LLNL-TR-678670

2015 LLNL NF Summer Program Report_Final

A. Kersting

October 28, 2015

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

2015 LLNL Nuclear Forensics Summer Program

Glenn T. Seaborg Institute
Lawrence Livermore National Laboratory
Physical and Life Sciences Directorate
Livermore, CA 94550

Director: Annie Kersting (kersting1@llnl.gov)
Administrator: Camille Vandermeer
Website: https://seaborg.llnl.gov/

Sponsors:
National Technical Nuclear Forensics Center, Domestic Nuclear Detection Office, Department of Homeland Security
LLNL: Glenn T. Seaborg Institute, Physical and Life Sciences Directorate

LLNL-TR-

Disclaimer

Auspices

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA273

PHOTO OF 2015 GROUP OF STUDENTS

Annie Kersting, Director, Glenn T. Seaborg Institute (far left), and 2015 Nuclear Forensics Summer Program Students.

The Lawrence Livermore National Laboratory (LLNL) Nuclear Forensics Summer Program is designed to give graduate students an opportunity to come to LLNL for 8–10 weeks for a hands-on research experience. Students conduct research under the supervision of a staff scientist, attend a weekly lecture series, interact with other students, and present their work in poster format at the end of the program. Students also have the opportunity to meet staff scientists one-on-one, participate in LLNL facility tours (e.g., the National Ignition Facility and Center for Accelerator Mass Spectrometry) to gain a better understanding of the multi-disciplinary, on going science at LLNL.

Currently called the Nuclear Forensics Summer Program, this program began 15 years ago as the Actinide Sciences Summer Program. The program is run within the Glenn T. Seaborg Institute in the Physical and Life Sciences Directorate at LLNL. The goal of the Nuclear Forensics Summer Program is to facilitate the training of the next generation of nuclear scientists and engineers to solve critical national security problems in the field of nuclear forensics and have the students participate in conducting research at LLNL. We select students who are majoring in physics, chemistry, geology, mathematics, nuclear engineering, chemical engineering and environmental sciences. Students engage in research projects in the disciplines of actinide chemistry, radiochemistry, isotopic analysis, computational analysis, radiation detection, and nuclear engineering in order to strengthen the “pipeline” for future scientific disciplines critical to DHS (DNDO), NNSA.

This is a competitive program with over 50 applicants for the 6-8 slots available. Students also come on paid internships from NNSA, DHS. Students come highly recommended from universities all over the country. For example, this year we hosted students from 7 different universities. (See Table 1). This year's students conducted research on such diverse topics as actinide (Np, U, Pu) isotopic fingerprinting, statistical modeling in nuclear forensics, environmental radiochemistry, heavy element separations chemistry, radiation detector physics development, nuclear chemistry, and scintillator materials development (see Table 2.) Graduate students are invited to return for a second year at their mentor's discretion. We encourage continuation of research collaboration between graduate student, faculty advisor, and LLNL scientists.

In addition to hands-on training, students attend a weekly lecture series on topics applicable to the field of nuclear forensics (see Table 3). Speakers are experts from both within LLNL and the national community. Speakers are able to discuss the importance of their work in the context of advances in the field of nuclear forensics.

Graduate and undergraduate students on fellowships such as the Nuclear Forensics Graduate Fellowship are invited into our summer program. They usually come for 8-9 weeks and can return the following summer or stay throughout the year depending on their research needs. This year we had 1 Nuclear Forensic undergraduate join our program (Table 1, noted by an asterisks). We also had 2 Nuclear Forensic graduate students and 7 returning graduate students that were funding on other nuclear science fellowships.

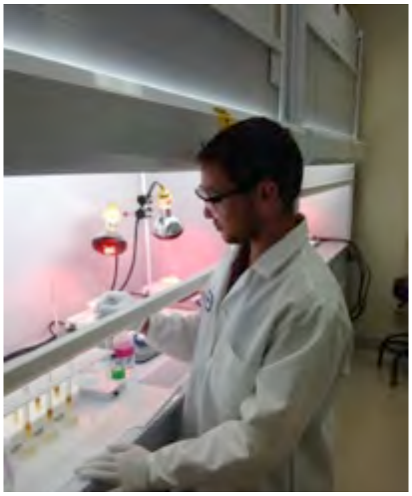
We also host students who are participating in the DOE-sponsored "Summer School in Radiochemistry" course held at San Jose State University and have recruited from this program. They come for a day, meet our summer students, see the research our students are doing, and tour our facilities.

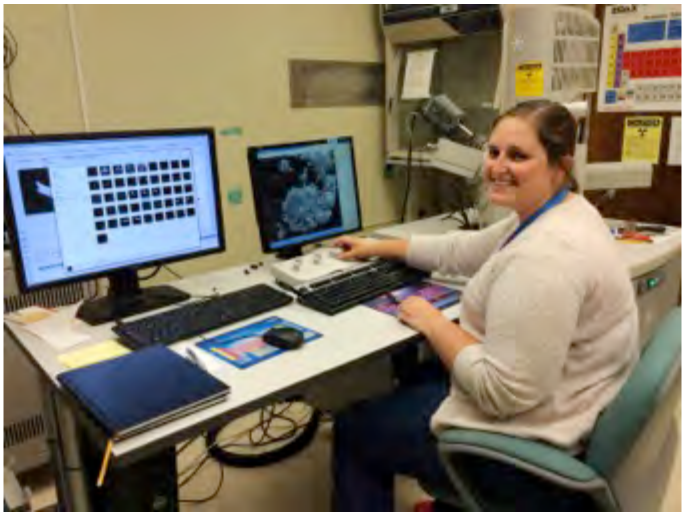
We use our summer program to help develop a successful pipeline of top-quality students from universities across the U.S. Since 2002, 30-40% have returned to conduct their graduate research at LLNL:

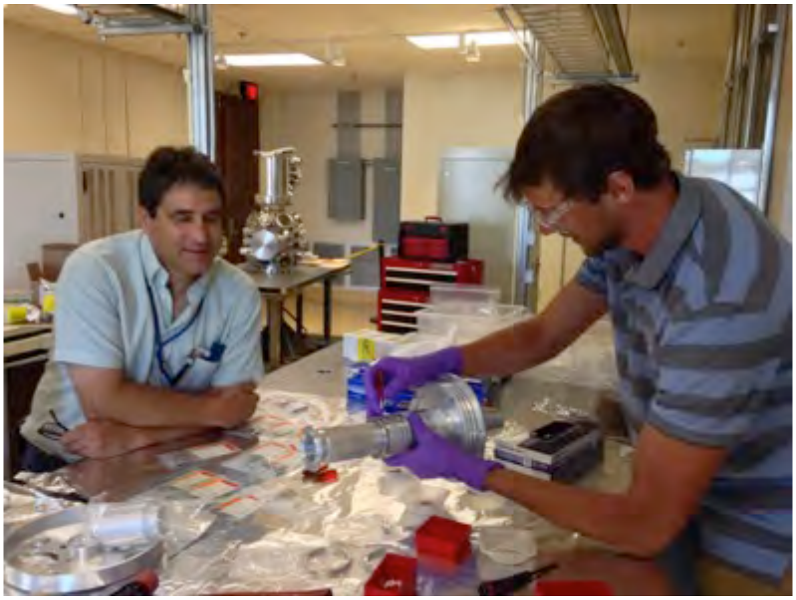
- 14 became postdoctoral fellows at LLNL.
- 6 became postdoctoral fellows at other national labs.
- 9 were hired as career scientists at LLNL.
- 3 were hired as career scientists at other national labs.
- 3 were hired as faculty in the area of nuclear forensics/radiochemistry/nuclear science.

