



Radiochemistry Renaissance

Radiochemists apply nuclear test experience and unique capabilities to new national security and scientific challenges.

ABOUT a century ago, the enduring dream of alchemists was realized when physicist Ernest Rutherford and his collaborators demonstrated that one element can change into other elements through the process of radioactive decay. Rather than turning lead into gold, Rutherford's discovery led to the founding of radiochemistry—the study of radioactive isotopes—and nuclear chemistry, which focuses on the properties of atomic nuclei and the processes involved in element transformation. Together, these fields form a pillar that supports Lawrence Livermore's nuclear security mission, a role they have held since the institution was founded in 1952. (See *S&TR*, June 2002, pp. 24–30.)

Radiochemists provided crucial contributions to the Laboratory's nuclear weapons test program. They created tracer components for test devices by using actinides—radioactive elements with atomic numbers from 89 through 103, the most common of which is uranium. They also assessed a weapon design's performance by studying the radioactive debris and gases produced in an experiment. Since the moratorium on underground nuclear testing began in 1992, radiochemistry research at Livermore has grown to encompass a wider range of national security and scientific missions.



Livermore scientists have engaged in radiochemistry, nuclear chemistry, and heavy-element research since the Laboratory's founding in 1952. In the photo above, Wes Hayes works in hot cells on debris collected from the Hutch Event, a 1969 underground nuclear experiment that produced large quantities of rare, heavy isotopes for debris analysis. At left, Roger Henderson prepares a uranium sample for electrodeposition onto a stub for testing a resonance ionization mass spectrometry technique.

Nuclear chemist Dawn Shaughnessy, who leads the experimental and nuclear radiochemistry group in the Physical and Life Sciences Directorate, notes that many potential collaborators and project sponsors are surprised by the breadth of radiochemistry capabilities at the Laboratory. Says Shaughnessy, "In the past, Livermore radiochemistry to most people really meant nuclear test analysis, although even in the heyday of underground testing, that was only part of the endeavor."

Today, Lawrence Livermore offers a unique recipe for radiochemistry research, combining nuclear testing expertise and resources, such as rare radioisotopes collected from past underground experiments, with robust materials handling capabilities and an array of

research and isotope production facilities, including the Center for Accelerator Mass Spectrometry (CAMS) and the National Ignition Facility (NIF). Nuclear chemist Narek Gharibyan observes, "We have places to safely perform irradiation, chemical separation, and nuclear counting, all on-site. CAMS also produces radioactive isotopes for a variety of chemistry experiments. It's unusual to have all of these facilities in one place."

Shaughnessy adds, "As radiochemists, we see NIF as a giant neutron source, one of the brightest in the world. For instance, it can help us make samples for nuclear forensics experiments." But for everything Livermore offers, the recipe would be incomplete without Shaughnessy's team of a dozen or so innovative chemists, working in such diverse areas as fission, nuclear

forensics, radioactive target fabrication, transactinide chemistry, and rapid radiochemical separations.

Mapping Fission's Outcomes

During fission, an excited nucleus splits into two (or occasionally more) lighter fragments and in the process releases by-products such as neutrons or photons in the form of gamma rays. Although the results of an individual fission event are random, the distribution pattern for the particles emitted for a given parent isotope and initiating energy is statistically predictable. Precisely determining these patterns benefits important national security efforts, from nuclear forensics investigations of postexplosion debris to nuclear reactor safety.

Gharibyan and his colleagues are refining techniques for measuring the products emitted during proton- and neutron-induced fission of several isotopes, including uranium-238. Researchers have extensively studied neutron-induced fission of uranium-238 because of its importance to nuclear power, but the proton-induced reactions are not as well understood. To examine these events, researchers stack uranium, aluminum, and yttrium foils at the end of an accelerator chamber at CAMS and bombard the target with protons accelerated to energies between

10 and 15 megaelectronvolts. The foils are thin enough for protons to pass through without losing much energy, yet thick enough to generate an adequate number of fission reactions for study. Yttrium foils act as a proton flux monitor, allowing the team to calculate the likelihood of a fission reaction occurring in the uranium foils.

