all workers with a reasonable potential for such intakes, using high-quality bioassay measurements and sophisticated statistical calculations to estimate any associated dose.

Gamma-emitting radionuclides, including fission products and activation products, are monitored in vivo using a whole-body radiation counter. Alpha- and beta-emitting radionuclides can be monitored only in vitro, from urine samples or other collected biological matter. Los Alamos routinely monitors workers' urine for plutonium, americium, uranium, and tritium intakes. The monitoring method and frequency are chosen to ensure that doses of regulatory concern are detected and to limit errors caused by uncertainty about when the intake occurred.

Radionuclides, such as T and many forms of U, that are cleared from the body quickly (that is, have short biological half-lives) require workers to be monitored frequently. In contrast, Pu and Am, which are slowly transported from the lung and metabolized into bone and the liver, are excreted gradually over many years and require less-frequent monitoring. Los Alamos workers who are monitored for T or U submit samples every two weeks, while those monitored for Pu or Am submit samples once or twice a year. On average, 400–500 routine samples are collected and analyzed monthly.

If a workplace incident involving a possible radionuclide intake occurs, more-aggressive sampling is initiated. These special bioassay samples are processed with expedited priority so that a dose estimate can be obtained as soon as possible following an intake. Inhalation of airborne radioactive material is the most common intake route, although ingestion and direct uptake to blood through a contaminated wound may also occur.

Chain of Custody and Quality Control

The Radiation Protection Services group (RP-SVS) manages Los Alamos' radiobioassay program, overseeing employee enrollment, sample collection, data interpretation, and reporting. The monitoring regimens for individual workers are assigned through the automated Dosimetry Evaluation System, which determines appropriate monitoring based on a worker's activities and work locations. RP-SVS transfers collected urine samples to the Nuclear and Radiochemistry group (C-NR) for analysis. Sample transfer and tracking follow a strict chain-of-custody protocol.

Once the samples arrive at the C-NR analytical laboratory, they are logged into the local tracking system and stored in an environmentally controlled secure environment until they are processed. Samples are batched into sets of 10–20 samples. Each set also includes a process blank, used throughout the analysis to monitor for the presence of radionuclide contamination, and a quality control (QC) sample with certified concentrations of the target radionuclides. The QC samples are prepared by an external laboratory, and their concentrations are not provided to the chemists or analysts processing the samples. Results from both the process blanks and QC samples are monitored to identify any problems arising during the analysis.

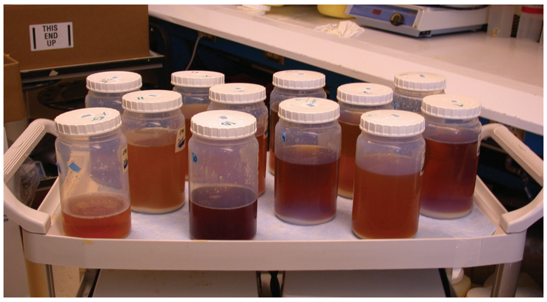
Radiochemical Sample Analysis

Carefully optimized radiochemical separations are used to isolate U, Pu, or Am from urine samples. Sample analysis begins with the documentation of each sample's physical characteristics, (e.g., volume and density). Each sample is then transferred to an appropriately sized clean vessel for processing. Samples are first acidified, then a known amount of an isotope dilution tracer is added to each sample. Tracers (see the margin table) are isotopes of the elements of interest that are absent from or of low abundance in the sample.

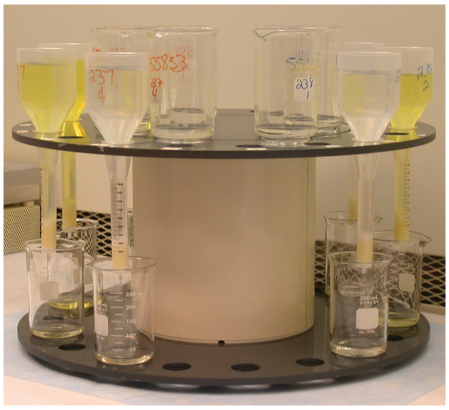
Isotope Dilution Tracers Used
for Routine Radioabioassay

