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## Magnetic Levitation Results in High-Purity Plutonium Metal



B2339-9 photo by Joe Riedel

Plutonium, a member of the actinide series of elements, exhibits seven unique crystal structures (phases) in the solid state that range in symmetry from simple monoclinic (sm) to face-centered-cubic (fcc). One phase, the easily worked fcc phase, denoted by  $\delta$ , is thermodynamically stable in pure plutonium from 319°C to 451°C and can be stabilized down to room temperature by small additions of gallium. The actinide series is characterized by the presence of 5f-electrons forming a narrow energy band at the Fermi energy ( $E_f$ ), with an increasing complexity in the electronic properties that culminates in plutonium.



B2610-6A photo by Mick Greenbank

Figure 1 (below). Levitation zone refining apparatus illustrated with a stainless steel rod loaded in the cold boat. The hot zone on the rod can be clearly seen from the red glow caused by the induction from the coil.



B2621-4 photo by Mick Greenbank

Figure 2 (left). Molten plutonium metal in a levitated state in the middle of the crucible. Enough gallium has been added to stabilize the  $\delta$  phase upon solidification (see Figure 3).

Figure 3 (left). Plutonium metal ( $\delta$ -phase alloy) half-sphere solid from a levitation distillation run.

*continued on page 2*

## Magnetic Levitation Results in High-Purity Plutonium Metal (*continued*)

Principal investigators on this project were **Michael S. Blau** (NMT-6) and **Jason C. Lashley** (MST-8).

The complex electronic structure coupled with small perturbations such as the presence of trace elemental impurities, has effects on both microscopic and macroscopic behavior. Overall, the primary metallic and metalloid impurities in plutonium are iron, uranium, magnesium, calcium, nickel, aluminum, potassium, and silicon. Oxides and hydrides, formed from surface reactions between the metal and oxygen and water vapor are equally undesirable. Additionally, small amounts of some common trace elemental impurities (thorium, aluminum, zirconium, and cerium) stabilize the  $\delta$  phase, while others affect the melting point. Iron and nickel, if present in sufficient amounts, form eutectics with plutonium that melt slightly above 400°C. Furthermore, plutonium decays over time into its daughter products, which contribute to the total impurity content. The primary plutonium decay products are isotopes of uranium, neptunium, and americium. One, Americium-241, is a  $\delta$  stabilizer and also interferes with a determination of nuclear cross sections.

A comprehensive knowledge is lacking for plutonium, compared to the level of knowledge for other elemental metals. The high degree of complexity in plutonium's intrinsic properties severely restricts extrapolation of knowledge from surrogate metallic systems. Consequently, fundamental measurements on well-characterized, research-grade (100 to 200 ppm total impurities) plutonium are required. Therefore, our efforts are directed at the preparation and characterization of large quantities (200 to 300 g) of research-grade plutonium, in support of fundamental experimentation.

Our approach to the preparation of research-grade plutonium metal is to start with doubly electrorefined, vacuum-cast plutonium metal and further purify it using levitation zone refining in concert with levitation distillation at reduced pressure. In particular, levitation zone refining targets metals and metalloids while levitation vacuum distillation targets decay products and gases. Double-electrorefined plutonium that has been chill-cast contains 500 to 600 ppm total impurities.

Impurity totals are derived from mass spectrometry and atomic emission data in which 75 to 80 trace elements are analyzed for and then quantified. Historically, 20 to 40 elements represent the typical range of elements documented in the early literature.

### Magnetic Levitation of Metallic Plutonium

Obtaining research-grade plutonium requires minimizing the contact of large amounts of plutonium with other materials at reduced pressure. Presently, levitation furnaces provide a tool for accomplishing this task. Radio-frequency-power-induced electric current flows into a crucible while the crucible acts as a transformer inducing a current in the direction opposite to the current in the induction coil. Magnetic fields in the crucible and the plutonium are opposed, causing repulsion and levitation between molten plutonium and the crucible walls. Magnetic levitation of plutonium metal at elevated temperatures (700°C to 1000°C) enables purification; eliminating plutonium/crucible interactions further minimizes the contact with other elements. Magnetic levitation is the fundamental operating basis for both the zone refining apparatus and the distillation apparatus.

The effectiveness of zone refining in reducing the concentration of impurities depends on the manner in which the impurity partitions itself in the liquid and solid states during the melting and solidification processes. The zone refining process involves casting a rod of unalloyed plutonium (usually 240 g) and then serially passing a molten zone through the rod in one direction at a slow rate (Figure 1). Impurities travel with, or opposite to, the direction of motion of the zone, depending on whether it lowers or raises the melting point of the rod metal, respectively. Consequently, impurities are swept and become concentrated in the ends of the rod, thereby leaving the remainder purified. The degree of separation approaches an infinitesimal limit as the number of passes increases.

Results to date have shown the reduction of impurities in double-electrorefined and vacuum-cast unalloyed plutonium from a total of 522.9 ppm ( $\pm 78.4$  ppm) impurities to 184 ppm ( $\pm 27.6$  ppm) through levitation zone refining; uranium accounts for 121 ppm of the measured 184 ppm. One important event, previously undocumented, is the absence of plutonium/crucible interaction; no crucible material has been detected in the plutonium by trace elemental analysis. In addition, in all cases, trace analysis showed impurities to have moved to the ends of the rod in accord with their predicted partitioning behavior. It was also determined that the slower rates of molten zone movement increased the purification efficiency. Additionally, reducing the atmosphere and a surface cleaning of the rod have proved beneficial.