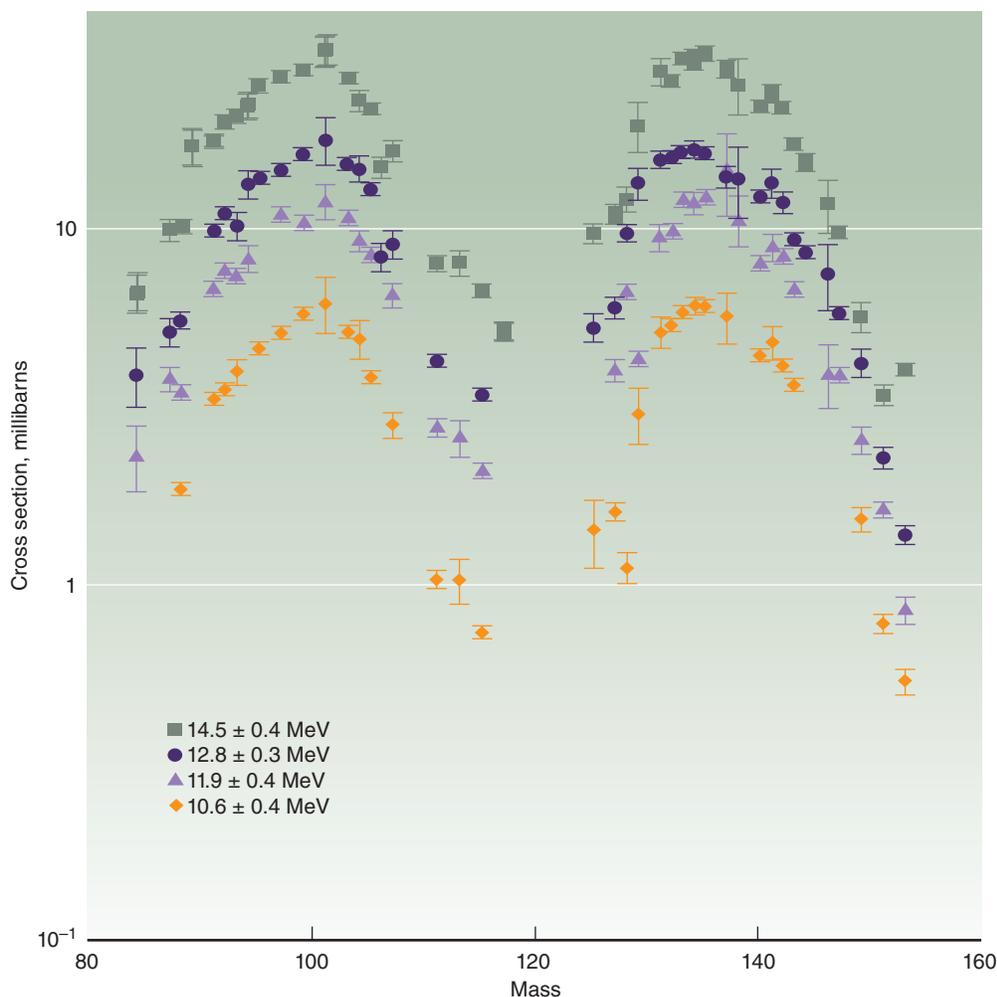
Most fission products are unstable and will decay by emission of a beta particle and characteristic gamma rays. High-purity germanium radiation detectors record the signatures of gamma rays emitted after decay, and automated analysis software processes the data to determine the identity and quantity of the gamma-emitting nuclides in the source. According to

Gharibyan, 40 to 50 spectra are collected and analyzed for each sample.

The more quickly samples arrive at Livermore's nuclear counting facility, the more radioactive products researchers are likely to detect. For many of the team's early experiments, samples received only 10 minutes of proton irradiation, to limit radiation levels and obviate the need for a cooldown period before sample removal and analysis. The fast turnaround enabled researchers to detect products with half-lives as short as 5 minutes.

