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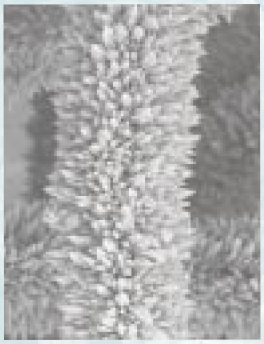
Experiments Aim to Extend the Limits of Magnetic Separation

Magnetic separation has received much attention recently from industrial, medical, and governmental researchers interested in selective separation technologies. Currently, we are developing technologies for single-particle capture of submicron actinide particles from forensic samples of interest. The retrieval and concentration of transuranic and fission products from the local environment or sample sources can also be used to learn about the environment around nuclear facilities.

High-gradient magnetic separation (HGMS) utilizes large magnetic field gradients to effectively separate micron-sized paramagnetic particles of actinide compounds. HGMS can extract and concentrate micron-sized actinides and actinide-containing particulates with no sample destruction. Most host materials such as air, water, and organic matter are diamagnetic, which will allow for a physical separation of the paramagnetic actinides from these materials. Typically, HGMS separators consist of a high-field solenoid magnet, the bore of which contains a fine-structured ferromagnetic matrix material. The matrix fibers locally distort the magnetic field, generating high-field gradients at the surface of the filaments. These areas then become trapping sites for paramagnetic particles and are the basis for the magnetic separation.



Using commercially available 45-micron-diameter stainless steel wool, the kaolin clay industry and soil remediation and water treatment processes have demonstrated HGMS of micron-sized materials.

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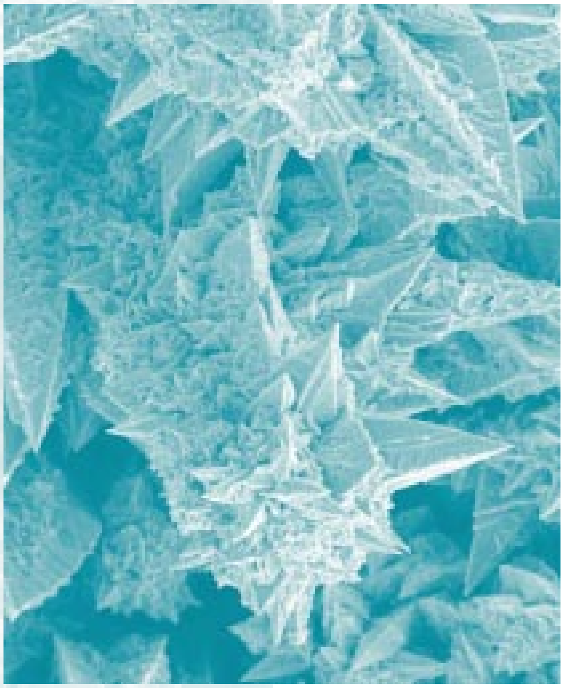
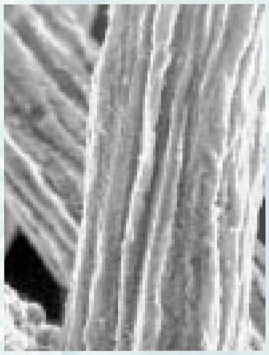




Figures. Scanning electron micrographs of extruded stainless steel matrix material (see pages 2 and 3).

Experiments Aim to Extend the Limits of Magnetic Separation *(continued)*

This article was contributed by **Laura A. Worl.** Other researchers on the project are **David Devlin, Dallas Hill,** and **Dennis Padilla,** all of NMT-6, and **F. Coyne Prenger,** (ESA-EPE).

The magnetic capture of smaller particles (submicron) can be obtained by increasing the magnetic force between the fibers and the paramagnetic particles. One approach towards increasing the magnetic force and improving separator efficiency is to reduce the size of the matrix. Others have examined submicron-sized spheres for the collection of nanometer-sized particles. In addition, fractionation methods for HGMS of nanometer particles are under development. We are investigating dendritic growth on surfaces and controlled corrosion of stainless steel wool in an effort to reduce the effective matrix capture diameter.

The matrix materials currently used for HGMS are inhomogeneous and have a complex cross section. In addition, the paramagnetic particles are nonspherical and include a range of particle sizes. All of these factors discourage precise analytical treatment. Therefore, our approach is semiempirical, combining a mechanistic analytical model with empirical input from controlled experiments.

Previously we derived a rate model from a force balance on individual paramagnetic particles in the immediate vicinity of a matrix fiber. The model assumes that if the magnetic capture forces are greater than the competing viscous drag and gravity forces, the particle is captured and removed from the flow stream. The rate model depends on the magnitude of the capture cross section (separation coefficient) as determined by the force balance on the particle. In this work we have expanded the model to include the loading behavior of particles on the matrix fibers using the continuity equation, and we utilize capture-rate data from the experimental results. The resulting analytical model predicts the critical separation parameters for submicron, single-particle collection presented in this article. It thus provides a predictive tool for HGMS tests conducted here and can be used for designing both prototype and full-scale units for specific applications.

We have conducted a series of HGMS experiments using particulate oxides of copper, praseodymium, or plutonium suspended in a liquid. The experimental data were correlated with the analytical model, which was developed previously with a systematic series of soil remediation tests.