### Levitation Vacuum Distillation

Removing Americium-241 from plutonium is possible because americium exhibits a high vapor pressure relative to plutonium. The Americium-241 is separated when plutonium metal is heated to the liquid state under reduced pressure ( $10^{-7}$  torr). The molten plutonium is levitated while Americium-241 is driven off and condensed onto a cold surface (Figure 2). The plutonium is cooled and solidifies to the shape of a button (Figure 3).

Recent results from levitation distillation show that the lowest americium level achieved was 1.50 ppm ( $\pm 0.30$  ppm). In addition, no crucible/plutonium interactions were evident. Plutonium in the liquid state appears as a viscous boiling liquid. Figure 2 shows a top view looking through the glove box window into the distillation apparatus vacuum chamber view port at the plutonium metal after 1 hour with the power supply at 40 kW. The effect of the levitation force that can be seen in the illustration is that the top surface of the plutonium is spherical instead of flat. Bubbles appear on the surface while the impurities are driven off in the vapor state. After 30 minutes the bubbling

rate slows down to the occasional formation of a large bubble, but no splatter occurs as a result.

### Summary

Large batches (100 g–300 g) of unalloyed plutonium were purified of trace elements to a level of 184 ppm, and uranium accounted for 66% of the total impurity level. In all batches the impurities traveled to the ends of the rod as predicted from their partitioning behavior. Trace analysis detected no plutonium/crucible interaction in either purification method. The lowest concentration of Americium-241 measured from the levitation distillation process was 1.50 ppm ( $\pm 0.30$  ppm). The purification hinges on levitating plutonium metal at elevated temperatures.

**One important event, previously undocumented, is the absence of plutonium/crucible interaction; no crucible material has been detected in the plutonium by trace elemental analysis.**

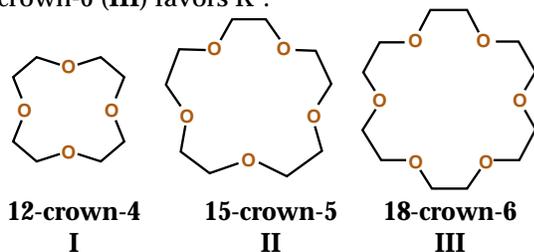
We thank Floyd Rodriguez of the Advanced Technology Group for his assistance in the laboratory. We are also grateful to Tom Yoshida, Amy Wong, and Debbie Figg of the Analytical Chemistry Group for the trace analysis. We are grateful to John Quagliano of the Analytical Chemistry Group for development of data analysis. We thank Galen Straub and John Wills of the Equation of State Group, James L. Smith of the Superconductivity Technology Center, Albert Migliori of the Condensed Matter Physics Group, Sig Hecker of the Materials Science Division Office, Mike Stevens, Roger Moment, and Mike Stout of the Structure/Property Relations Group, David Olivas, Karl Staudhammer, and Ramiro Pereyra of the Physical Metallurgy Group, and Dave Embury of the Center for Materials Science. We are grateful for the joint funding support from Stephen Sterbenz of the Los Alamos Neutron Scattering Center, Eugene Farnum of the Structure/Property Relations Group; Alan Picklesimer, Dean Preston, and Miles Baron of the Nuclear and Hydrodynamic Applications Group, and Don Wolkerstorfer of the Nuclear Weapons Technology Program Office.

## Researchers Prepare and Characterize First Transuranic Crown Ether Complex

Researchers on this project are **David L. Clark, D. Webster Keogh, Phillip D. Palmer, Brian L. Scott, and C. Drew Tait.**

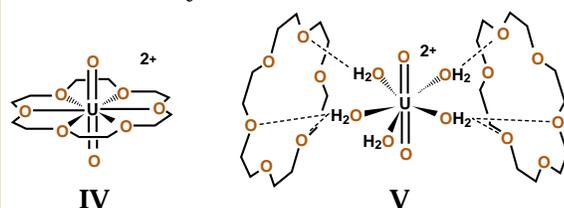
The complete encapsulation of the  $\text{NpO}_2^+$  ion by a crown ether ligand under any conditions is unprecedented and represents the first structural and spectroscopic characterization of any transuranic crown ether complex.

Crown ether ligands have the ability to selectively bind metal ions of a characteristic size; thus, it's not surprising that crown ether ligands have been considered as potential extractants for actinide ions. They are a special type of polydentate ligand in which the ligating atoms lie approximately in a plane about the central metal atom, and the remainder of the molecule lies in a "crown" arrangement. All of the oxygen atoms of the polyether "point" inward towards the metal atom, and these macrocyclic ligands have the unusual property of forming stable complexes with alkali metal ions. This exceptional stability is related to the cavity size of the ligand, with different cavity sizes favoring specific alkali metal ions. For example, 12-crown-4 (I) selectively forms a complex with  $\text{Li}^+$ , 15-crown-5 (II) forms a complex best with  $\text{Na}^+$ , and 18-crown-6 (III) favors  $\text{K}^+$ .