Longer-lived and lower-yield products experience fewer decay events and thus can be more difficult to detect. To create these elusive particles in greater

A team of nuclear chemists at Livermore is refining techniques for precisely determining the unique patterns of isobars—nuclides of different elements with the same mass number—produced by the fissioning of various parent isotopes at different energies. This graph shows the likelihood of various isobars being produced during fission of uranium-238 when the proton inducing the reaction is moving at different speeds. Colored symbols indicate proton energy measured in megaelectronvolts (MeV); 1 millibarn is equivalent to 10^{-27} square centimeters.



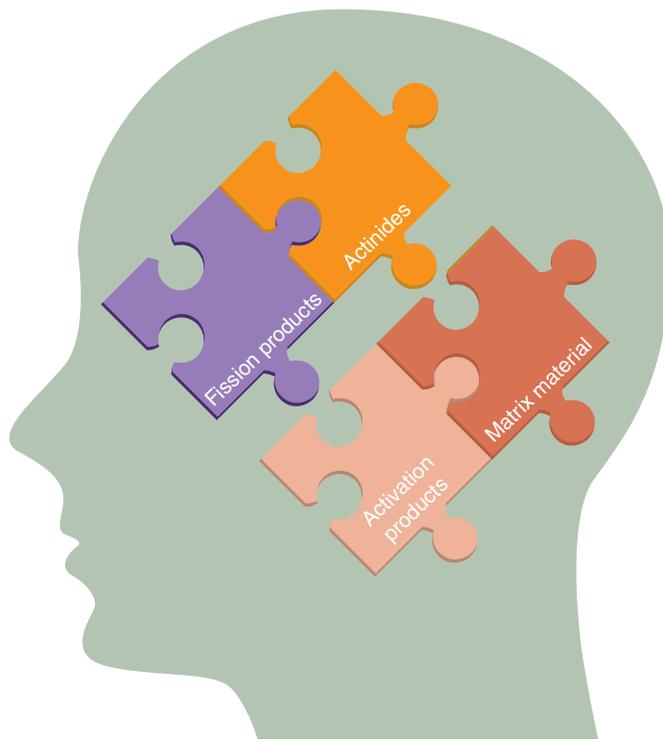
numbers, the Livermore team increased the irradiation period to a full day and the nuclear counting period to two months. After days or weeks, the interfering signatures produced by many of the shorter-lived fission products are eliminated, so that longer-lived and lower-yield products are somewhat easier to distinguish.

Chemically isolating and removing selected fission products from some samples before nuclear counting also helps the researchers fill in data gaps. “Radiochemistry allows us to detect emissions produced in small quantities or those that have interferences,” says Gharibyan. In one uranium-238 experiment, the researchers demonstrated that, by chemically separating samples, they could measure fission yields for about 50 percent more isobars—nuclides of different elements with the same mass number—than they could identify by nuclear detection alone. In future experiments, the team will measure fission product distributions for other actinide isotopes.

Mixing a Radionuclide Cocktail

If an illicit nuclear explosive were detonated on U.S. soil, nuclear forensics experts would be tasked with examining rubble from the explosion for traces of fissile material, fission products, and activation products—nearby debris or structural components of the bomb made radioactive by neutron activation. The more information experts could glean by characterizing these materials, the better able they would be to trace the weapon’s design and origin.

To ensure readiness in the event of such a scenario, research teams at Los Alamos, Pacific Northwest, and Lawrence Livermore national laboratories have, for the past decade, engaged in isotope identification exercises using simulated debris samples. Exercises last from days to weeks and involve both chemical analysis and computer modeling. Samples



Nuclear forensics readiness exercises use samples of synthetic nuclear debris to test participants’ skills at isotope identification. The current method for preparing samples is to irradiate a single fuel in a reactor and collect the fuel and its fission products. A truly realistic sample would include all the pieces of the puzzle—fuels plus fission and activation products mixed in the right proportions and embedded in a matrix of dirt and debris.

are prepared at one facility, typically by irradiating uranium in a reactor and splitting it into chunks. The samples are then sent to the participating laboratories for analysis.