Single-Particle Collection

Assuming a spherical particle with a known density, we can calculate the concentration of a specific-diameter particle. For a concentration of 4 parts per billion (ppb) of a 0.8-micron particle, there would be approximately 1300 plutonium oxide particles in 1 ml of solution. In the initial feed concentrations for our experiments, we typically use starting plutonium concentrations in the range of 2–15 ppb and an initial volume of 100 ml. This would translate to approximately 6500 particles with a 0.8-micron diameter in the feed solution. In these applications, we attempt to extract all the 6500 particles to get below the single-particle threshold.

To obtain a concentration of less than 3 x 10^{-11} M (~3 ppt) (parts per trillion) of plutonium oxide, the small but finite solubility of PuO_2 in water demanded that we examine alternate carrier fluids. Though the PuO_2 solubility constant is very low, in slightly basic conditions plutonium (IV) in water solutions at pH 8 can be found at concentrations up to 10^{-7} M. Preliminary HGMS tests conducted in pH 8 water failed to remove plutonium from the feed samples. For the remaining HGMS tests, we have examined dodecane as a carrier fluid to enhance the insolubility of the plutonium. Plutonium oxide particles sized from 0.2–0.8 microns were removed below 6 ppt. The separation efficiencies for these tests were over 99%. This value is the detection limit of the current analytical method (liquid scintillation counting) without a preconcentration step in the sample preparation. The data are in general agreement with the analytical model.

Matrix Material

The experiments discussed here used a matrix material based on extruded stainless steel fibers. Figure 1 shows a scanning electron micrograph of the extruded material. The multiple ridges in the material form a continuum

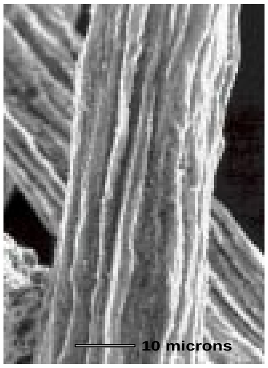


Figure 1. Scanning electron micrograph of extruded stainless steel matrix material. Results of experiments show that maximum separation effectiveness is obtained when the matrix fiber diameter approaches the diameter of the particles to be captured.

of sharp axial edges that generate large magnetic field gradients and serve as trapping sites for the submicron particles. The extruded sample developed for this program contains a much higher density of edge locations compared with traditional HGMS shaved stainless steel wool materials. The extrusions produce small matrix fiber diameters and high matrix loading capacities.

The effect of matrix diameter was examined experimentally by determining HGMS effectiveness for four different matrix materials with different cross-sectional areas. The results indicate that for selective small-particle capture, very fine matrix fibers are required. For particles below 0.2 µm, HGMS separation is much more effective with smaller wire diameters (5 µm).

The effect of changing the applied magnetic field for the same matrix size from 7 T to 2.5 T is not nearly as significant as the effect of reducing the matrix size. At 2.5 T the matrix material is nearly saturated magnetically, and any further increase in the applied field has a small effect on the separation. Increasing the matrix residence time will also increase the separation effectiveness, but at extremely low superficial velocities the resulting particle settling can be a significant problem.

To greatly enhance performance and to achieve a single-particle collection threshold, it has become apparent through model predictions and experimental data that the matrix fiber diameter is a crucial separation variable. Tests have been initiated to develop new matrices with submicron-sized fiber diameters. Two different approaches are being studied to generate these materials. One approach is controlled corrosion studies on 25-µm-sized drawn stainless steel wool material, and the second approach is the growth of micron-sized nickel dendrites on stainless steel wool fibers by chemical vapor deposition.

Nickel dendrites were deposited on the stainless steel matrix material using a hot-wall reactor. Nickel dendrite structures were uniformly deposited on the surface throughout the wool structure. The length of the dendrites is 1–2 orders of magnitude smaller than the diameter of the wool fiber substrate, shown in Figure 2. The resulting matrix material has a very high surface area containing fine points that may greatly enhance the high field gradients. In addition to magnetic characterization of the material, HGMS testing on these materials is planned in the future. This material has the potential to advance HGMS towards subnanometer particle collection. We are currently evaluating the HGMS performance of the new materials.

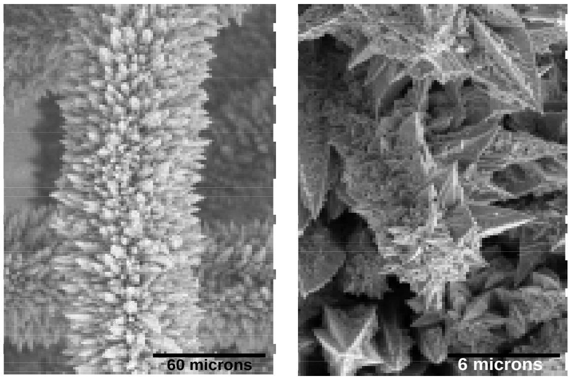


Figure 2. Scanning electron micrograph of extruded stainless steel matrix material with nickel dendrites grown on the surface of the material. This is one approach in the development of new matrices with submicron-sized fiber diameters. The other is controlled corrosion studies on 25-µm-sized drawn stainless steel wool material.