Crown ether ligands have been shown to afford actinide extraction in hydrocarbon-water systems, and many of these studies invoke the standard cavity-size argument to explain the observed results. However, in spite of the observed extraction behavior, we note that there are relatively few examples of actinide crown ether complexes wherein the actinide ion is actually coordinated to the crown ether ligand by one or more oxygen donor atoms of the crown ligand itself. Examples of inclusion compounds of actinide trans dioxo cations  $\text{AnO}_2^{n+}$  completely encapsulated by a crown ether ligand are limited to only two uranium examples,  $[\text{UO}_2(\text{18-crown-6})]^{2+}$  (IV) and  $[\text{UO}_2(\text{dicyclohexano-18-crown-6})]^{2+}$ , with non-coordinating perchlorate or triflate counterions in the crystal lattice. It has been argued that the synthesis of these rare uranyl crown ether inclusion complexes could be achieved

only by the use of weakly coordinating anions, nonaqueous conditions, and proper choice of cavity size in the crown. Indeed, the majority of reports on actinide crown ether complexes reveal that the crown ether ligand prefers to reside in the outer sphere of the actinide ion and engage in second-sphere hydrogen bonding between the crown ether oxygen atoms and water molecules coordinated to the actinide metal center (as illustrated in V). Well-known examples of second sphere crown ether complexes would include  $[\text{UO}_2(\text{H}_2\text{O})_5 \cdot 2(\text{18-crown-6}) \cdot \text{H}_2\text{O} \cdot 2\text{CH}_3\text{CN}][\text{ClO}_4]_2$  (V) and  $[\text{UO}_2(\text{H}_2\text{O})_5 \cdot (\text{18-crown-6})][\text{CF}_3\text{SO}_3]_2$ . There are no known examples of crown ether inclusion complexes (such as IV) containing a transuranic ion in any oxidation state.



In an attempt to employ this well-known ability of crown ether ligands to form second-sphere hydrogen-bonded complexes of trans dioxo ions (as in V), we reacted the  $\text{NpO}_2^{2+}$  ion with 18-crown-6 in order to isolate single crystals of the  $\text{Np}(\text{VI})$  aquo ion. This effort is part of our "Actinide Molecular Science" LDRD (Laboratory-Direct Research and Development) project with the Seaborg Institute. We were quite surprised to observe the unexpected and complete encapsulation of the  $\text{NpO}_2^+$  ion in acid solution by the 18-crown-6 ligand. Addition of one equivalent of 18-crown-6 to a stirring solution of  $\text{NpO}_2^{2+}(\text{aq})$  in 1M perchloric or triflic acid results in reduction of  $\text{Np}^{\text{VI}}$  to  $\text{Np}^{\text{V}}$ , and deposition of large turquoise crystals of  $[\text{NpO}_2(\text{18-crown-6})][\text{X}]$ ,  $[\text{X} = \text{ClO}_4, \text{CF}_3\text{SO}_3]$ , after 12 to 24 hours. Near infrared (NIR) electronic absorption spectra of the crystalline solids dissolved in 1M  $\text{HClO}_4$  confirms that reduction of  $\text{Np}^{\text{VI}}$  to  $\text{Np}^{\text{V}}$  has occurred based on the presence of the strong electronic absorption feature at 980 nm ( $\epsilon = 395 \text{ M}^{-1}\text{cm}^{-1}$ ) characteristic of the  $\text{NpO}_2^+$  ion.

Even in the presence of ozone ( $O_3$ , a strong oxidant)  $Np^{VI}$  reduction and deposition of turquoise crystals of the  $Np^V$  crown complex was observed when 18-crown-6 was added. Ultimately, we find that 1M HX solutions of  $Np^V$  in the form  $NpO_2^+$  (aq) react smoothly with 18-crown-6 to give the  $[NpO_2(18\text{-crown-6})][X]$  product in nearly quantitative crystalline yield.

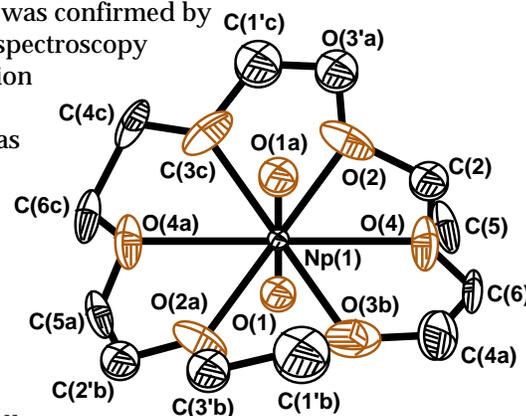
A single-crystal x-ray diffraction study revealed that  $[NpO_2(18\text{-crown-6})][X]$  contains an  $NpO_2^+$  ion completely encapsulated by a 18-crown-6 ligand. A thermal ellipsoid diagram of the  $[NpO_2(18\text{-crown-6})]^+$  ion (Figure 1) shows two trans oxo ligands and six approximately coplanar crown ether O atoms coordinated to the  $NpO_2^+$  unit, forming an approximate hexagonal bipyramidal coordination environment about the Np center. The  $Np=O$  distance of 1.800(5) Å is unusually short for an  $NpO_2^+$  ion, (generally ca. 1.85 Å) while the average equatorial  $Np-O$  distance of 2.594(10) Å is unusually long for a neutral O-donor ligand. Coordination of  $\sigma$ -donor ligands about the equatorial plane of an actinide trans dioxo ion generally results in a slight lengthening of the  $Np=O$  bond and a concomitant decrease in the equatorial  $Np-O$  bonds. In  $[NpO_2(18\text{-crown-6})][X]$  however, the coordination of 18-crown-6 about the equatorial plane results in the opposite effect, namely a shortening, and presumably strengthening of the  $Np=O$  bond.