About three years ago, Livermore nuclear chemists, led by Kevin Roberts, began designing more realistic debris to further challenge their fellow chemists and modelers. A fully realistic sample would include a carefully curated selection of fuels, fission products, and activation products embedded in a matrix of dirt and debris. Drawing on the Laboratory’s experience in analyzing nuclear test debris (see *S&TR*, April/May 2012, pp. 11–13) as well as the results of Gharibyan’s fission investigations and other research efforts, the team is determining how best to create a “radionuclide cocktail” with ingredients in the right amounts and proportions.

Using a mix of different fuels and reaction energies will likely achieve the most realistic results. Laboratory researchers have access to isotopes from past experiments and can generate new materials using accelerators, test reactors, and other sources. In conjunction with the Crocker Nuclear Laboratory at the University of California at Davis, the Livermore team completed several practice runs to demonstrate sample production

in 2012 and two round-robin exercises with Los Alamos, Pacific Northwest, and the United Kingdom’s Atomic Weapons Establishment in 2013.

Nearby facilities such as CAMS and the cyclotron at Davis (about 135 kilometers or 85 miles north of Livermore) are preferred for sample preparation because many of the fission and activation products are short-lived. Samples must be created and shipped promptly so that exercise participants can measure the more ephemeral products. In fact, logistics and handling are no small part of the research project. Roberts notes that at first, his group adopted radiochemical methods from the underground test program because those approaches were established and effective. Now, the researchers want to modernize the techniques so they can prepare testing materials more efficiently and safely. “Making this kind of sample is not a trivial exercise,” says Roberts. “The debris can end up being fairly radioactive, and not many facilities can handle such materials. We can, and we couple it with the weapons knowledge here.”

As part of the sample preparation effort, Livermore researchers have partnered with scientists at the University of Nevada at Las Vegas (UNLV) to fabricate a potential matrix material made of equal parts

glass and concrete dust. The substance is then combined with fuels irradiated at a test facility at the Nevada National Security Site, and the resulting samples are characterized. The Laboratory team also is investigating the feasibility of using additive manufacturing to create samples that can be precisely reproduced, which would aid in data intercomparison.

Kimberly Budil, who manages the Nuclear Counterterrorism Program in Livermore's Global Security Principal Directorate, stresses the importance of using realistic debris samples for the readiness exercises. "It's important to challenge the participants in a way that mimics the response to an actual incident and at the same time to thoroughly test their diagnostic capabilities."

Roberts notes that his team is 5 to 10 years from routine production of truly realistic samples, but those developed for the round-robin exercises in 2015 should have materials in the proper proportions. By engaging in readiness exercises and sample development, Livermore researchers are helping to establish a significant national capability and fostering stronger partnerships with forensics specialists at other laboratories and with sponsors in the Departments of Defense and Energy.

A Source for Radioactive Targets

In addition to their work on nuclear fission and forensics, the radiochemists in Shaughnessy's group are fabricating

radioactive sources and targets for Laboratory experiments that require a broad range of isotopes. Some of these materials are created in facilities such as CAMS. Others are acquired by dipping into the Laboratory's archive of isotopes collected from various sources, including Oak Ridge and Savannah River national laboratories. The archive is one of a kind, offering such items as the world's only supply of a metastable form of americium-242 and the only separated batch of plutonium-244. Nuclear chemist Roger Henderson, who leads the fabrication efforts, says, "At Livermore, we have access to unique, irreplaceable source materials. Part of our job is stewardship of these materials because no one knows when they will be produced in experimentally usable quantities again."