Summary

We have derived a model from a continuity equation that uses empirically determined capture cross-section values. The model allows us to predict high-gradient magnetic separator performance for a variety of materials and applications. The model can be used to optimize the capture cross-section values and thus increase the capture efficiency. Results show that maximum separation effectiveness is obtained when the matrix fiber diameter approaches the diameter of the particles to be captured.

Experimentally, we obtained a single-particle capture limit with 0.8-µm PuO_2 particles with dodecane as a carrier fluid. The finite solubility of plutonium in water prevented the complete removal of the contaminants when using water as the carrier fluid.

The development of new matrix materials is being pursued through the controlled corrosion of stainless steel wool and the deposition of nickel dendrites on the existing stainless steel matrix material. The new materials are promising for the submicron collection of paramagnetic particles. HGMS experiments on the new materials are planned.

XANES Reveals Oxidation State of Plutonium

This article was contributed by **D. Kirk Veirs** (NMT-11). Other researchers on the project include **S. D. Conradson** (MST-8), **D. L. Clark** (NMT-DO), **D. W. Keogh, M. P. Neu,** and **S. D. Reilly** (CST-18), **W. Runde** and **P. D. Palmer** (EM-ET), and **J.B. Tracy** (NMT-11).

Oxidation state and chemical speciation define the chemistry of plutonium and other actinides. These properties underlie the behavior of plutonium in a wide range of systems, from separation processes to transport properties in the environment. Predicting the fate of plutonium in the environment, designing remediation processes for plutonium-containing residues, and evaluating stabilization technologies for unstable residues all rely to some extent on knowledge of the oxidation state and speciation.

In all of these systems the plutonium content can be low, and determination of these fundamental chemical properties can be problematic. Standard methods for elemental analysis yield no information on oxidation state or speciation. X-ray absorption spectroscopy (XAS) is an established technique for determination of oxidation states and speciation in transition metals and is beginning to be used to study actinides. XAS is sensitive, requires no sample preparation, is applicable to liquids and to solids, whether or not the solids are amorphous or crystalline, and can be applied to complex and opaque matrices. In this work we are concerned with the oxidation state; however, it is recognized that speciation information can be acquired at the same time by extending the energy range over which the data are collected.

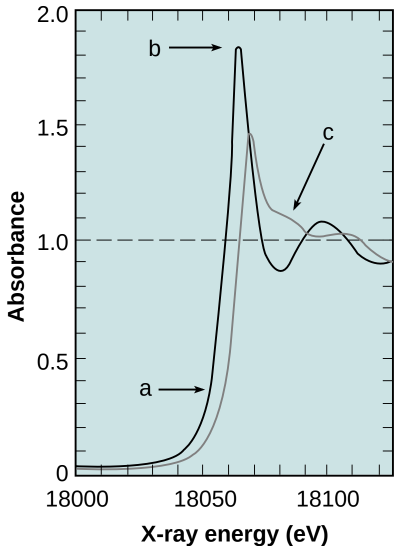


Figure 1. XANES spectra of Pu(III) (black) and Pu(VI) (gray) aquo ions. The absorption edge (a) and "white line" maximum (b) generally shift to higher energy for higher oxidation states. Dioxo cations have a characteristic shoulder (c) and reduced "white line" intensity. XAS spectra are normalized to an edge jump absorbance of 1.

Our work on the aquo ions of plutonium represented our first effort to study the effect of oxidation state on the x-ray near edge structure (XANES) spectrum. It was found that the edge energy of XANES spectra increases by about 1.7 eV per oxidation state in going from Pu(III) to Pu(VI). Still to be determined was the influence of the speciation and the physical state (liquid or solid) on the XANES spectrum. In order to sort out these effects, we studied a large number of well-characterized plutonium samples. The goal of our work is to develop a methodology to determine oxidation states from the XANES spectrum of actinides in any matrix. The work includes understanding the instrumental and data reduction limitations on determining precise energies of the XANES features.

In the XANES spectrum the L_{III} absorption edge of plutonium occurs at about 18050 eV. It arises from allowed optical transitions between the $2p_{3/2}$ core state to the unoccupied $6d_{3/2}$ states and / or to the continuum. The uncertainty of the final state arises from different interpretations of the "white line" feature of actinide XANES spectra. The XANES spectra of Pu(III) and Pu(VI) aquo ions illustrate characteristic features of actinide XANES spectra and the types of changes in those features that allow oxidation state determination, as shown in Figure 1. The XANES spectra of the III and IV oxidation states of plutonium share similar features—a strong, narrow "white line" followed by deep EXAFS oscillations. In contrast, the dioxo species typically found in the V and VI oxidation states have a much weaker "white line" feature, a shoulder rather than the deep oscillation, and a somewhat flat transition to the EXAFS (extended x-ray fine absorption structure) region. These features are typical of all actinide L_{III} XANES spectra.

Theoretical calculations of the XANES edges of actinides using multiple scattering theory quantitatively accounts for all observed features. It attributes the "white line" mainly to multiple scattering, either atomic XAFS or electron scattering of the low-energy electrons from the neighbors, with a small contribution from the atomic transition. Theoreticians also conclude that the Fermi level is not necessarily the midpoint of the edge jump in the XANES.