For trans dioxo ions, the Raman-active  $\nu_1$  vibrational mode of the  $O=An=O$  unit is a much better indication of bond strength than bond length determined by an x-ray diffraction analysis. For the  $[NpO_2(H_2O)_5]^+$  ion, with  $Np=O = 1.85\text{Å}$ , the  $\nu_1$  vibrational mode is 767  $cm^{-1}$ . Raman spectra of  $[NpO_2(18\text{-crown-6})][X]$ , showed a strong, higher-frequency band at 778  $cm^{-1}$  consistent with a stronger  $Np=O$  bond than in the aquo ion. To confirm this spectroscopic assignment, an electrochemical labeling method was used to incorporate  $^{18}O$  into the  $Np=O$  unit.

$^{18}O$ -enriched  $H_2O$  (98%  $^{18}O$ ) was added to 0.56 M  $NpO_2^+$  (aq) in 1M  $HClO_4$  and reduced electrochemically at -0.2 V to a mixture of

aquo  $Np^{3+}/Np^{4+}$ , thereby removing the oxo ligands). The potential was reversed, and the aquo  $Np^{3+}/Np^{4+}$  reoxidized to  $Np^{18}O_2^{2+}$  (aq), where the oxo ligands were then enriched in  $^{18}O$ . Oxidation state purity was confirmed by NIR electronic absorption spectroscopy using the 1223 nm absorption feature ( $\epsilon = 45 M^{-1}cm^{-1}$ ) of  $NpO_2^{2+}$  (aq). 18-crown-6 was added, and aquamarine crystals of  $[NpO_2(18\text{-crown-6})][ClO_4]$  formed after the mixture cooled to 5°C overnight. The Raman spectra of  $^{18}O$ -enriched  $[NpO_2(18\text{-crown-6})][ClO_4]$  crystals show  $\nu_1$  stretching frequencies for all three isotopic compositions:  $^{18}O=Np=^{18}O$ ,  $^{18}O=Np=^{16}O$ , and  $^{16}O=Np=^{16}O$  at 734, 751, and 780  $cm^{-1}$ , respectively, confirming the original assignment.

The complete encapsulation of the  $NpO_2^+$  ion by a crown ether ligand under any conditions is unprecedented and represents the first structural and spectroscopic characterization of any transuranic crown ether complex. The relative ease of encapsulation in aqueous solutions contrasts with the necessary use of anhydrous conditions and poorly coordinating counter-ions to insure bonding of crown ether O atoms to the inner sphere of the related  $UO_2^{2+}$  ion. This difference attests to the ability of crown ether ligands to separate ions of nearly identical chemical behavior, and the apparent preference for  $Np^V$  over  $Np^{VI}$  may be related to the differing ionic radii of these ions. The complete encapsulation illustrates the additional point that the preferential encapsulation of a pentavalent actinide ion would never have been observed by studying uranium only, since uranium does not form a stable pentavalent state in aqueous solution. The potential ability of crown ether ligands to extract actinide ions selectively from radioactive process streams or nuclear waste solutions is particularly intriguing because of its economical and environmental clean-up implications.



**Figure 1.** Thermal ellipsoid plot showing the molecular structure of the  $[NpO_2(18\text{-crown-6})]^+$  cationic unit of  $[ClO_4]$  (ellipsoids drawn at the 50% probability level).

## Editorial

**“Excess” Nuclear Materials Hold Keys to Medicine, Research, Space Power**

**K. K. S. Pillay**  
is the Project  
Leader for  
Waste  
Management,  
NMT-DO.

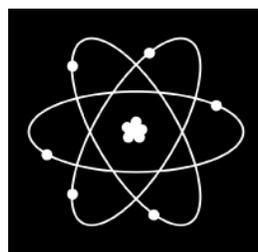
The U.S. Department of Energy (DOE) has significantly downsized its nuclear weapons complex (facilities, infrastructure, and work force) over the past several years, and the process is continuing with the eventual goal of maintaining a small, environmentally benign, efficient operation. As part of this ideal goal, the DOE is embarked on a number of programs to dispose of nuclear materials presently considered excess to national security needs. Although several government agencies as well as private industries and universities have potential uses for these materials, disposition strategies for all excess nuclear materials are being evaluated solely by the DOE's nuclear material integration (NMI) program. Since DOE's current mission is to clean up the environmental legacies of the past, excess materials are considered a liability.

The purpose of this article is to voice my concern and to alert the scientific community of an opportunity to participate in a thoughtful process of planning to preserve some of the valuable materials within the DOE complex for the future. A number of these materials may be considered excess to national security, but they are extremely valuable resources for the future of nuclear science and technology. Unfortunately, some of these unique materials have already been dumped into high-level waste tanks in the name of “mortgage reduction,” (reducing legacy waste) and are not replaceable in the near future.