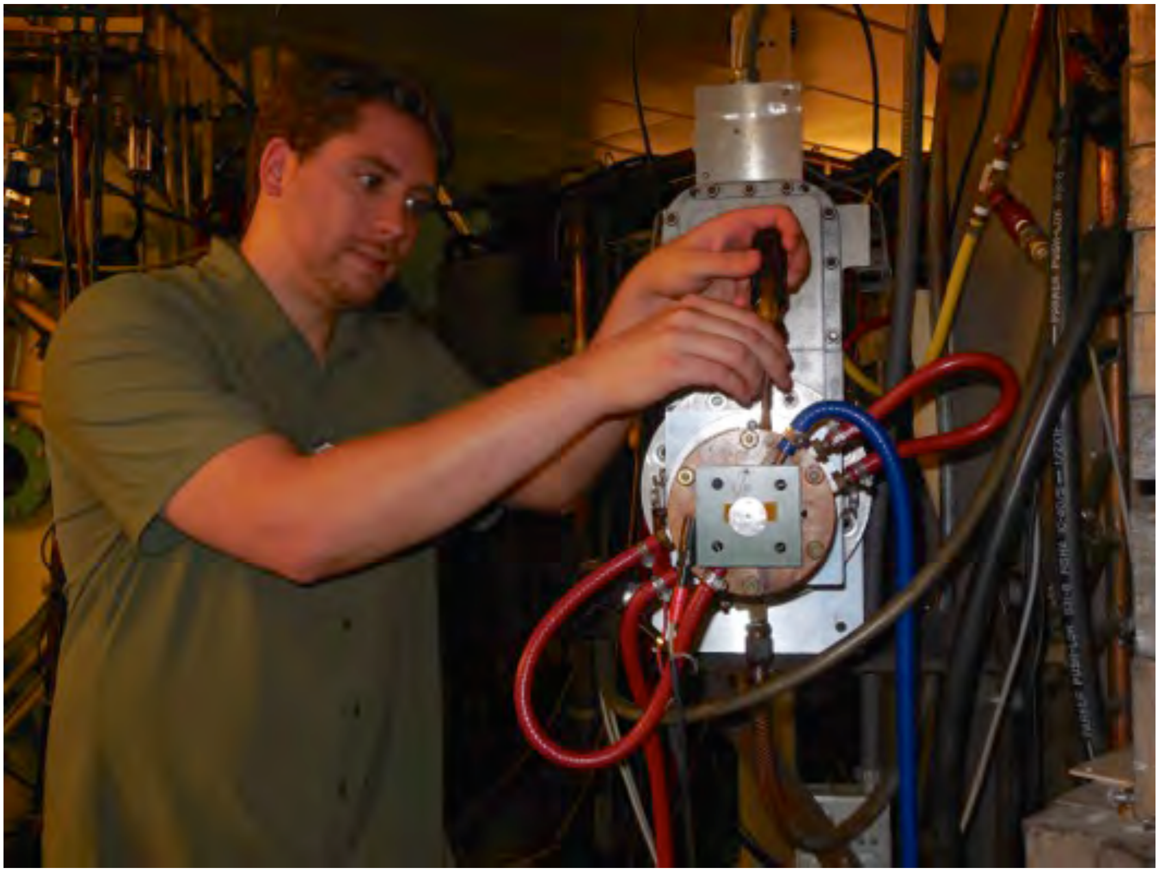
A big factor in the success of this program is the dedication of the staff scientists who volunteer to mentor the summer students. In FY14, funding from the Nuclear Forensics Graduate Mentoring Program (sponsor: DNDO) helped to partially support the time staff took to teach the summer interns. Staff scientists were able to take the necessary time to develop an appropriate summer project for their student, oversee necessary safety training, and dedicate more time to helping the interns maximize their productivity and scientific potential.

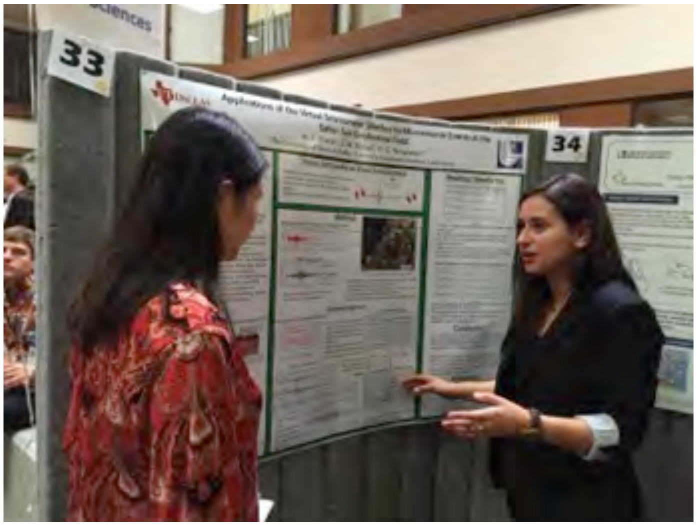
The posters presented at our Laboratory Student Poster Day are included at the end of this report.