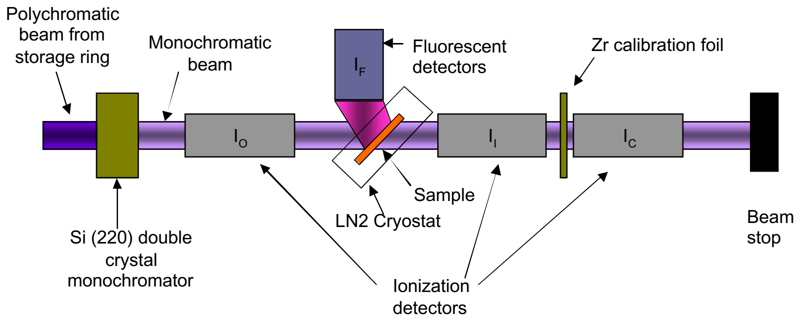
XANES spectra can be fit using an arc tangent function for the edge jump and any number of line shapes for the "white line." The dioxo species require additional peaks in the fit in order to obtain an adequate fit. The position of the arc tangent is generally reported as the absorption edge. The "white line" peak position reported here is obtained by determining the energy of the peak maximum from the first derivative with respect to energy. The peak maximum obtained using the derivative is not dependent upon choices of peak line shape or initial parameters from a fit of the data; thus, it is more closely tied to the observed data.

XAS data are collected in both transmission and fluorescence in most cases (Figure 2). Synchrotron emission passes through a double Si-crystal monochromator, and the intensity is measured with an ionization chamber. This monochromatic beam impinges upon the sample, and fluorescence is detected using an array of germanium energy-dispersive detectors. The remaining beam passes through a second ionization chamber, a zirconium calibration foil with a K absorption edge energy of 17999.35 eV, and a third ionization chamber before termination. The transmission data are more reliable for XANES measurements and are used here. Data for solid samples are collected at near liquid-nitrogen temperature to minimize Debye-Waller motion. Data for liquid samples are collected at room temperature.

The reproducibility of the XANES spectrum was evaluated using fifteen scans of ten different proprietary resin samples with adsorbed Pu(IV). The adsorbed species are identical so any observed changes in the XANES spectra are due to limitations in the data. Reproducibility of the edge energies, s = 0.31 eV, and the "white line" peak maximum, s = 0.20 eV, was found to be adequate for distinguishing between oxidation states based on the 1.7 eV separation observed for aquo ions.

Thirty well-characterized plutonium samples of varying speciation and physical state were examined. The range of speciation spanned weak oxo ligands such as nitrate to halogens such as chloride. The XANES spectra varied considerably in the intensity of the "white line" feature and the overall width of the transition as measured by the difference between the edge position and the peak position. However, there was remarkably little variation in the energy of the peak position. The range of the peak positions is ±2.4s based on the resin data; thus, it does not appear that the peak position changes. In two cases plutonium surrounded by the same ligands was prepared in both the solid state and in solution, which allowed direct measurement of the effect of physical state on the XANES spectra. The solid state XANES spectra is always more broad, and the "white line" are always of lower intensity than in the XANES spectra of the same species in solution.

Uranium, neptunium, and americium were examined in addition to plutonium, and trends were observed. The general rules described below apply to these four actinides and can be used to determine their oxidation state in many matrices. The dioxo cations V and VI are distinguished from III and IV by the characteristic dioxo shoulder about 10 eV higher in energy than the "white line." The peak maximum of III is 3 to 4 eV lower in energy than the peak maximum of IV. The peak maximum of V is lower in energy by 2 eV from the peak maximum of VI and is lower in energy by about 1 eV from the peak maximum of IV. The energy of the peak maxima alone cannot distinguish the dioxo cations from IV.



Sample absorbance = $\log(I_I/I_O)$ Transmission
Sample absorbance = $\log(I_F/I_I)$ Fluorescence
Zr calibration absorbance = $\log(I_C/I_I)$ Transmission

Figure 2. Schematic of data collection at the Stanford Synchrotron Radiation Laboratory. XAS data are usually collected in both transmission and fluorescence. The synchrotron emission passes through a double Si-crystal monochromator, and the intensity is measured with an ionization chamber. This monochromatic beam impinges upon the sample, and fluorescence is detected using an array of germanium energy-dispersive detectors. The remaining beam passes through a second ionization chamber, a zirconium calibration foil, and a third ionization chamber before termination.

Editorial

Fruitful Research Collaboration Follows Common Guidelines

This article was contributed by **Kyu C. Kim,** NMT Chief Scientist.

The Nuclear Materials Technology (NMT) Division has a wide range of research collaborations with universities, national laboratories, industrial companies, and several international organizations. The division presently carries out active research collaborations with about three dozen external entities. The nature of these collaborations ranges from individual-researcher-initiated research projects with external collaborators to institutionally backed projects. If one includes the co-authorship in research papers published in scientific journals, this number becomes even larger.

University collaborations typically take the form of conducting joint research on campuses or at Los Alamos with students participating as part of their academic degree programs. These collaborations can be particularly helpful for students as they make the transition from their formal training to career-oriented research. NMT provides a unique environment where nuclear materials can be handled safely for those interested in nuclear materials research. The nation's universities typically lack resources in this area because of the specialized facilities involved and the safety and oversight requirements that must be met.