Tracer	Target Radionuclides
^{233}U	^{234}U, ^{235}U, ^{236}U, and ^{238}U
^{242}Pu	^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu
^{243}Am	^{241}Am

Once tracer equilibration is complete, the radionuclides are co-precipitated from the urine with calcium phosphate, and the remaining urine is decanted to remove as much of the matrix as possible. The precipitate is then dissolved, and the radionuclides are purified from the solution using anion exchange chromatography. This process uses columns containing resin beads that bind the radionuclides of interest while allowing the other sample constituents to pass through. The chemical conditions in the columns are then adjusted to release the bound radionuclides as a purified sample.



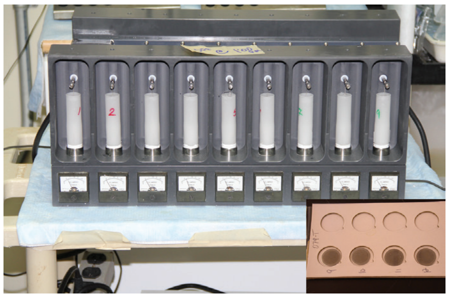
Urine samples ready for radiochemical processing.



Initial anion exchange purification of radiobioassay samples.

Next, samples of Pu are electrodeposited onto stainless steel planchettes for alpha spectrometry analysis, which is used to determine the activities of ^{238}Pu and $^{239+240}$Pu in the sample. Alpha spectrometry is the sole technique used to measure ^{238}Pu due to its relatively short half-life (87 years) and the potential of ^{238}U to interfere with mass spectrometry techniques. However, alpha spectrometry cannot resolve the alpha peaks of ^{239}Pu and ^{240}Pu, so these isotopes are subsequently measured by thermal ionization mass spectrometry (TIMS). Samples of Am and U are dissolved in dilute acid, and the concentrations of ^{241}Am, ^{235}U, ^{236}U, and ^{238}U are determined by inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS provides the isotope ratios necessary to differentiate the natural U that is present in all urine samples from depleted or enriched U present because of occupational exposures.

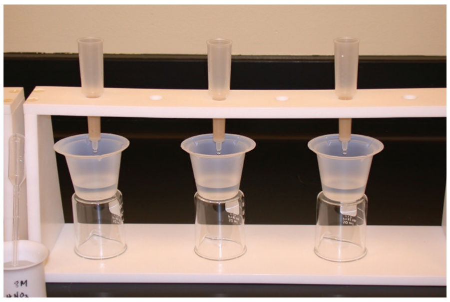
TIMS Analysis of Plutonium Samples



Electroplating instrumentation used to prepare samples for alpha spectrometry. The inset shows electroplated discs prior to alpha spectrometry analysis.

After alpha spectrometry analysis, Pu samples are further processed in preparation for measurement by TIMS. For most of the Pu isotopes, TIMS provides higher resolution and lower detection limits than other methods provide, which makes it possible to detect much lower exposure levels. Preparing samples for TIMS involves stripping the Pu samples from the stainless steel alpha spectrometry planchettes using nitric acid and further purifying the Pu using anion exchange chromatography. This separation process is similar to that used for the initial sample purification prior to alpha spectrometry analysis, but on a much smaller scale. Samples are electroplated onto rhenium filaments, which both fixes the sample to the filament surface and provides a final purification step. The filaments are then introduced into the high-vacuum chamber of the thermal ionization mass spectrometer, where they are resistively heated to 1500°C–1700°C. Filament heating results in volatilization/ionization of the sample. The ions are focused through an electrostatic lens system and magnetic field, which separates them by mass before they are collected and measured along a focal plane behind the magnet. The resulting data are then processed by using isotope dilution to calculate the abundance of each isotope of interest.

Quantification via Isotope Dilution Methods



Anion exchange purification prior to TIMS analysis.