The U.S. weapons complex at one time had the only facilities and resources in the free world to produce some of the uncommon and uniquely valuable nuclear materials. Those facilities are being eliminated altogether in the name of “mortgage reduction.” Since there is no chance that such facilities will be rebuilt in the foreseeable future, we should at least consider saving, (as “national treasures” for the future) some of the unique resources they produced.

A number of man-made elements and radioactive isotopes are unique and should be saved from being discarded as waste or declared excess to national security needs. Unfortunately, the definition of “national security needs” is too narrow to include future needs of science and technology. Therefore, the ongoing discussions about nuclear material disposition do not include a strategy to save some of these rare gems for future generations. Pleas made by many distinguished scientists, including Dr. Glenn Seaborg, as early as 1994, have yet to produce any tangible results. As a result, future generations will be learning about the golden days of nuclear technology in the U.S. as we are presently learning about the dinosaurs.

The origins of many of the presently known applied nuclear technologies worldwide can be traced to U.S. research. However, the past two decades have shown a serious deterioration of the role of our nuclear sciences as evidenced by the closing of academic programs and nuclear facilities in universities and elimination of national support for such programs. In the frenzy to reduce nuclear weapons and pursue the ideal goal of eliminating all weapons of mass destruction, we have in-



voluntarily succumbed to the abandonment of all beneficial uses of nuclear technologies. Since we know that today's technology innovations are based on yesterday's re-

search, it is hard to fathom where tomorrow's technologies are going to come from under these conditions. Somehow, we have lost the initiatives and leadership in this area as the rest of world is moving forward and reaping the benefits of past nuclear research to better their lives.

The uniqueness of some of the incidentally gathered material resources of the DOE complex can be illustrated using their potential value to nuclear medicine. According to the

Institute of Medicine of the National Academy of Sciences, in the U.S., isotopes are used daily in more than 36,000 diagnostic imaging procedures and in close to 100 million laboratory tests annually.

These isotopes also play a major role in treatment. The continuing growth in radioimmunotherapy and the rapid developments in the new field of brachytherapy for localized



cancer treatment are areas that require special attention during the NMI process because most of the active ingredients used here are short-lived alpha-emitters. These, in turn, are derived from a variety of long-lived heavy isotopes of unique characteristics, not available outside the DOE complex.

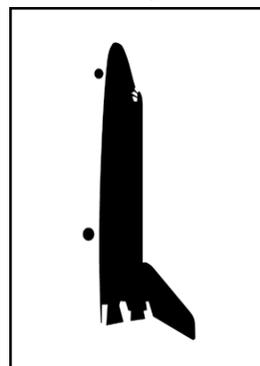
Typical examples include  $^{229}\text{Th}$ ,  $^{227}\text{Ac}$ , and  $^{225}\text{Ac}$ , which are intermediates separated and purified from various DOE source materials (namely  $^{233}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$ ). These intermediates are used primarily for the production of their daughters,  $^{231}\text{Bi}$ ,  $^{223}\text{Ra}$ , and  $^{212}\text{Bi}$ , which are the short-lived alpha emitters used in therapy. Although it is theoretically possible to use a high-flux reactor to produce  $^{229}\text{Th}$  and  $^{227}\text{Ac}$  from  $^{226}\text{Ra}$ , we are limited by the insufficient availability of high-flux neutron sources within the U.S. Even if we decided to use foreign facilities for irradiation, the starting materials ( $^{233}\text{U}$ ,  $^{235}\text{U}$ ,  $^{232}\text{Th}$ , and  $^{226}\text{Ra}$ ) would have to be preserved from the current inventories within the DOE complex.

At one time, the DOE complex was the sole source of transuranic elements used by universities and research to study the beneficial applications of such elements and to use them to increase our knowledge of the world around us. One unique example is that of the isotope  $^{252}\text{Cf}$ , a spontaneous fission source and efficient source of neutrons. In addition to its many beneficial uses in medicine,  $^{252}\text{Cf}$  has been used in industry for neutron radiography and activation analyses, and by the weapons

complex for testing the safety of nuclear weapons. Since this is an isotope with a relatively short (2.65 years) half-life, it is important to preserve the parent nuclides such as  $^{243}\text{Am}$ , and  $^{244}\text{Cm}$  to produce this material in the future. Rare isotopes are also necessary in our search for the island of stability in the periodic table beyond presently known elements. Limited quantities of Am, Cm, Bk, and Cf now available within the DOE complex are likely to end up in high-level waste tanks if a deliberate effort is not made to salvage them.

As a practical matter we also need  $^{238}\text{Pu}$  as a reliable source of thermoelectric power for extended space missions and a variety of terrestrial applications.

Presently, the supply of  $^{238}\text{Pu}$  in the U.S. is the lowest ever. At the same time, we are told that there is now a wish list of 40 NASA missions requiring  $^{238}\text{Pu}$  radioactive thermoelectric generators for power.