For one Laboratory project, Henderson created 60 monitor foils of uranium-235 enclosed in aluminum holders to calibrate dosimeters being designed for field deployment following a nuclear accident. He also crafts targets for experiments to study nuclear reactions, most of which are relevant to both stockpile stewardship and fundamental science research. "Target making is a specialty process," says Henderson. "No two clients have identical specifications. There's always some difference in the substrate, size, amount of material, or other specifications."

Henderson often prepares targets for Livermore physicist Ching-Yen Wu, who studies neutron-induced reactions

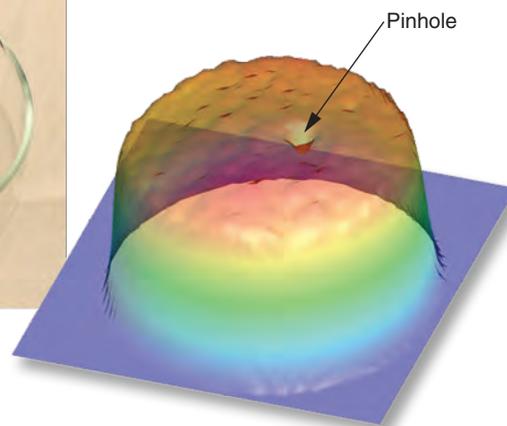
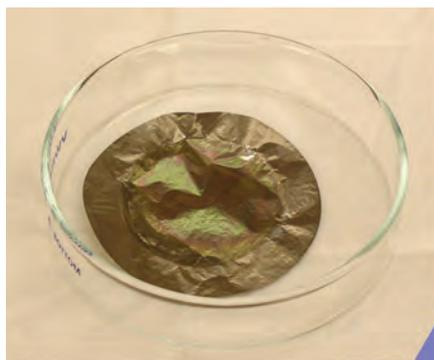
in uranium and plutonium isotopes in experiments at the Los Alamos Neutron Science Center. Wu's targets are made of freestanding foils, each only a few micrometers thick but up to 4 centimeters in diameter—quite large for heavy-element experiments. In addition, the fragile foils often require uranium or plutonium on both sides instead of the standard one side. To limit handling, Henderson developed an apparatus that electroplates both sides of the foils simultaneously. He also built an instrument that generates a three-dimensional map of the target surface, allowing researchers to characterize how smoothly and evenly the radioactive material is deposited on each surface.

Having an in-house capability to supply quality-tested radioactive sources and targets has been a boon for Livermore researchers. In particular, the electroplating technique and the surface-mapping tool have increased the consistency of radiochemistry experiments. Collaborators at GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany, are also interested in using the automated mapping system to characterize their targets.

Extracting Elemental Behavior

Other radiochemists at Livermore are using Henderson's target foils to explore the chemical behavior and fundamental properties of elements at the far end of the periodic table, which have short life spans and low production yields. Examining the transactinides, elements 104 and above, is especially challenging. Their high nuclear charge causes the inner electron orbitals

An automated surface mapping system developed at Livermore examines targets such as the foil on the left and produces a three-dimensional surface map such as the one on the right. This information allows researchers to evaluate coating consistency, which could affect an experiment, and to characterize features such as the pinhole in the foil.