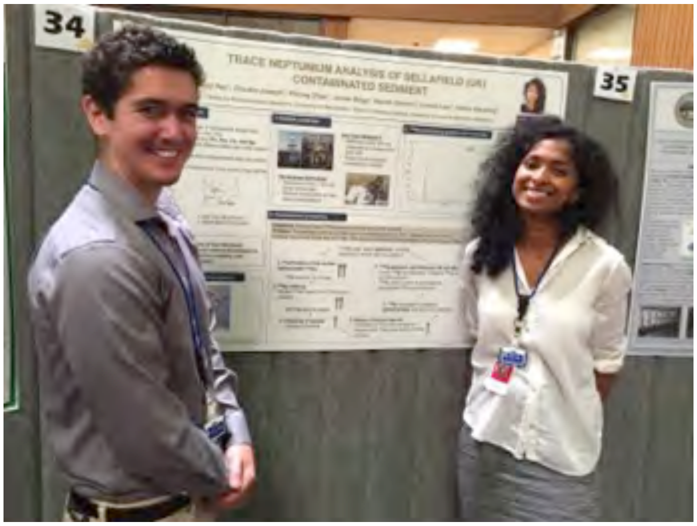









33
34


34
TRACE NEPTUNIUM ANALYSIS OF SELLAFIELD (UK) CONTAMINATED SEDIMENT
35

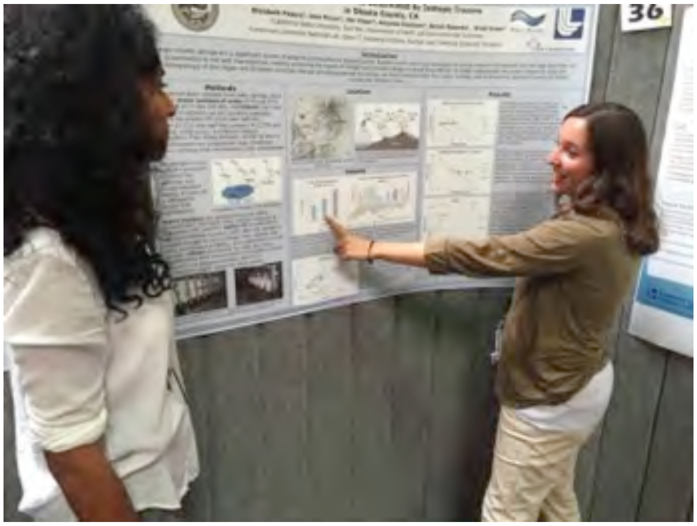

36

Table 1. Summer Students

Student	Major	University	Year
Merritt Earle**	**Environmental Engineering and Earth Sciences**	**Clemson University**	**Undergrad**
John “Jack” Goodell	**Nuclear Chemistry**	**University of Maryland, College Park**	**Grad**
Kathryn “Katie” Hoffman	**Chemistry**	**University of Cincinnati**	**Grad**
Rachel King Lopez	**Civil and Environmental Engineering and Earth Sciences**	**University of Notre Dame**	**Grad**
Elizabeth Peters	**Geology**	**California State University East Bay**	**Grad**
Andrea Rhode	**Geosciences**	**University of Texas at Dallas**	**Grad**
Colin Thomas	**Nuclear Engineering**	**Georgia Institute of Technology**	**Grad**

*= Nuclear Forensics Graduate Fellows ** = Nuclear Forensics Undergraduate Intern

Table 2. Student Projects and Mentors

Student	Mentor	Project
Merritt Earle**	**Mavrik Zavarin Annie Kersting**	**GC-MS Characterization of Plutonium Interaction with Acetohydroxamic Acid**
John “Jack” Goodell	**Brian Bandong Christine Egnatuk**	**Simulation of Activation Product Gamma-Ray Spectra for Nuclear Forensics**
Kathryn “Katie” Hoffman	**Ruth Kips Mike Kristo**	**Preparation of Uranium Oxide Dispersions for Nuclear Forensics Morphological Analysis**
Rachel King Lopez	**Amy Gaffney Theresa Kayzar**	**A New Tool in the Nuclear Forensics Tool Box: Exploring Thorium Isotope Compositions of UOCs and Ore-UOC Pairs**
Elizabeth Peters	**Brad Esser**	**Groundwater Properties Determined by Isotopic Tracers in Shasta County, CA**
Andrea Rhode	**Eric Mazel Dennise Templeton**	**Applications of the Virtual Seismometer Method to Microseismic Events at the Salton Sea Geothermal Field**
Colin Thomas	**Brett Isselhardt**	**Modeling Tools for Resonance Ionization Mass Spectrometry**

* = Nuclear Forensics Undergraduate Intern **= Nuclear Forensics Graduate Fellows

Table 3. Seminar Schedule

Date	Speaker	Topic
6/18/14	**Ruth Kips** Staff Scientist, Chemical and Isotopic Signatures Group, Nuclear and Chemical Sciences Division	**Nuclear Forensic Research: Science for National Security**
6/25/14	**James Begg** Staff Scientist, Environmental Radiochemistry Group, Nuclear & Chemical Sciences Division	**Biogeochemistry and the Fate of Plutonium in the Environment**
7/2/14	**Dawn Shaughnessy** Group Leader, Experimental Nuclear and Radiochemistry, Nuclear & Chemical Sciences Division	**Superheavy Element Discovery at LLNL**
7/15/14	**Amy Gaffney** Staff Scientist, Chemical & Isotopic Signatures Group, Nuclear & Chemical Sciences Division **Brett Isselhardt** Staff Scientist, Chemical & Isotopic Signatures Group, Nuclear & Chemical Sciences Division	**Chronometry of Geologic and Nuclear Materials** **Resonance Ionization Mass Spectrometry Analysis for Nuclear Forensics**
7/23/14	**Brad Esser** Group Leader, Environmental Radiochemistry, Nuclear & Chemical Sciences Division	**Characterizing California Groundwater with Isotopes: Applications to the Drought and Climate Change**
7/28/14	**Gareth Law** University of Manchester's School of Chemistry and the Dalton Nuclear Institute	**Shining Light on the UK Nuclear Legacy**
8/7/14	**Annie Kersting** Director, Glenn T. Seaborg Institute, Physical and Life Sciences Directorate	**Closing out the Program**

GC-MS Characterization of Plutonium Interaction with Acetohydroxamic Acid

Merritt Earle[1], Mavrik Zavarin[2], James Begg[2], Claudia Joseph[2], Roald Leif[2], Mark Lane[2]
[1]Clemson University, 101 Calhoun Drive, Clemson, SC 29634
[2]Lawrence Livermore National Lab, 7000 East Ave. Livermore, CA 94550

Background

Acetohydroxamic acid (AHA) has been identified as a possible salt-free organic reagent to control concentrations of tetravalent plutonium and neptunium in UREX (modified PUREX) processes that use single cycle flowsheet and centrifugal extractors.[1]

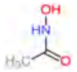
Besides chelation, the hydroxylamine group of AHA is a strong reductant, and reduction of the metal also leads to a significant decrease of their extractability.[2]

Gas chromatography – mass spectrometry is well suited for the task of determining the presence and concentration of compounds. Many samples of interest are aqueous and require extraction into an organic solvent.

Approach

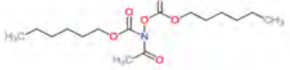
Gas chromatography-mass spectrometry analyses were performed on an Agilent 6890 gas chromatograph coupled to an Agilent 5973 MS detector. Samples were introduced into the GC using a splitless/purge injector with a 4mm id single taper injection liner.

AHA was insoluble in an organic solvent for analysis in the GC-MS. A derivatization reaction was utilized in order to detect and quantify the amount of AHA present.



AHA

n-hexyl chloroformate



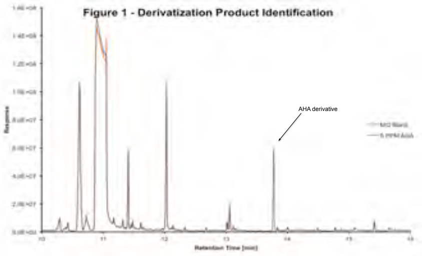
Acetohydroxamic acid derivative

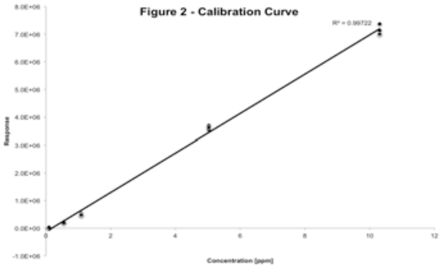
After performing the derivatization the products were analyzed in the GC-MS. Total ion chromatograms were used to compare various solutions and identify the target compound. (Figure 1)

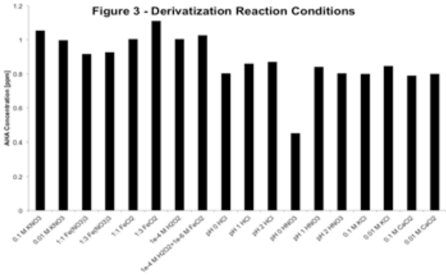
Solutions of varying AHA concentration were then analyzed and used to build a calibration curve for quantifying future samples. (Figure 2)

The derivatization was performed under a range of conditions in order to determine how robust the reaction was.