This problem can be solved by creatively using two other isotopes available within the DOE complex— $^{237}\text{Np}$  and  $^{241}\text{Am}$ —that are considered excess to national security. Both these isotopes can be readily converted into  $^{238}\text{Pu}$  via neutron irradiation. Such an approach would address the problems of these three isotopes at the same time.

So-called “excess materials” now within the DOE complex are invaluable resources that should be preserved for the future of medicine, research, and space exploration. The investments required to stabilize and store these valuable resources are minuscule compared to investments already made by U.S. taxpayers to create them. The DOE NMI program must recognize that proper management of these resources is absolutely essential to the future of science and technology and to the future of the nation.

*K. K. S. Pillay*

The recommendations in this editorial are mine; they do not represent the opinion of Los Alamos National Laboratory, the University of California, the Department of Energy, or the U.S. Government.

## LANL Develops TRU Waste Mobile Analysis Methods for RCRA-Listed Metals

This article was contributed by Cynthia Mahan (NMT-1). Other technology developers on this project are Randy Drake, Debbie Figg, and Dave Wayne (NMT-1), and Steve Goldstein (CST-9). This project was funded by Environmental Management-LDRD.

DOE plans to dispose of approximately 6.2 million cubic feet of transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP) site over a 25-year disposal period. Analytical characterization is a critical compliance activity required for most TRU waste destined for treatment and/or disposal. This waste is located at various DOE sites throughout the nation and, generally speaking, the required analytical capabilities for characterization do not exist at the majority of storage sites. Thus, the waste will require costly, difficult, and highly regulated transport to a facility with the requisite capabilities. To help DOE in its characterization activities, researchers in CST and NMT Divisions are working to develop a mobile analytical laboratory capable of measuring metals that fall under the Resource Conservation and Recovery Act (RCRA)(i.e., As, Ba, Cd, Cr, Hg, Pb, Se, Ag.). In addition, Sb, Be, Ni, Tl, V, and Zn are also regulated and must be characterized. The estimated savings of using a mobile laboratory as an alternative to transporting the waste is nearly one hundred million dollars.

In this study, several direct chemical analysis techniques were chosen as potentially suitable for mobile deployment. Direct chemical analysis techniques measure analytes in a solid sample without the need for acid digestion, thus minimizing sample handling and improving analytical throughput (i.e., turnaround time). This research targeted the following techniques: glow discharge mass spectrometry (GDMS), laser induced breakdown spectroscopy (LIBS), dc arc atomic emission spectroscopy (DC-ARC-AES) using a charge injection device (CID) as a detector, laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS), and energy dispersive x-ray fluorescence (EDXRF). This project was supported by Laboratory-Directed Research and Development funds.

The method-development phase of this study involved devising sample preparation procedures, instrument parameter optimization (e.g., analyte wavelength selection, laser power settings, etc.), and determination of analytical figures of merit. Each technology developer (see sidebar) was provided with surrogate cemented waste samples. These surrogates, obtained from the Idaho National Engineering and Environmental Laboratory, are actual samples used in the WIPP Analytical Laboratory Performance Demonstration Program (PDP). All laboratories that intend to characterize WIPP waste must qualify their analytical methods through this program.

Following successful development of the analytical method, another set of PDP samples was distributed to each of the researchers in a blind, round-robin format. The Quality Assurance Program Plan for the Transuranic Waste Characterization Program (TWCP) describes the performance criteria for TRU waste characterization, including PDP analysis, that must be met to demonstrate effective analytical performance. The concentrations of analytes in the PDP samples were not known at the time of analysis. After the EDXRF and DC-ARC analytical results were compiled, values for the expected concentration of analytes in each of the evaluation samples were obtained from the Idaho National Energy Laboratory, and results were compared to the known values. Accuracy and precision of the analysis were evaluated using TWCP data-quality objectives.

### Evaluation of EDXRF

All analyses were performed using a commercial EDXRF spectrometer. A nearly identical field-transportable instrument is also available, so performance of this method should be similar under field conditions. The instrument has an x-ray tube source with variable source current and voltage up to 1 mA and 50 kV, which permits optimization of excitation conditions for the element of interest. It also uses a high-resolution, electrically cooled Si(Li) detector, which permits

simultaneous collection of x-rays of variable energy with minimal spectral interference. The instrument is capable of rapid, multi-element standardization and quantitation of the acquired spectra. Samples were analyzed using an auto-sampling turret in the automated mode overnight; throughput is presently about 10 to 15 samples per day (see figure).

The EDXRF technique meets detection limit requirements for 11 of the 14 metals. Exceptions are V, Hg, and Be; the latter is not detected by EDXRF. The detection limit for vanadium is only a factor of 2 above the required limit, so it is likely that the required limit could be met by increasing data acquisition time by a factor of 4 or by increasing sample size. However, the required detection limit for mercury is a factor of 40 lower and apparently unattainable by direct EDXRF techniques. Additional field-based techniques, which can more sensitively measure both mercury and beryllium, are required for waste characterization of these RCRA metals.