International collaborations are being developed in many research areas aimed at reducing the global nuclear danger—safeguarding nuclear materials through detection and instrumentation, safe storage and disposition of fissile materials, development of waste treatment technologies, etc. Industrial partnerships have been forged through CRADAs (cooperative research and development agreements) for a number of new or advanced process engineering projects.

The goals of these collaborations vary widely. However, one common objective among all these collaborations is to enrich and to advance the science and technology in the specific areas of each collaboration. In some cases, we are also able to recruit unique scientific resources and talents through our university interactions. Traditionally, these interactions with universities have provided a significant portion of the human resources needed for the research and programmatic activities carried out in the national laboratories. These are, therefore, the key elements to our future progress.

NMT Division, as a science and technology organization, has generally encouraged all forms of individual and institutional collaborations, internal and external, within the bounds of our institutional mission. The success of these external collaborations has been outstanding. That said, any collaboration should meet some of the basic premises of research collaboration in NMT Division and, on the larger scale, in the Laboratory. Some of these premises are stated in the following:

1. The area of the collaboration has to be defined by the collaborators. The research areas within NMT Division are very broad, and these are documented in division science and technology strategic plans. The division strives to maintain four core technical capabilities:

plutonium metallurgy, actinide process chemistry, actinide materials science including actinide ceramics, and nuclear facility operation. In each of these core capabilities, there may be specific capabilities needed to enhance science and technology activities. When a collaborative work is proposed, it is therefore desirable and necessary to conduct a relevance check of the proposed work against the division's core capabilities.

2. Technical merits of the proposed work should be evaluated and reviewed by competent independent reviewers. As we strive to achieve excellence in our research work, this is perhaps one of the most important criteria. If the proposed work has some outstanding technical merits or potential payoffs, there may be alternative ways of supporting such work in this Laboratory besides the Division. We do not wish to miss out on the opportunities. The Laboratory Directed Research and Development program is just such a mechanism.

3. The scope of the collaboration has to be defined and agreed upon. Once the proposed work is realistically sized, there have to be sufficient resources in terms of budget, personnel, and facility. Additionally, one has to consider the right mix of talents, steady funding sources to carry the work to conclusion, and a suite of required research equipment.

4. The need for the collaboration has to be justifiable with relatively high priority. In the real world of limited science and technology budgets, we have to prioritize our work so that we get maximum benefits for the dollars spent. We recognize that not all scientific endeavors lead to immediately useful results or applications. With limited resources, however, it is essential to prioritize our tasks and to plan within the agreed upon scope for long-term stability of our research activities.

5. Finally, it is important to recognize that NMT Division is not a funding organization for a variety of internal and external collaborations. Unlike government or private grant awarding organizations, the Laboratory's operating funds are allocated for specific missions. It is safe to say that all funds in this Laboratory are associated with our mission-oriented programs, small and large, and resource allocation is performed by the program offices throughout the Laboratory. This means that the program offices should be made to see the benefits of the proposed collaborations and to support the work as an essential part of the program planning and execution. There is no excess in today's Laboratory operating budget, and we must use our resources sparingly.

Aside from the formalized collaborations described above, there are examples of numerous informal collaborations in the scientific community. Collaboration has become nearly synonymous with any scientific work in today's world, and it is expected to be more so in the future. It's a necessity as well as a driving force for scientific progress.

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

Researchers Evaluate Isotope Ratio Techniques for Actinide Analysis

This article was submitted by **David M. Wayne** (NMT-1.) Others contributing to this work are **Wei Hang** and **Vahid Majid** (CST-9) and **E. Larry Callis, Debbie Figg, Diane McDaniel,** and **Cris Lewis** (NMT-1).

Isotope ratio and isotope dilution analyses play a key role in the characterization of nuclear materials for both defense and energy applications. In many cases we use thermal ionization mass spectrometry (TIMS), which offers optimum accuracy and precision: <0.001% relative standard deviation (RSD). However, in cases where less-precise and less-accurate data (~0.5% to 3.0% RSD) will meet customer needs, or when very rapid results are required, isotope ratio analysis can be undertaken by other means. Quantitative elemental and isotopic data can be obtained directly from the sample surface through the use of cathodic sputtering (glow discharge mass spectrometry—GDMS), laser ablation (laser ablation inductively coupled plasma mass spectrometry—LA-ICPMS), or by ion beam bombardment (secondary ion mass spectrometry—SIMS). In this article, we describe the capabilities of two plasma-based isotope ratio analysis techniques: GDMS and ICPMS.

ICPMS is the method of choice for most trace element determinations in radioactive materials at LANL. The ICP ion source is an extremely efficient ion generator that operates at near-atmospheric (~760 torr) pressures. Nearly complete analytical coverage of the periodic table is available from ICPMS. Samples may be introduced as solutions, slurries, or suspensions of very fine particles generated by laser ablation. Samples are nebulized, ignited in an rf-generated argon plasma at >7000°C, and sampled into the mass spectrometer through a series of cones. The sampling cones, along with a powerful differential pumping system, permit ions to make the transition from the high-pressure ion source region to the low-pressure (~10^{-7} to 10^{-8} torr) mass analysis region.