Results





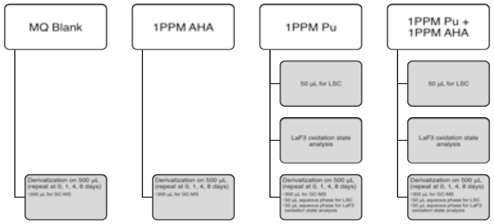


Conclusions

GC – MS is a viable method for quantitative determination of concentration of AHA. The derivatization reaction is robust, performing similarly in many environments. The derivatization, done in the aqueous phase, may be applied to other systems requiring similar treatment.

Future Work

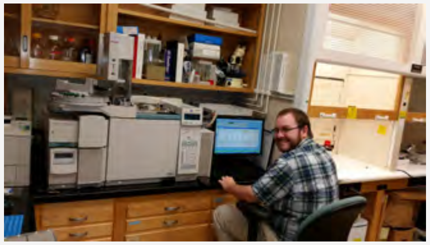
Derivatize and analyze AHA + Pu solutions.



MQ Blank
1PPM AHA
1PPM Pu
1PPM Pu + 1PPM AHA
50 µL for LSC
50 µL for LSC
LaF3 oxidation state analysis
LaF3 oxidation state analysis
Derivatization on 500 µL (repeat at 0, 1, 4, 8 days)
-300 µL for GC-MS
Derivatization on 500 µL (repeat at 0, 1, 4, 8 days)
-300 µL for GC-MS
Derivatization on 500 µL (repeat at 0, 1, 4, 8 days)
-300 µL for GC-MS
-50 µL aqueous phase for LSC
-50 µL aqueous phase for LaF3 oxidation state analysis
Derivatization on 500 µL (repeat at 0, 1, 4, 8 days)
-300 µL for GC-MS
-50 µL aqueous phase for LSC
-50 µL aqueous phase for LaF3 oxidation state analysis

Explore effects of various oxidation states of plutonium on derivatization reaction and complexation with AHA.

Further refine methodology in order to optimize detection limits, clarity of peaks, and reproducibility of results.



This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344.
This material is based upon work supported by the U.S. Department of Homeland Security under Grant Award Number 2012-DN-130-NF0001-02.
The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

References
[1]R. J. Taylor. I. May, I. S. Denniss, A. L. Wallwork, G. Hunt, S. Hutchison, V. Richards, N. J. Hill, Proc. RECOD 98, European Nuclear Society, Nice, 1998, p. 417.
[2]Taylor R. J., Dennis I. S., May I., 2000 Hydroxamic Acids – Novel Agents for Advanced Purex Process, Atalante 2000, Avignon, France, P2-15.

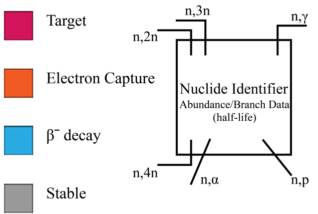
Simulation of Activation Product Gamma-Ray Spectra for Nuclear Forensics

J. J. Goodell[1], C. M. Egnatuk[2], B. B. Bandong[2]
1) University of Maryland – Department of Chemistry & Biochemistry
2) Lawrence Livermore National Laboratory – Nuclear & Chemical Sciences Division, Physical & Life Sciences Directorate

INTRODUCTION: Nuclear forensics is the science of source and route attribution of nuclear materials – what is it? where did it come from? who is responsible? The process of developing diagnostic tools and material/device signatures to answer these questions has become increasingly reliant on simulations due to the ban on nuclear testing and limited availability of resources. Signatures for fission products and the actinides are well understood, but there is little information available regarding the activation products of elements in more commonly used materials. To remedy this, we simulate the activation of these more common elements to identify any nuclides having high diagnostic value. This is accomplished through high-resolution gamma-ray spectroscopy using a high-purity germanium detector (HPGe). Here we present the resulting simulated gamma-ray spectra from the activation of 2 transition metals: gold (Au) and titanium (Ti).

OBJECTIVE: Identify activation products (APs) of commonly used materials which have high diagnostic value – easily distinguishable characteristic gamma-ray peaks with appropriate half-lives – to strengthen the nuclear forensics toolkit.

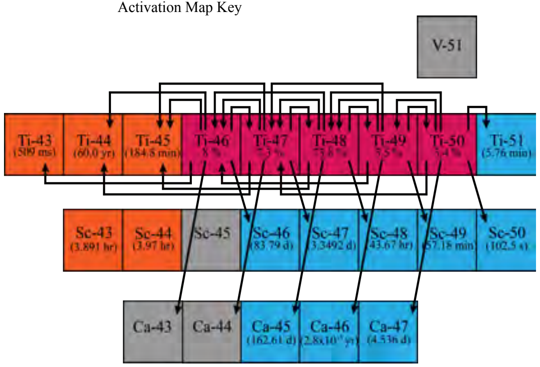
- Primarily interested in the 3d transition metals, some of the 5d transition metals, and a small selection of other metals
- Evaluate the APs and their decay chains resulting from 6 different neutron activation reactions



Activation Map Key

Neutron Reactions:

1. $^{A}X1_{n}\ (n,\gamma)\ ^{A+1}X1_{n+1}$
2. $^{A}X1_{n}\ (n,2n)\ ^{A-1}X1_{n-1}$
3. $^{A}X1_{n}\ (n,3n)\ ^{A-2}X1_{n-2}$
4. $^{A}X1_{n}\ (n,4n)\ ^{A-3}X1_{n-3}$
5. $^{A}X1_{n}\ (n,p)\ ^{A}X2_{n+1}$
6. $^{A}X1_{n}\ (n,\alpha)\ ^{A-3}X3_{n-1}$



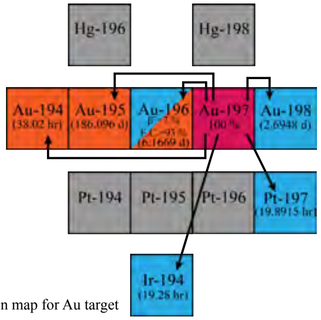
Activation map for Ti target

METHOD:

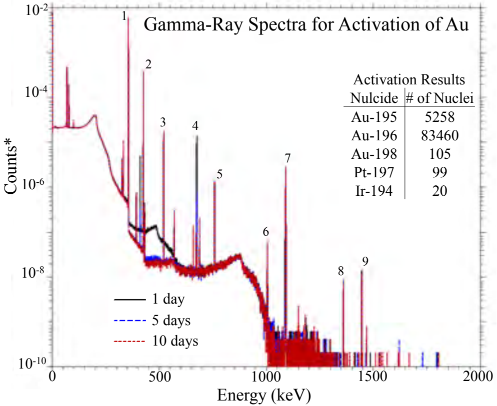
1. Use a known neutron energy distribution to simulate the activation of a given element
2. Calculate the activity of each AP and its daughter products up to a total decay time of 10 days
3. Use the activity data at time "t" to define the source for the simple HPGe simulation using MCNP6
4. Identify the energies and nuclides associated with easily distinguishable peaks in the gamma-ray spectra

Simulation Details:

- Neutrons produced through the (d,n) reaction on a ^{9}Be target – simulating the UC Davis cyclotron setup
- Neutron energy ranges from 7-20 MeV
  - average = 11.78 MeV
- Uses a simple planar HPGe model
  - 2.94 cm radius, 5.78 cm length
- Source to detector distance is 6.625 cm



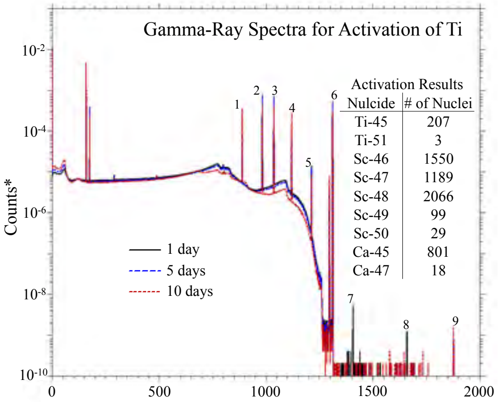
Activation map for Au target



Activation Results

Nulcide	# of Nuclei
Au-195	5258
Au-196	83460
Au-198	105
Pt-197	99
Ir-194	20

*Probability of registered count per photon



Activation Results

Nulcide	# of Nuclei
Ti-45	207
Ti-51	3
Sc-46	1550
Sc-47	1189
Sc-48	2066
Sc-49	99
Sc-50	29
Ca-45	801
Ca-47	18

*Probability of registered count per photon

Spectrum Table

Target Element	Peak #	Spectrum Energy (keV)	Library Match Nuclide	Library Match Energy (keV)
Au	1	355.83	Au-196	355.73
	2	426.32	Au-196	426.1
	3	521.56	Au-196	521.4
	4	676.04	Au-198	675.88
	5	759.28	Au-196	759.1
	6	1006	Au-196	1005.7
	7	1091.5	Au-196	1091.4
	8	1361.5	Au-196	1361
	9	1446	Au-196	1446.3
Ti	1	889.65	Sc-46	889.28
	2	983.89	Sc-48	983.53
	3	1037.6	Sc-48	1037.52
	4*	1120.6	Sc-46	1120.55
	5	1213.4	Sc-48	1212.88
	6	1297.4	Ca-47	1297.09
	7*	1408.2	Ti-45	1408.1
	8	1661.1	Ti-45	1660.9
	9	1877.9	Ca-47	1878

*Multiple nuclides may produce this peak

CONCLUSION: The results presented here represent a very small portion of the work that needs to be done to better understand the role that APs play in nuclear forensics. This work illustrates the utility of simulations to generate useful data when resources are limited. Identifying the prominent gamma lines in activation products is only the first step in developing new diagnostic tools and material/device signatures for nuclear forensics.

FUTURE WORK:

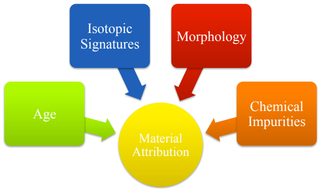
- Create a more accurate model of the HPGe detector
- Simulate AP production from other element targets
- Expand simulations to include different neutron sources and energy distributions – McClellan TRIGA reactor and Flattop-25 critical assembly
- Incorporate other residual nuclides into the gamma-spectroscopy simulation
- Combine AP spectra with each other and expected fission product spectra and re-analyze
- Validate simulations against experimental data

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. **IM Review & Release # LLNL-POST-675558**

Preparation of uranium oxide dispersions for nuclear forensics morphological analysis

Katie Hoffman[1], Ruth Kips[2], Michael Kristo[2]
Department of Chemistry, University of Cincinnati[1]
Nuclear and Chemical Sciences Division, Lawrence Livermore National Laboratory[2]

Introduction



Today morphological analysis is one of the main areas of focus for nuclear forensics research. While techniques such as scanning electron microscopy (SEM) are well-establish as tools for visually capturing nuclear particle morphology, objective and universal methods for extracting information from the resulting images are still under development and discussion. Morphological features can potentially be identified as a signature left by the material's processing history, but only if images can be reliably analyzed. The Morphological Analysis for Material Attribution (MAMA) software being developed at Los Alamos National Laboratory (LANL) seeks to help achieve this goal for nuclear forensic samples specifically.

Sample Preparation ➡ SEM ➡ MAMA ➡ Quantification

It has been observed that sample preparation plays a large role in the effectiveness of the MAMA software. A spatially even, monolayer dispersion of particles is most compatible with the software, but several sample preparation methods are currently in use across the field, all with varying results. This project seeks to identify the best sample preparation method for these purposes, using uranium ore concentrate (yellowcake) as a test material.

Objectives:

- Evaluate the effectiveness of current sample preparation methods for use with SEM and MAMA software
- Determine and optimize the best sample preparation method necessary for quantitative image analysis as it applies to nuclear forensics

Scanning Electron Microscopy

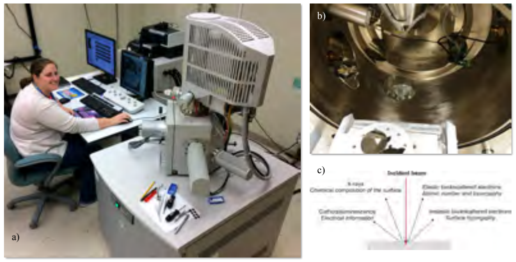


Figure 1. a) Instrument with computer interface **b)** inside chamber **c)** signals produced during SEM

Preparation Methods & Results

Sequential Carbon Tape Method

- Carbon mount (10 mm-dia) with double sided organic adhesive coating stuck to surface of aluminum stub (12 mm-dia)
- Stubs are gently pressed together to gradually decrease the amount of material collected across four stubs

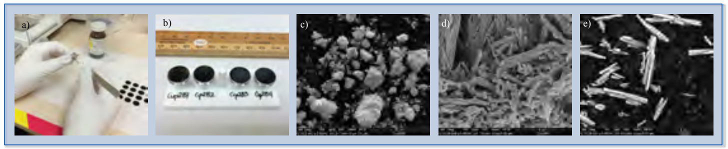


Figure 2. a) Pressing aluminum stubs with carbon tape together **b)** Material deposited on stub **c)** *Magnification: 2,303x* – heterogeneous mixture & many agglomerations **d)** *Magnification: 26,694x* – agglomeration **e)** *Magnification: 26,851x* – smaller particles can be found but are agglomerations