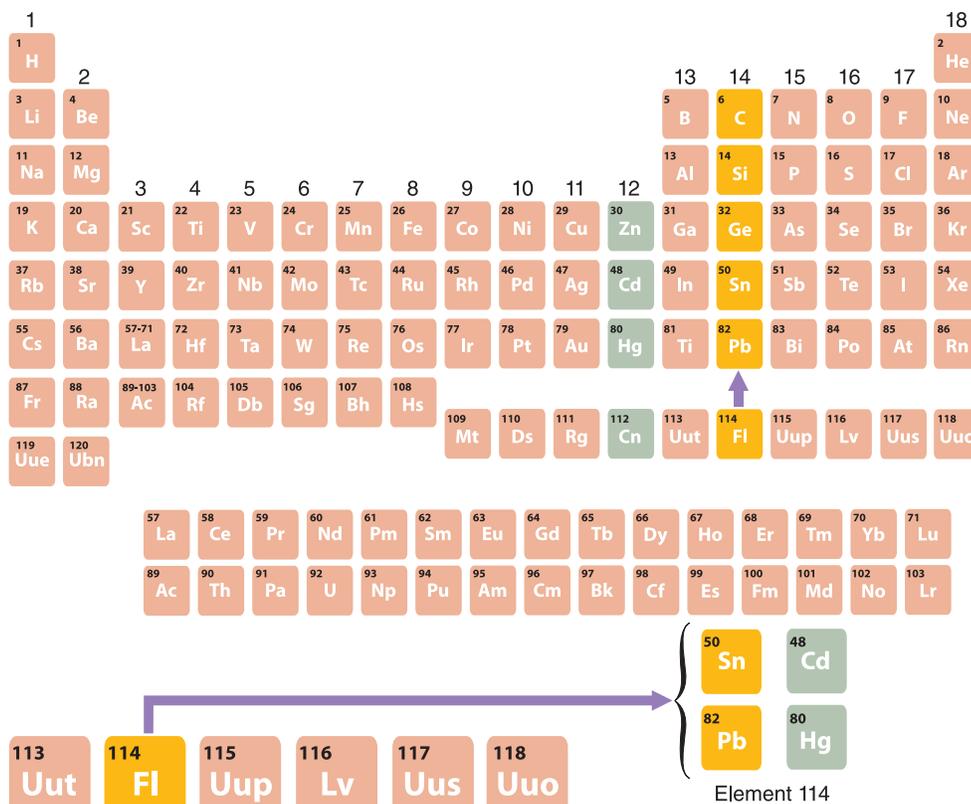


to move very close to the speed of light, which can affect an element's atomic and chemical properties. This relativistic effect may become more extreme for the heavier transactinides, making their characteristics and behavior more difficult to predict.

Six of the newest and heaviest transactinide elements were discovered by Livermore researchers in collaboration with colleagues at the Flerov Laboratory of Nuclear Reactions (FLNR) in Russia. (See the box on p. 10.) While an element's atomic number is determined by the number of protons in its nucleus, the element's placement in the periodic table is based on the chemical properties it shares with elements nearby. The question that intrigues Lawrence scholar John Despotopulos is whether the newest elements belong where they are currently situated. "Flerovium, element 114, is just beneath lead on the periodic table, so these two elements should have similar chemical properties," says Despotopulos. "But some scientists predict that flerovium is more like mercury or an inert gas such as radon."

Two gas-phase experiments of flerovium produced contradictory results. Wet-chemistry experiments, which are more complicated than gas-phase studies, would provide more insight into where the element fits in the periodic table. Despotopulos and colleagues at Livermore and UNLV are thus devising efficient and precise wet-chemistry methods to isolate the two elements. To evaluate these methods, they are using surrogates—lighter elements with putatively similar properties to the transactinides and more atoms available for study. (See *S&TR*, September 2011, pp. 4–10.)

A short nuclear lifetime and low production rate prevent flerovium from reaching chemical equilibrium in its environment. As a result, measuring the element's chemical reactivity is difficult. The Livermore and UNLV collaborators are working with carrier-free isotopes to more accurately replicate that behavior in the surrogates. In a carrier-free isotope, all the atoms of a given element consist of the same radioisotope; no stable



An element's position in the periodic table is based on its properties. Because the heaviest elements are short-lived and produced only in tiny quantities, scientists must extrapolate their characteristics by systematically studying related but longer-lived elements. For example, the properties of flerovium (Fl) may be similar to tin (Sn) and lead (Pb) or cadmium (Cd) and mercury (Hg).

isotopes are present. Carrier-free isotopes of bismuth and lead are isolated from samples of uranium-232, while antimony and tin are created at CAMS. The flerovium surrogates, lead and tin, are then mixed together, as are the element 115 surrogates, bismuth and antimony.