In a glow discharge (GD) ion source, direct atomization and ionization are achieved via cathodic sputtering of the sample surface in a low-pressure (0.1 to 10 torr) argon atmosphere. Unlike other direct sampling techniques (e.g., SIMS or LA-ICPMS), the GD ion source exhibits relatively uniform elemental response and can rapidly produce quantitative trace analyses (parts per billion) without the need for strictly matrix-matched standards. The GD ion source is highly efficient and is capable of measuring ~99% of the elements in the periodic table. Its chief limitation is that samples must conduct electricity. For ceramics, soils, and other insulating materials, bulk analyses are performed by mixing a powdered sample with a conducting metal binder, or by using a tantalum (Ta) secondary cathode. A radiofrequency-powered GD ion source also permits direct sputter atomization of insulating materials.

Mass bias in mass spectrometry arises when physical phenomena present during ionization, sampling, or analysis result in the preferential loss of either light or heavy ions from an ion population. Thus, the measured isotope ratio is different from the actual value. Although mass bias in ICPMS and GDMS is a predictable function of element mass and can be corrected, it is generally far more severe than in TIMS. For this reason, isotope ratio measurements made using plasma-source mass spectrometry are inherently less accurate than TIMS measurements.

Extensive research has been done on isotope ratio analysis using both double-focusing single collector and “multicollector” ICPMS. The latter are equipped with up to nine independent detectors that measure multiple ion beams simultaneously and can attain sensitivity and precision that rivals that of multicollector TIMS instruments. Even so, single-collector, double-focusing ICPMS (and GDMS) instruments are far less expensive, easier to maintain, and offer exceptional analytical versatility. For “real-world” samples, a double-focusing, single-collector ICPMS is capable of accuracy and precision of 0.5% to 2.0% RSD, depending on the actual concentration of the isotopes in the unknown. Isotope dilution analysis, preconcentration, and on-line separations for key elements are also possible using solution-based ICPMS.

In contrast, only a few investigators have used GDMS to measure isotope ratios. NMT-1 researchers have measured isotope ratios of several elements (B, W, Tl, Pb, U) in a variety of metal and glass standards using a double-

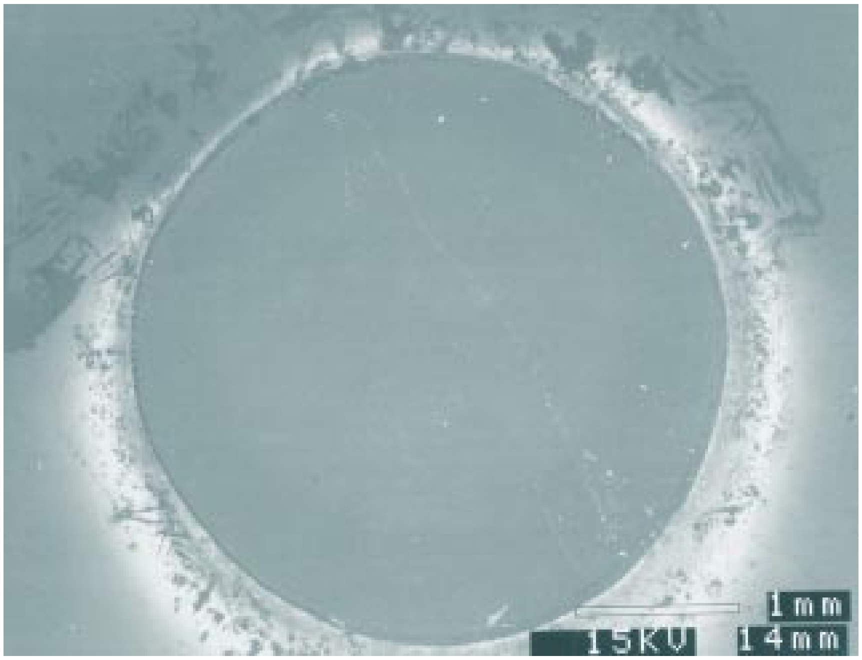


Figure 1. Scanning electron microscope image of a sputter crater in glass after 5 hrs. of analysis using a secondary cathode. The bright areas around the perimeter of the crater are coated with Ta sputtered from the secondary cathode.

focusing, single-collector GDMS instrument. The mass ranges can be selected and scanned by changing the magnetic field intensity. Total elapsed time required for each analysis (i.e., 8 to 10 sets of 8 to 15 scans) was 30 to 40 minutes. All uncertainties are reported at the 2-σ level.

First, we performed isotope ratio analyses of tungsten (W, 0.102 wt. %) and lead (Pb, 240 ppm) in a steel standard (NIST SRM 1264a). The precision of W isotope ratios measured using GDMS was ~0.4% to 1.5% RSD, and the accuracy was <1% RSD. Mass bias in Pb isotopes was estimated using the departure of the ^{186}W / ^{183}W ratio from the known value, and assuming an exponential mass fractionation law. The precision of Pb isotope ratios in SRM 1264a, measured by GDMS, was ~1.5% to 3.6% RSD.