Sandwich (Rubbing) Method

- Vitreous carbon planchets (25 mm-dia), no adhesive
- Material is "sandwiched" between two planchets and they are rubbed together to disperse the material

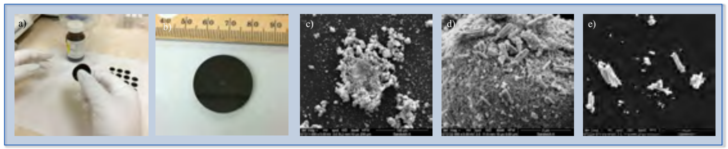


Figure 3. a) Rubbing two carbon planchets together gently **b)** Material deposited on planchet **c)** Magnification: 1,000x – agglomerations as well as dispersions of finer particulates present **d)** Magnification: 32,000x – agglomeration, different texture from above method **e)** Magnification 24,675x – small individual particles

Vacuum Impactor (VI) Method

- Same planchets used, planchet sits inside impactor (see Figure 2a)
- Material is vacuumed off any surface (i.e. container lid, wipe, another planchet)

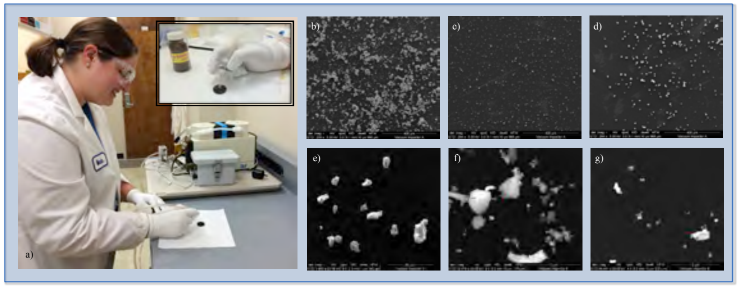


Figure 4. a) Vacuuming material off of smooth surface (planchet), *inset:* material is deposited onto second planchet that is inside plastic impactor. **Top right row:** All images at same magnification: *259x* **b)** the center **c)** the inner ring **d)** the outer ring of the planchet. **Bottom right row: e)** *Magnification: 1,806x* – large agglomerations or particles with spherical nature **f)** *Magnification: 32,839*x – particles still agglomerate with this method **g)** *Magnification: 46,441* – most individual particles look spherical rather than like a rod.

MAMA

This software was designed to help provide robust and accurate quantification of morphological features in nuclear material microscopy images. An associated lexicon of image descriptors has also been developed to facilitate the use of nuclear forensic image databases. Both are most effective when applied to a monolayer of material.

Segmentation & Quantification

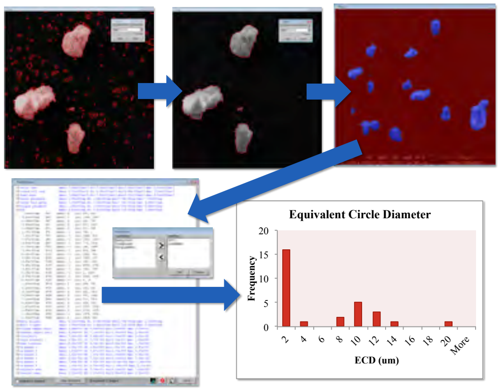


Figure 5. An example of possible steps in the MAMA software to obtain quantitative values from an SEM image. MAMA segments the image into particles, which can then be adjusted and assigned a label. A particle analysis will then produce a list of parameters that have been measured and calculated for each particle.

Conclusions

- There is little control over the amount of material deposited during the sequential carbon tape method. This method is ill-suited for quantitative analysis, but quick if only qualitative information is needed
- The sandwich method decreases agglomeration of the material, but doesn't provide an even overall dispersion of particles.
- Using a vacuum impactor with a high flow rate and a low sample amount will provide the most even dispersion of particles for quantification, but original material morphology is effected (particles become spherical)
- For VI, particles are sorted by size and velocity so the area of analysis on the planchet can greatly effect the quantitative results.
- Future work: Thorough characterization the behavior of various materials in the vacuum impactor to improve the quantitative output from MAMA

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. We thank the U.S. Department of Energy's National Nuclear Security Administration, Office of Defense Nuclear Nonproliferation Research and Development, for financial support.

LLNL-POST-675629

A new tool in the nuclear forensics toolbox:
Exploring thorium isotope compositions of UOCs and Ore-UOC pairs

King Lopez, Rachel[1,2]; Kayzar, Theresa[1]; Gaffney, Amy[1]
[1]University of Notre Dame, South Bend, IN; [2]Lawrence Livermore National Laboratory, Livermore, CA

Introduction

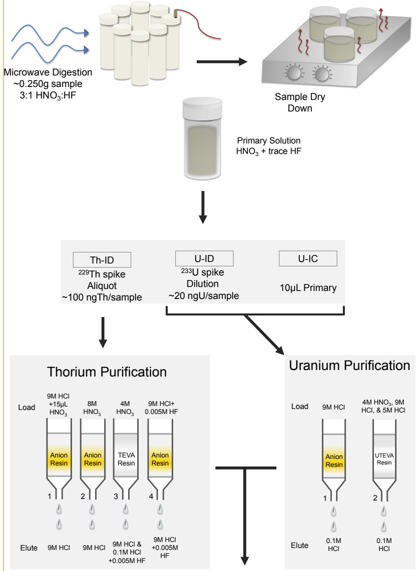
Isotopic analysis of uranium ore concentrates (UOC, also known as 'yellowcake') has been demonstrated to be a useful analytical technique to aid in identifying the parent material of a sample. Previous studies investigated the rare earth elements, transition metals, and various actinide isotope ratios to determine whether these signatures are preserved through UOC processing[1-3]. However, many of these geochemical signatures change through the mining, milling, and conversion process used to transform uranium ore to UOC. Th-230 forms from the decay of U-234, whereas Th-232 reflects the local geology of the ore deposit. Therefore, the $^{230}Th/^{232}Th$ composition of uranium ores varies as a function of age, weathering, as well as the initial U and Th concentration of the ore.[4]

This study focuses on:

- $^{230}Th/^{232}Th$ and Th concentration analysis of U ores and UOC using MC-ICP-MS
- Investigating the variation in $^{230}Th/^{232}Th$ between a paired ore and UOC

Through the analysis of UOCs and ore-UOC pairs, this study examines the potential use of the $^{230}Th/^{232}Th$ composition as a nuclear forensic signature.