Isotope dilution methods are used to determine the concentrations of the isotopes of interest from alpha and mass spectrometry data. As described earlier, the isotope dilution method begins with the addition of a known amount of an isotope dilution tracer to each acidified sample. The isotope dilution tracer is then chemically equilibrated with the sample via heating and stirring to ensure that the tracer material behaves identically to the radionuclides of interest. Assuming complete equilibration, the measured spectrometric signals directly reflect the concentrations of the isotope of interest in a sample and the isotope dilution tracer, or

$$\frac{N_s}{N_t} = \frac{X_s}{X_t} \quad ,$$

where N_s and N_t are the concentrations of the radionuclide of interest and the isotope dilution tracer, respectively, and X_s and X_t are the corresponding spectrometric signals. The value of N_t is known and X_s and X_t are measured; N_s can then be calculated for each radionuclide of interest:

$$N_s = N_t \left(\frac{X_s}{X_t} \right) \quad .$$

These results are then converted from an atom scale to activity units and reported to the RP-SVS for individual dose calculation and assessment.

TIMS filament-electroplating system. The inset shows a close-up of a filament set up for sample electroplating.

Radiobioassay Dose Assessment

The results of the radiochemistry analysis—the concentration of the radionuclide in urine with the associated measurement uncertainty—are analyzed statistically to determine whether a radionuclide intake has occurred and if so, to estimate the resulting dose. The dose is reported as CED, a quantity that accounts for both the potential of different types of radiation to produce biological damage and the radiosensitivity of different body tissues. The word "committed" reflects the fact that radionuclides may remain in the body for an extended time, delivering further doses to exposed tissues. The CED is the total dose delivered over 50 years following the intake.

Internal dosimetry requires modeling the metabolism of each radionuclide in the body as well as the dose delivered to each tissue from radionuclides deposited in other tissues. The modeling depends on the isotopes involved; the intake route; the chemical and physical form of the material, in particular, particle size and solubility; and the affinity of different elements for particular tissues in the body—and often some of these parameters are not known.

We use a statistical inference process to estimate the intake parameters from the bioassay data. This approach can provide a much more accurate characterization of the intake and hence a more accurate dose estimate. It is very data intensive, however, as multiple bioassay measurements are generally needed to converge on a likely range of intake parameters and narrow the credible limits of the dose assessment.

Specifically, we use Bayesian inference for this process, which allows us to incorporate historical experience about the frequency, magnitude, and parameters of intakes that occur at Los Alamos. The method yields a probability distribution for dose and intake parameters, making it possible to quantitatively assess the likelihood that the intake occurred before a particular date and the probability that the dose exceeds the regulatory limit. We report a final dose when the statistical credible limits are sufficiently narrow to preclude serious misinterpretation of the scale or circumstances of the intake. In most cases, the worker will continue to submit routine bioassay samples throughout their employment at Los Alamos, and the additional data will be used to refine the dose estimate.

The ability to detect and quantify radionuclide intakes using these methods can vary greatly, depending on the material involved. The most challenging cases involve ^{238}Pu, which has a high specific activity and for which isobars such as ^{238}U preclude the use of sensitive mass spectrometry methods. Even with multiple measurements, it can be difficult to reach firm conclusions regarding intakes of 1000 mrem CED or less. The use of mass spectrometry for ^{239}Pu, a method pioneered at Los Alamos, allows internal doses of less than 100 mrem to be quantified with confidence, a first in Pu dosimetry. Tritium, which has a biological half-life of just 10 days, can be reliably detected in urine at levels that deliver very little dose to a worker. In fact, it is possible to detect and quantify T doses in the microrem range.

Uranium presents a different set of challenges. Uranium is present in the environment and is routinely consumed in drinking water and diet. Every person excretes U in urine, at levels that vary from person to person over two or more orders of magnitude. Our statistical methods, which look for sudden increases in excretion followed by a gradual drop-off, can identify intakes resulting in doses of several hundred millirems but are not reliable at lower levels. If the U can be identified by isotopic ratio as enriched or depleted, extremely small doses (less than 1 mrem) can be identified and quantified, since the dietary component can be mathematically separated from the occupational intake.