The research team then uses extraction chromatography to separate the desired isotopes. For this technique, a resin coated with an extractant is affixed inside a glass column along with a small amount of the sample. When the column is flushed with a solvent, usually hydrochloric or nitric acid, the component of interest adheres to the extractant. Everything else is washed through the column. The extractants selected for the Livermore experiments are crown ethers, cyclical molecules that selectively bind with certain metals.

Tests on the four surrogates in varying concentrations of solvent showed that

crown ethers extracted the targeted surrogate efficiently and precisely. Despotopulos and his colleagues are extending the extraction study to include mercury and cadmium, which may share properties with flerovium. They are also synthesizing various crown ethers to determine the best combination of extractant properties for different elements.

Chemistry at the Push of a Button

Producing enough atoms to study the heaviest transactinides requires weeks or months of accelerator beam time. Because these rare, short-lived elements can form at any time, scientists must constantly monitor the experiments. With funding from Livermore's Laboratory Directed Research and Development Program, radiochemists in Shaughnessy's group are collaborating with researchers at UNLV and Texas A&M University to design

A Smashing Collaboration

In 1989, nuclear chemists Ken Hulet from Lawrence Livermore and Georgy Flerov, founder of the Flerov Laboratory of Nuclear Reactions (FLNR) in Dubna, Russia, met at a conference and decided to work together to synthesize new elements. (See *S&TR*, October/November 2010, pp. 16–19.) Transcending international politics and intense competition within the heavy-element research community, scientists from the two institutions have built an enduring research partnership and discovered six new elements, 113 through 118.

The names chosen for elements 114 and 116, the two newest additions to the periodic table, pay tribute to that collaboration. Flerovium, the name for element 114, honors Flerov and FLNR, and livermorium, for element 116, recognizes Lawrence Livermore and its hometown, Livermore, California. Bill Goldstein, the Laboratory's deputy director for Science and Technology, says, "These names honor not only the individual contributions of scientists from the two laboratories to the fields of nuclear science, heavy-element research, and superheavy-element research, but also the phenomenal cooperation and collaboration that has occurred between scientists in the two countries."

Element discovery is a lengthy process. Before an element can be added to the periodic table and named, its existence must be detected independently at more than one laboratory and preferably through more than one method. Elements 114 and 116 were first glimpsed by the Livermore–FLNR team in 1998 and 2001, respectively. (See *S&TR*, January/February 2002, pp. 16–23.) In May 2012, the International Union of Pure and Applied Chemistry (IUPAC) officially accepted the element names. In its decision, IUPAC stated that it found the name livermorium appropriate because of Livermore's breadth of nuclear and radiochemical research.

On June 24, 2013, Laboratory employees and the city of Livermore celebrated the discovery and naming of livermorium and flerovium with a daylong celebration, attended by members of the U.S. and Russian discovery

team and Dubna city officials. The festivities began with a Laboratory-hosted colloquium, titled "Elemental Science: Livermorium and the Periodic Table." In one lecture, Livermore nuclear chemist Ken Moody discussed the history of heavy-element research and the long-standing collaboration between Lawrence Livermore and FLNR. "A collection of people with good will and shared vision can make wonderful things happen," he observed. Following the colloquium, the city of Livermore hosted a dedication ceremony at the newly renamed Livermorium Plaza and unveiled a plaque dedicated to the discovery team.

All elements with more protons than uranium, element 92, are radioactive and were discovered in a laboratory. None of these elements has a half-life long enough to have survived since Earth's formation. Essentially all transuranic elements were first synthesized at one of three facilities—FLNR, Lawrence Berkeley National Laboratory, or the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany—where inside an accelerator, a stream of lighter atoms was smashed into a heavier atom for hours or days until, finally, a pair combined. Synthesis experiments for many of the newest and heaviest elements yield only a single atom with a lifetime ranging from microseconds to a few seconds, making detection and study a challenge. Despite the difficulties, scientists persist with these investigations because each addition to the periodic table expands their knowledge of atomic structure and behavior.