Methods and Analytical Technique



Microwave Digestion
~0.250g sample
3:1 HNO_3:HF

Sample Dry Down

Primary Solution
HNO_3 + trace HF

Th-ID	U-ID	U-IC
^{229}Th spike Aliquot ~100 ngTh/sample	^{233}U spike Dilution ~20 ngU/sample	10µL Primary

Thorium Purification

	1	2	3	4
Load	9M HCl +15µL HNO_3	8M HNO_3	4M HNO_3	9M HCl+ 0.005M HF
	Anion Resin	Anion Resin	TEVA Resin	Anion Resin
Elute	9M HCl	9M HCl	9M HCl & 0.1M HCl +0.005M HF	9M HCl +0.005M HF

Uranium Purification

	1	2
Load	9M HCl	4M HNO_3, 9M HCl, & 5M HCl
	Anion Resin	UTEVA Resin
Elute	0.1M HCl	0.1M HCl

Analysis conducted on Nu Plasma MC-ICP-MS

Sample Description

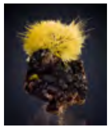


Figure 1. Specimen of Uraninite (UO_2).[5]

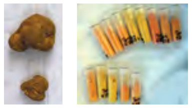


Figure 2. Examples of uranium ore (left) **and UOC powders** (right)[6].

Name	Location	Deposit Type	U-Mineral	Mining Method	Other
Argentina-Unspecified	n/a	Sandstone, Surficial	Pitchblende	Open Pit	Two mills for several mines, possible blending?
Canada-Faraday	Bancroft, ON	Intrusive	Uraninite	Underground	On-site Mill
Gabon-Moauana	n/a	n/a	Francevillite	n/a	
Germany-Wismut	Various	Veins, black shale, tabular/rollfront ss, lignite	Pitchblende, Coffinite	Open Pit Underground	
Netherlands-Delft	-	-	-	-	No mines, only enrichment facility
Paired Samples from Vaal Reef Deposit, South Africa					
Ore 12850-14	Kopanang, Great Noligwa and Moab Khotsong Mines	Conglomerate	Uraninite	Underground	Gold mine, powders mixed at processing
Ammonium Diuranate (ADU) 12851-07					
U_3O_8 12851-09					

Table1. Background information of the samples analyzed in this study.[7] See figure 3 for processing schematic for the paired samples.

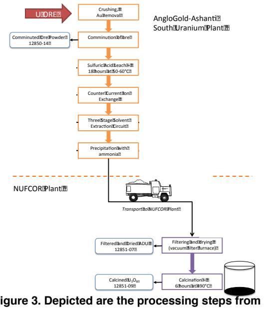
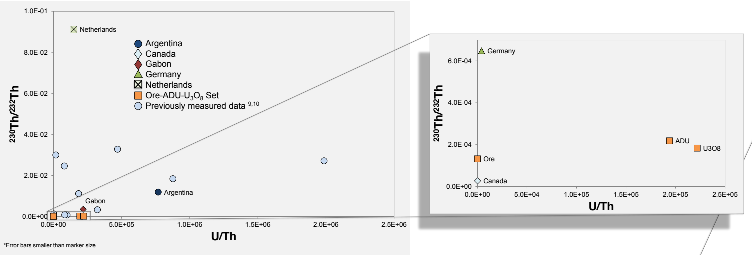


Figure 3. Depicted are the processing steps from conversion of ore to U_3O_8 at the AnglGold-Ashanti South Uranium Plant and the NUFCOR Plant.[8] The samples studied here are depicted by the blue boxes.

Results and Interpretation



*Error bars smaller than marker size

Figure 4. Thorium isotope variation of UOCs and ore relative to U/Th. The $^{230}Th/^{232}Th$ compositions of the UOCs range from $2.66x10^{-5}$ to $9.12X10^{-2}$. The $^{230}Th/^{232}Th$ compositions of individual UOCs vary outside of analytical uncertainty. Therefore the $^{230}Th/^{232}Th$ composition of a UOC may be a unique signature. The $^{230}Th/^{232}Th$ variation between different localities is much greater than the variation among the ore-UOC set from South Africa (highlighted in the graph on the right). Therefore it is possible that the $^{230}Th/^{232}Th$ signature is preserved through the ore to UOC conversion process. The increased U/Th in the ADU and U_3O_8 reflects the removal of impurities during the ore to UOC conversion process.

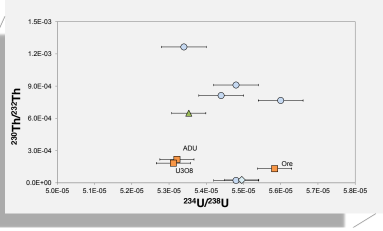


Figure 7. Isotope variation between ore-ADU- U_3O_8. The processed samples have lower $^{234}U/^{238}U$ and higher $^{230}Th/^{232}Th$ than the ore.

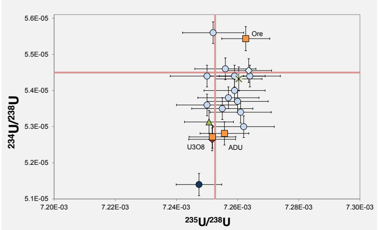


Figure 5. Uranium isotope composition of the UOCs and ore. All samples have natural $^{235}U/^{238}U$ compositions. The $^{234}U/^{238}U$ compositions are more variable than the $^{235}U/^{238}U$ compositions. ^{234}U is formed by alpha decay of ^{238}U,which may eject ^{234}U from a crystal structure and therefore results in preferential leaching of ^{234}U in uranium bearing rocks.

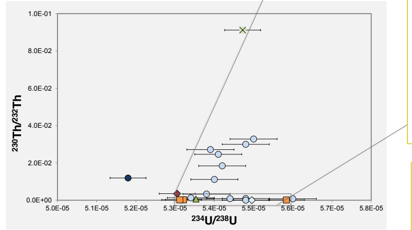


Figure 6. Isotope variation of $^{234}U/^{238}U$ and $^{230}Th/^{232}Th$ within the UOCs and ore sample. The variation of $^{230}Th/^{232}Th$ among the UOCs is larger than the variation of $^{234}U/^{238}U$ composition. The $^{234}U/^{238}U$ composition of the ore-ADU-U_3O_8 set changes among samples taken from different stages within the processing—see Figure 7.

Summary

- This study measured the variation of $^{230}Th/^{232}Th$ in UOCs from a variety of localities and one ore-ADU-U3O8 set.
- The $^{230}Th/^{232}Th$ variation of the UOCs is greater than analytical uncertainty. This variation does not correlate with U/Th.
- The variation of $^{230}Th/^{232}Th$ within the ore-ADU-U3O8 set is smaller than the $^{230}Th/^{232}Th$ variation between UOC localities. Therefore $^{230}Th/^{232}Th$ may be a useful signature worth exploring for use in nuclear forensics.

Future Work

- Investigate sample powder homogeneity.
- Analyze duplicate samples
- Investigate variability of samples within a mine.
- Explore $^{230}Th/^{232}Th$ of ore-UOC pairs from different conversion processes.