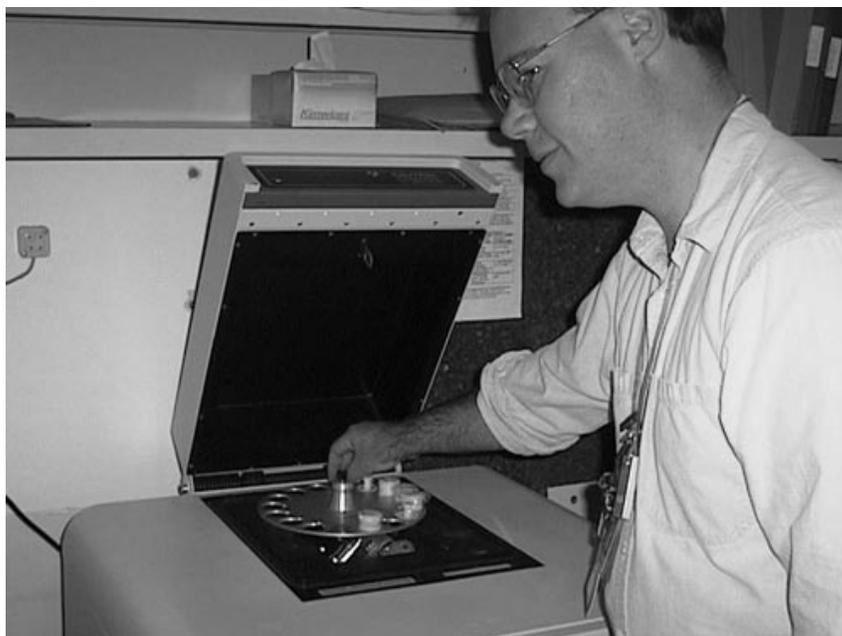
Results of the round-robin analysis show the majority of results meet the TWCP data quality objectives for percent recovery ( $\pm 20\%$ ) and relative percent difference ( $\pm 30\%$ ). Only chromium and mercury deviated slightly from the required recovery for two of the blind samples. Vanadium recoveries for two samples were low, but not enough to reduce the analytical score. Further studies are needed to determine the effects on method performance of inherent radiation of the samples and matrix variability, although these effects are expected to be relatively minor.

### Evaluation of DC-ARC-AES

DC-ARC-AES is a bulk-solids analytical technique that uses a solid-state integrating detector to measure the spectral emission intensities produced when a sample is vaporized and excited by a dc arc. The CID detector represents relatively new technology that has the potential to improve analytical performance over the traditional dc arc and conventional spectroscopic techniques. Samples are pulverized, mixed with graphite powder, and

burned in the lower of two vertically mounted graphite electrodes. The detector chip is similar to a photographic plate in that it provides for continuous wavelength coverage; hence, most elements in the periodic table can be determined if present in sufficient quantity. Potential analytical benefits over conventional spectroscopic methods include full elemental fingerprinting of the sample, the ability to detect weak spectral lines in the midst of strong matrix signals, improved sample throughput, simultaneous background correction, minimal sample preparation, and instrumental ruggedness.

**Figure 1. Steve Goldstein (CST-9) loads the autosampler on an EDXRF instrument.**



The DC-ARC technique did not perform as well as expected on the round-robin test. Only 3 analytes (Ba, Be, and Ag) met the detection limit criterion. Detection limits obtained for Sb, Cd, Cr, Pb, and Tl were high by approximately a factor of 2. They may be improved by further optimization. The reason for the high detection limits is that interfering elements, especially Fe, produce background

*continued on page 10*

The estimated savings of using a mobile laboratory is nearly one hundred million dollars.

## ...RCRA-Listed Metals (continued)

spectral interference on most of the target analytes. Fe is present in these samples at relatively high concentrations (>6000 ppm). The low detection criterion for Hg precludes analysis by dc arc as well as any other emission technique. Results of the blind round-robin test show element recoveries ranging from 72%–133%, except for the 47% recovery for V on one of the blind samples. The majority of elements that failed the TWCP objective for percent recovery failed by less than 10%.

The correction of two major problems may improve the results. First, background correction must be more precise. The five-fold dilution of the matrix, as tested, results in concentrations of interfering elements at very high levels. Over- or undercorrection of these interferences results in biases. Secondly, the technique has poor precision. It is believed this is due to a nonhomogenous sample with varying particle sizes. Better sampling, grinding, and sieving processes could result in improved precision and accuracy. An improved method with a greater dilution of the sample with graphite powder has been tested, and the preliminary results show improvements in the detection limits and recoveries for several of the elements.

### Conclusion

EDXRF appears to have great potential for TRU waste characterization for the majority of regulated metals, with the exception of Hg and Be. A solid-sampling, automated, cold vapor, atomic absorption spectrometer has been used to qualify Hg analysis for the PDP program. This instrument is small, rugged, and can be readily installed in a mobile laboratory. While the GDMS, LA-ICPMS, and LIBS work is not complete, emission techniques can measure Be accurately at very low concentrations. LIBS, which is compact, portable, and cost-efficient, will probably prove to be the technique to use for Be determinations.

## Recent Publications (July 1998–August 1998)

The expanded NMT Division comprises many authors of journal articles, formal reports, status reports, and conference reports. *Actinide Research Quarterly (ARQ)* no longer has room to publish a comprehensive publications list. Therefore, the new policy is to list only invited talks, *published* journal articles, *published* conference proceedings, books, book chapters, and formal LA reports, except in unusual circumstances. Authors need to provide complete information when their articles, book chapters, or books are published. In addition, this issue of *ARQ* goes to press early to close out the fiscal year, so only July and August publications are listed. September publications will be included in the next issue.