For the next set of analyses, we analyzed a Na-Ca-Al silicate-based glass-ceramic standard (NIST SRM 611) using a Ta secondary cathode (Figure 1). The standard glass contains trace amounts of Pb (426 ppm), Tl (62 ppm), and U (461.5 ppm). Furthermore, the isotope ratios of Pb (^{208}Pb / ^{206}Pb and ^{207}Pb / ^{206}Pb) in this material have been characterized using TIMS. Isobaric interference from $(\mathrm{TaNa})^+$ ion clusters (mass = 203.9378 amu) prevented the collection of ^{204}Pb at a mass resolution of 1500, although the remaining Pb isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) were interference-free. Mass bias, measured using ^{205}Tl / ^{203}Tl, varied from –0.7% to +0.9% over 9 runs, much lower than typical values for ICPMS (> 1.5%). These data also support our theoretical calculations, which predict that mass bias in the GD ion source is less severe than in the ICP ion source. The GDMS Pb isotope determinations were typically accurate to within 1% of TIMS Pb isotope measurements and precise to < 2% RSD.

GDMS permits the collection of multi-element isotope ratio data in a single run; thus, a uranium isotope ratio (^{235}U / ^{238}U) was also measured in the glass standard, along with Pb and Tl. The extremely low abundance of ^{235}U (ca. 1 ppm) resulted in low signal intensities, and the ^{235}U / ^{238}U ratios obtained by GDMS were less precise (2.3% to 9.3% RSD) and less accurate (0.4% to -7.8% RSD) than the Pb and Tl measurements. However, the uranium isotope ratio data are still useful. The GDMS analyses indicated that the U in the glass standard was depleted in ^{235}U (^{235}U / ^{238}U = 2.2×10^{-3} to 2.5×10^{-3}). This was confirmed by NIST personnel and in published reports. Note that the characterization of depleted U in the glass standard took less than 1 hour by GDMS.

Conclusions

Most commercial, magnetic-sector ICPMS and GDMS instruments are single-collector, double-focusing mass spectrometers designed for rapid determinations of trace and major elements. However, sector GDMS and ICPMS may also be used to acquire reasonably precise and accurate (0.5% to 2.0% RSD) isotope ratios on trace and major elements. Both techniques are very rapid and require minimal sample preparation but with decreased sensitivity, accuracy, and precision relative to TIMS. Moderate-precision data may be useful in some applications; however, isotope ratios acquired using GDMS and ICPMS may be most useful as screening techniques before TIMS data are obtained from selected samples.

NMT Division Completes Annual Division Review

Reported by **Octavio Ramos,** CIC-1.
Photos by **Gary Warren,** CIC-9.

On May 11–14, 1999, NMT Division held its Science and Technology Assessment (also called the "Division Review") at the J. Robert Oppenheimer Study Center and TA-55. This year's topics included pollution prevention, analytical chemistry, separations science, materials science, and nuclear materials management. In addition, there were 43 poster papers covering a broad range of NMT's scientific and technological activities.

On May 11 the Division Review Committee (see Figure 1) met with Laboratory and NMT management for an executive opening session, which was followed by morning overview sessions presented by Nuclear Weapons Directorate Deputy James A. Mercer-Smith and NMT Division Director Bruce Matthews. The afternoon session covered topics such as facilities and infrastructure, NMT's major programs, and personnel and collaborations.

For the next day and a half, the committee listened to a number of presentations, including an update from the Seaborg Institute; an overview of analytical chemistry; highlights from separations science actitivities, materials science, and nuclear materials management; and an overview of waste treatment, environmental compliance, and pollution prevention.

Poster sessions presented the second afternoon showcased NMT's science and technology activities and accomplishments. This year, the committee selected five posters it felt were outstanding. The top five were as follows:

- Synthesis and Characterization of Uranium(IV)-bearing Members of the (NZP) Structural Family, H. T. Hawkins, D. R. Spearing, and D. K. Veirs (NMT-6); J. A. Danis and W. H. Runde (CST-7); D. M. Smith (CST-11); C. D. Tait (CST-4); M. N. Spilde (University of New Mexico); and B. E. Scheetz (Pennsylvania State)
- Coordination Chemistry of Hexa-valent Actinide Ions (Uranium, Neptunium, and Plutonium) Under Highly Alkaline Conditions, D. L. Clark (NMT-DO); S. D. Conradson (MST-11); D. W. Koegh and B. L. Scott (CST-18); R. J. Donohoe, D. E. Morris, and C. D. Tait (CST-4); M. P. Neu (CST-11); and R. D. Rogers (CST-7)
- Magnetic Separation for Nuclear Material Detection and Surveillance, L. A. Worl and D. Padilla (NMT-6); D. Devlin (MST-7); and D. D. Hill and F. C. Prenger (ESA-EPE)
- Membranes for Selective Metal Ion Separation, G. D. Jarvinen, M. E. Barr, and J. S. Young (NMT-6); T. M. Mcleskey, D. S. Ehler, N. N. Sauer, and Q. T. Le (CST-18); N. C. Schroeder, K. D. Abney, R. M. Chamberlin, E. A. Bluhm, and E. Bauer (CST-11); T. W. Robinson and B. F. Smith (CST-12); R. C. Dye, B. S. Jorgensen, and D. R. Pesiri (MST-7); A. Redondo, L. R. Pratt, and S. L. Rempe (T-12)
- Electronic Structure of Plutonium Metal: High-resolution Core Level and Resonant Valence Band Photoemission Spectroscopy at the Advanced Light Source, J. H. Terry, Jr., R. K. Schulze, T. G. Zocco, and D. Farr (NMT-11); J. Lashley (MST-8); E. Rotenberg and D. Shuh (Lawrence Berkeley National Laboratory); and J. Tobin (Lawrence Livermore National Laboratory)

Figure 1. Division Review Committee Members (left to right) Dr. Ned Wogman (chair), Dr. Darleane Hoffman, Dr. Todd LaPorte, Dr. Lamar Miller, Dr. Robert Uhrig, Dr.Anthony Rollett, Dr. Richard Bartsch, and Dr. Darryl DesMarteau.