Monitoring Los Alamos workers for intakes of radionuclides has long been a priority of our occupational health and safety program. We apply the most-sensitive measurement techniques in the DOE complex to detect minute quantities of radionuclides in urine and evaluate results by using sophisticated statistical methods to produce accurate dose estimates.

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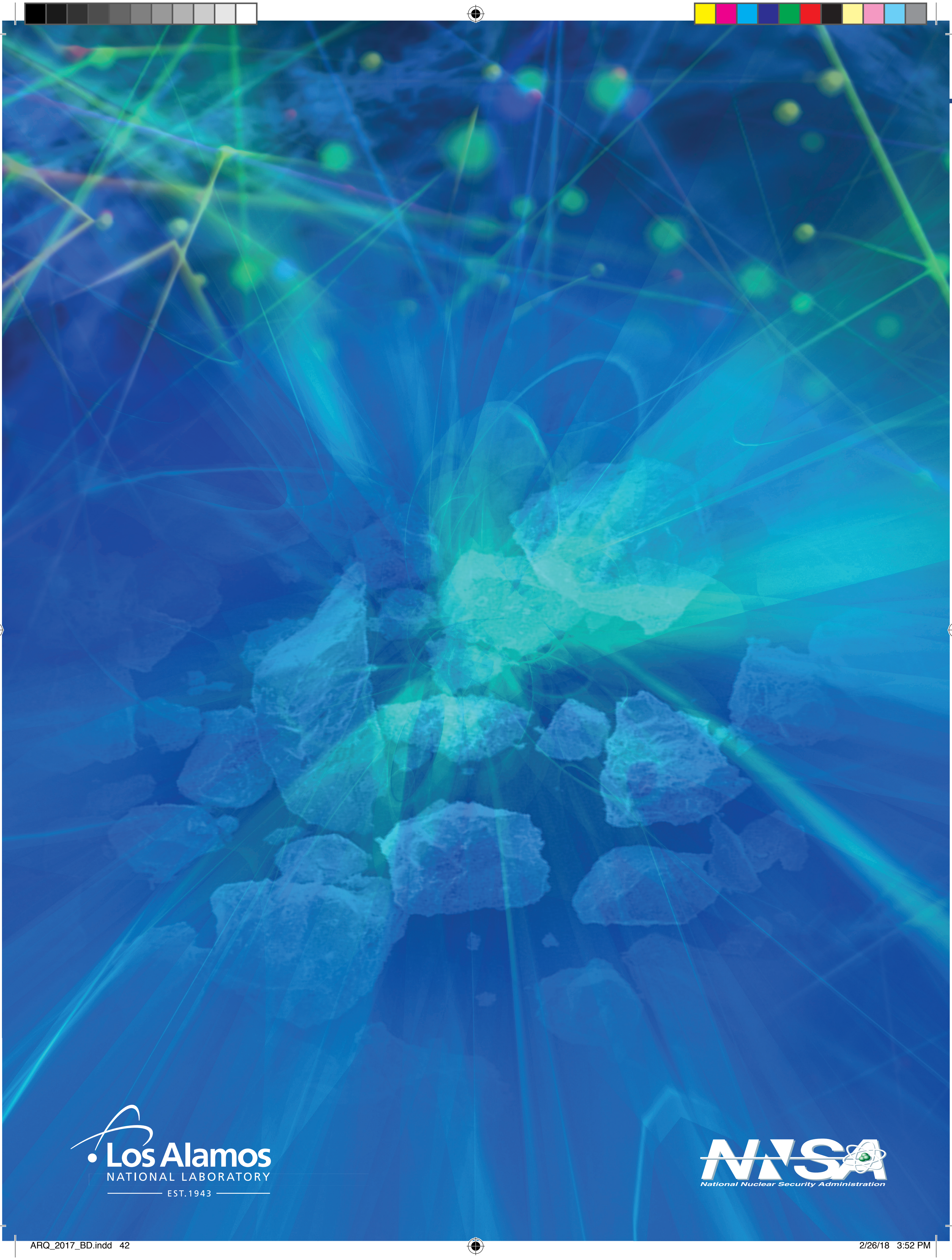

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