Timothy G. George (NMT-9), "Monthly Progress Report Heat Source Technology Programs—July 1996," LA-13491-PR (July 1998).

Timothy G. George (NMT-9), "Monthly Progress Report Heat Source Technology Programs—August 1996," LA-13492-PR (July 1998).

Ming G. Moy (NMT-1) and Craig S. Leasure (NMT-11), "Minimum Analytical Chemistry Requirements for Pit Manufacturing at Los Alamos National Laboratory," LA-13482-MS (July 1998).

Robert Villarreal (NMT-11), "Selection of Actinide Chemical Analogues for WIPP Tests," LA-13500-MS (August 1998).

Thomas G. Zocco (NMT-11), Luis A. Morales (NMT-11), Ramiro A. Pereyra (NMT-11), William B. Hutchinson (NMT-11), Tom Baros (NMT-11), Joseph L. Lowery (NMT-11), William R. Blumenthal (MST-8), and George T. Gray, III (MST-8), "Microstructural Analysis of a Plutonium-Gallium Alloy Tested in a Kolsky Bar Apparatus," LA-13483-MS (July 1998).

Thomas G. Zocco (NMT-11), Luis A. Morales (NMT-11), Ramiro A. Pereyra (NMT-11), and Joseph L. Lowery (NMT-11), "Microstructural Observations of a Post-Test Visar Wave Profile/Release Experiment (SHOT #55-40-219)," LA-13484-MS (July 1998).

## Secretary Richardson Dedicates ARIES

Secretary of Energy Bill Richardson dedicated the Advanced Recovery and Integrated Extraction System (ARIES) during his visit to the Laboratory September 11 (Figure 1). ARIES integrates the technologies needed to remove plutonium from the core of surplus nuclear weapon pits and convert it to unclassified metal pucks or plutonium oxide. The product of the ARIES Demonstration Line (Figure 2) will then be packaged for long-term storage and subsequent disposition. For disposition the plutonium may be blended with other materials to make mixed-oxide fuel for use in existing domestic power reactors, or it may be encased in ceramic for disposal as high-level waste. The unclassified long-term storage package and the disposition activities allow the plutonium to be inspected and its composition and quantity verified in accordance with international safeguards regimes.

The ARIES prototype is being developed jointly by Los Alamos and Lawrence Livermore National Laboratories. Sandia National Laboratory is developing some of the robotics for the system. Information gained from the ARIES Demonstration Line will be used in designing the United States' pit disassembly and conversion facility, which will probably be located at either the Pantex Plant or the Savannah River Site.

Richardson recognized the efforts of his fellow New Mexicans working on the ARIES project, saying with pride, "Their efforts to dismantle nuclear weapons are making the world a safer place."

**Figure 2. The ARIES Demonstration Line integrates key components of the ARIES prototype that have been proven in earlier experiments. These modules include pit bisection, hydride-dehydride processing, conversion of the pit plutonium metal to an unclassified metal puck or plutonium oxide form, packaging for long-term storage, electrolytic decontamination of the material storage container, and nondestructive assay of the long-term storage package. ARIES Project Leader Tim Nelson explains the process to Secretary Richardson as Vic Reis, John Browne, and David Nelson (ESA-EPE) listen.**



**Figure 1. Secretary of Energy Bill Richardson dedicated ARIES, a prototype technology housed in the Lab's Plutonium Facility. The U.S. will use ARIES to disassemble plutonium components from retired nuclear weapons and convert the resulting plutonium into a form suitable for disposition and international inspection. Looking on (from left to right) are Lab Director John Browne; Vic Reis, DOE's assistant secretary for defense programs; Dana Christensen (in back row), deputy division director for Nuclear Materials Technology (NMT); and NMT Division Director Bruce Matthews.**



NewsMakers

■ Sixteen NMT members received the **1998 NMT Division Science and Technology awards**. Each received a certificate and cash award for exceptional contribution to communicating science, technological innovation, and accomplishment through significant publication efforts from July 1997 to July 1998. The recipients of the 1998 awards are as follows: **David L. Clark** and **Noah G. Pope** (NMT-DO); **Joel D. Williams** and **Stephen L. Yarbrow** (NMT-2); **John J. Park** (NMT-5); **Mary E. Barr**, **Timothy O. Nelson**, **Louis D. Schulte** and **Wayne H. Smith** (NMT-6); **Andrew J. Montoya** (NMT-7); **Thomas W. Blum** and **Derek J. Gordon** (NMT-8); **Gary L. Silver** (NMT-9); and **Barbara Martinez** and **Thomas G. Zocco** (NMT-11).

■ **Plutonium Futures—The Science**

A second in the conference series “Plutonium Futures—The Science” is slated for July 2000 in Santa Fe. The conferences are designed to be an interdisciplinary forum to present and discuss current research on the physical and chemical properties of plutonium and other actinide elements. Once again the forum will have international participation to discuss the latest and emerging science of actinides (chemistry, physics, materials science, actinides in the environment), relevant to reducing the global nuclear danger. For more information visit the conference Web site at <http://www.lanl.gov/Pu2000.html>.

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