A mural at Livermorium Plaza in downtown Livermore, California, commemorates the U.S.–Russian collaboration that led to the discovery of six heavy elements.

a system that captures, prepares, and measures samples with limited interaction from researchers.

The system, which is being tested at CAMS, will connect directly to the beamline where the element is produced. After screening out the incomplete fission products, it will collect complete products, dissolve them in solution, and subject them to automated chemical processing, including ion exchange or extraction

chromatography. The development team estimates that the system will reduce the time spent on chemical separation tasks by a factor of up to 10.

A system that automates some of the repetitive and time-consuming activities in chemistry has numerous other applications. Roberts, for instance, wants to apply the technique to expedite nuclear forensics research. "Urgency was not always a pressing concern for

scientists working on underground nuclear experiments," he says. "They did need to capture the short-lived fission products, but they had more time to analyze their results. We would face a much different scenario in the event of a nuclear explosion. We'd need results immediately." An automated wet-chemistry system could also be used for medical imaging and treatment, astrophysical research, or even



Livermore nuclear chemist John Despotopoulos works with the Laboratory's automated ion chromatography fraction collection system, which can chemically separate up to 12 samples simultaneously.

environmental remediation—for example, by accelerating the extraction of lead and mercury, two heavy-metal pollutants. (See *S&TR*, November 1999, pp. 17–19.)

Portability is a key design consideration for the automated system because it will likely be transported to partner facilities for element synthesis and characterization efforts. A reasonably compact system could also facilitate field deployment for nuclear forensics and environmental purposes. In a complementary effort, the team is evaluating a slimmed-down design for an extra-sensitive germanium detector to rapidly identify specific isotopes at remote locations. With improved nuclear counting techniques, the detector could identify certain isotopes in the presence of others, thus eliminating the chemical separation step—a process Roberts compares to “finding the needle without removing the haystack.”

Radiant Prospects

Budil adds that the expertise developed by Shaughnessy's group is broadening the scope of nuclear forensics research at a national level. “In the nuclear forensics community, we are continually looking

for new approaches to address evolving threats,” says Budil. “NIF is a great example. It offers unique capabilities for exploring nuclear science and nuclear chemistry at a fundamental level, but forensic scientists need to learn to apply these capabilities to our mission space. The radiochemistry team is helping us define the role for NIF experiments in current and future research.”

An effort to build a new accelerator center at Livermore has begun to gather momentum. The proposed center would include a medical cyclotron, a larger accelerator that could be used for nuclear science and as a rare isotope source, and a facility with modular laboratory spaces. “Our current facilities for nuclear science are not flexible enough for 21st-century experiments,” says Budil. “We need to be able to modify work areas to accommodate new technologies as they become available. We also want to design spaces that foster collaboration and cross-talk among scientists—not just with our teams at Livermore but with the nuclear forensics community at large.”

If the accelerator project reaches fruition, Lawrence Livermore will likely

serve as a magnet for nuclear research. In the meantime, radiochemistry researchers are working to secure beam time on other large accelerators, such as the 88-inch cyclotron at Lawrence Berkeley National Laboratory.

Whatever the future holds, the need for expertise in radiochemistry and nuclear chemistry is unlikely to wane. “Issues involving radioactivity will never go away,” says Roberts. “Even if we were to get rid of our weapons stockpile, we’d need to understand nuclear weapons and radioactivity for nuclear waste disposal, for example.” As they have demonstrated in the posttesting era, Livermore's radiochemistry researchers are ready to respond to new challenges as national needs change.

—Rose Hansen

Key Words: actinide, activation product, carrier-free isotope, Center for Accelerator Mass Spectrometry (CAMS), crown ether, extraction chromatography, fission yield, flerovium, Flerov Laboratory of Nuclear Reactions (FLNR), heavy elements, high-purity germanium radiation detector, isotope, livermorium, National Ignition Facility (NIF), nuclear chemistry, nuclear forensics, radioactive decay, radiochemistry, transactinide.

For further information contact Dawn Shaughnessy (925) 422-9574 (shaughnessy2@lnl.gov).