During the close-out session the Division Review Committee made several positive comments. “Without NMT, many other divisions at the Laboratory could not conduct advanced science and technology,” noted Dr. Ned A. Wogman, the committee’s chair. “Furthermore, they could not share their knowledge through publication to the entire world. NMT should be proud to be the source of such proliferation.” As to the committee’s final report, Wogman had this to say: “Our final report will have a strong message, a good message. And we have even greater expectations as to NMT’s future.”

NMT Division Review Committee

Dr. Ned A. Wogman, 1999 Chair
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Dr. Anthony (Tony) W. Thompson, CA

Dr. Robert E. Uhrig
Nuclear Engineering Department
The University of Tennessee

Publications and Invited Talks
(March 1999–May1999)

Cournoyer, M. E., and W. H. Smith, “Parametric Optimization of the MEO Process for Treatment of Mixed Waste Residues,” *in Proceedings of the Waste Management ’99 Symposium*, Laser Options, Inc., Tucson, AZ (in press).

Gibbs, F. E., “Review of the Effect of Iron and Nickel Content on the Homogenization Response and Performance Properties of Delta Phase Stabilized Plutonium-Gallium Alloys,” *Defense Research Review* (April 1999).

Jarvinen, G. D., and J. A. Thompson (PolyIonix Separation Technologies, Inc.) “Polymer Filtration Using Water-Soluble Polymers and Ultrafiltration to Remove Dissolved Metal Ions,” *Filtration & Separation Magazine* (April 1999).

Jarvinen, G. D., B. F. Smith, T. W. Robison, and K. M. Kraus and J. A. Thompson (PolyIonix Separation Technologies, Inc.) “Removal and Recovery of Metal Ions from Process and Waste Streams Using Polymer Filtration,” in *Metal Separation Technologies Beyond 2000: Integrating Novel Chemistry with Processing*, K. Nona, C. Liddell, and David J. Chaiko, eds., Mineral, Metals & Materials Society, Warrendale, PA, June 1999.

continued on page 12

Two awards were presented at the NMT Annual Division Review on Thursday, May 13, 1999. *Gordon Jarvinen* was presented with the 1999 R.D. Baker Award in Science and Technology, and *Diedra Yearwood* received the 1999 William J. Maraman Award for Excellence in Facility Operations.

Publications and Invited Talks (March 1999–May 1999) *continued*

Manner, W. L., Jane A. Lloyd, and Mark Thomas Paffett, "Reactivity of Formic Acid (HCOOD and DCOOH) at Uranium and Uranium Oxide Surfaces," *Surface Science*, (April 1999).

Miskowski, V. M., Stefan Franzen, Andrew P. Shreve, Mark R. Ondrias, Stacie E. Wallace-Williams, Mary E. Barr, and William H. Woodruff, "Distortional Isomers of a Mixed Valence Binuclear CU Complex," *Inorganic Chemistry*, (April 1999).

Morales, L. A., J. A. Haschke, and T. H. Allen, "Kinetics of Reaction Between Plutonium Oxide and Water at 25°C to 350°C: Formation and Properties of the PuO_{2+X} Phase," Los Alamos National Laboratory report LA-13597-MS (May 1999).

Park, Y., D. G. Kolman, H. Ziraffe, C. Haertling, and D. P. Butt, "Gallium Removal from Weapons-Grade Plutonium and Cerium Oxide Surrogate by a Thermal Technique," in *Proceedings of the MRS Fall Meeting 1998*, Materials Research Society, Warrendale. PA.

Ramos, O., Jr., and D. Herrera, "Helping the Nuclear Materials Technology Division at Los Alamos National Laboratory Change Deeply Rooted Perceptions About Diversity," *Hubbard & Hubbard, Inc., Newslink*, Vol. 1, No. 1 (March 1999).

Veilleux , J. M., M. S. El-Genk, Edwin P. Chamberlin, Carter P. Munson, and John R. Fitzpatrick, "Etching of UO_2 in NF_3 RF Plasma Glow Discharge," *Nuclear Materials/Sevier Science BV*, (in press).

Veilleux , J. M., M. S. El-Genk, Edwin P. Chamberlin, Carter P. Munson, and John R. Fitzpatrick, "Plasma Decontamination of Depleted Uranium Oxide from Stainless Steel Surfaces," in Annals of the New York Academy of Sciences for the Plasma-99 Symposium, HEAT AND MASS TRANSFER UNDER PLASMA CONDITIONS, April 19–23, 1999, Antalya, Turkey (in press).

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