References

1.Varga, Z.; Wallenius, M.; Mayer, K., Origin assessment of uranium ore concentrates based on their rare-earth elemental impurity pattern. *Radiochim Acta* **2010,** *98*, 771-778. **2**.Balcaen, L.; Moens, L.; Vanhaecke, F., Determination of isotope ratios of metals (and metalloids) by means of inductively coupled plasma-mass spectrometry for provenancing purposes--A review. *Spectrochimica Acta Part B* **2010,** *65* (769-786). **3.** Brennecka, G. A.; Borg, L. E.; Hutcheon, I. D.; Sharp, M. A.; Anbar, A. D., Natural variations in uranium isotope ratios of uranium ore concentrates: Understanding the 238U/235U fractionation mechanism. *Earth and Planetary Science Letters* **2010,** *291*, 228-233. **4.** Anomalous U234/238 in nature. *Journal of Geophysical Research* **1962**, *67* (4518-4520). **5**. http://www.mindat.org/photo-252233.html **6.** https://str.llnl.gov/str/March05/Hutcheon.html 7. LLNL Internal report **8**. Marks, N.; L., B.; Eppich, G. R.; Gaffney, A. M.; Genetti, V. G.; Hutcheon, I. D.; Kristo, M. J.; Lindvall, R. E.; Ramon, C.; Robel, M.; Roberts, S. K.; Schorzman, K. C.; Sharp, M. A.; Singleton, M. J.; Williams, R. W., Technical Report on the Behavior of Trace Elements, Stable Isotopes, and Radiogenic Isotopes During the Processing of Uranium Ore to Uranium Ore Concentrates. *Internal Report for Lawrence Livermore National Laboratory* **2015**. **9**.LLNL measured data. **10**. LANL measured data.

Prepared by LLNL under Contract DE-AC52-07NA27344.
LLNL-POST-

Groundwater Properties Determined by Isotopic Tracers in Shasta County, CA

Elizabeth Peters[1], Jean Moran[1], Ate Visser[2], Amanda Deinhart[2], Sarah Roberts[2], Brad Esser[2]
[1]California State University, East Bay, Department of Earth and Environmental Sciences
[2]Lawrence Livermore National Lab, Glenn T. Seaborg Institute, Nuclear and Chemical Sciences Division

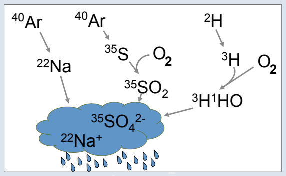
Introduction

Large-volume springs are a significant source of water to communities in Shasta County. Aquifers in this region are developed in young volcanic formations and the age and flow of groundwater is not well characterized, making predicting the impact of drought and climate change on spring flow difficult. To better understand the water resources and the hydrogeology of the region and to better constrain the age of water produced by springs, we have sampled water from wells, springs, and a stream for isotopic tracers of water source and residence time.

Methods

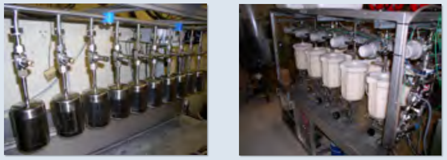
We analyzed water samples from wells, springs, and a creek for **stable isotopes of water** ($\delta^{18}O$ and $\delta^{2}H$), **sulfur-35** (87.4 day half-life), and **tritium** (12.3 year half-life). In addition, we are currently analyzing samples for krypton-85 (10.8 year half-life), sodium-22 (2.6 year half-life), carbon-14 (5,730 year half-life), noble gases, and helium isotopic composition. From these analyses, we will be able to gain information on groundwater ages (residence times), recharge area and elevation, and groundwater flow.

The isotopes in this study are produced by cosmic ray spallation and nuclear weapons testing. Krypton-85 is released by nuclear fuel reprocessing.



Precipitation of isotopes in the atmosphere.

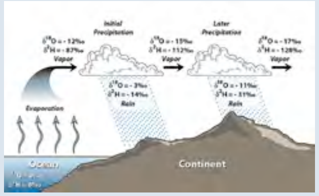
Stable isotopes are analyzed by a Los Gatos Research DLT-100 liquid water isotope analyzer to determine $\delta^{18}O$ and $\delta^{2}H$; **Sulfur-35** is analyzed by liquid scintillation counting (LSC) after the sample is passed through an ion exchange resin, eluted with NaCl, precipitated as $BaSO_4$, and suspended in a LSC cocktail; **tritium** is analyzed by noble gas mass spectrometry after accumulation of daughter product helium-3 in a degassed sample stored in a hermetically sealed vessel for three weeks.



Tritium samples are shown on degassing lines. Samples (right) are being frozen with dry in preparation for analysis of helium-3.

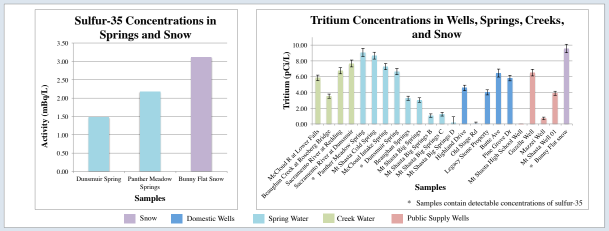
Location

Sampling locations for groundwater, springs and creeks.



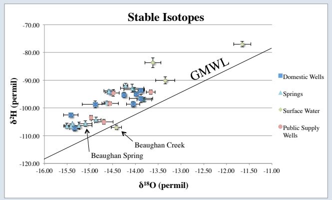
Schematic showing how stable isotopes of the water molecule fractionate during evaporation and precipitation.

Results



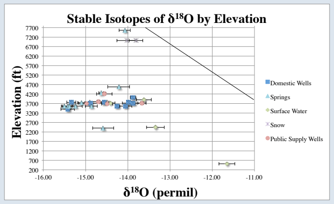
Sulfur-35 activities (mBq/L) for springs and snow. Detection of sulfur-35 indicates the presence of a fraction of recently (<1-2 years) recharged groundwater. Only two springs had detectable sulfur-35.

Tritium activities (pCi/L) for wells, surface water, creeks, and snow. Higher tritium activities generally indicate more recently recharged water. Tritium activities for wells and springs vary significantly indicating a range in groundwater ages.

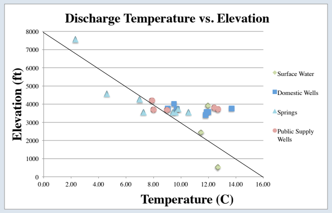


Water in the region plots on a local meteoric water line that parallels but is slightly offset from the Global Meteoric Water Line (GMWL). Groundwater well and spring water samples exhibit the same range of values. Surface water samples exhibit heavier isotopic values, except for Beaughan Creek, which plots on the lower left due to its higher elevation and closer proximity to Beaughan Springs.

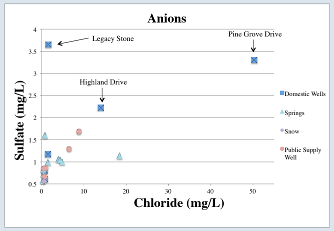
Results



The isotopically heaviest waters are measured in low elevation samples. The relatively large range of $\delta^{18}O$ values in spring and groundwater samples from approximately 3200-4200 ft may indicate that water from these locations recharged over a range of elevations not represented by the sample elevations. The heavier samples from this elevation range may have had shorter flow paths than the lighter samples.



Mean annual air temperature decreases by 2'C for every 1000 ft elevation gain. A similar trend is expected for water recharge temperatures. Significantly colder discharge temperatures in spring and well waters than in surface waters sampled at the same elevation likely indicates groundwater recharge at higher elevations. There is no indication of geothermal heating in the groundwater.



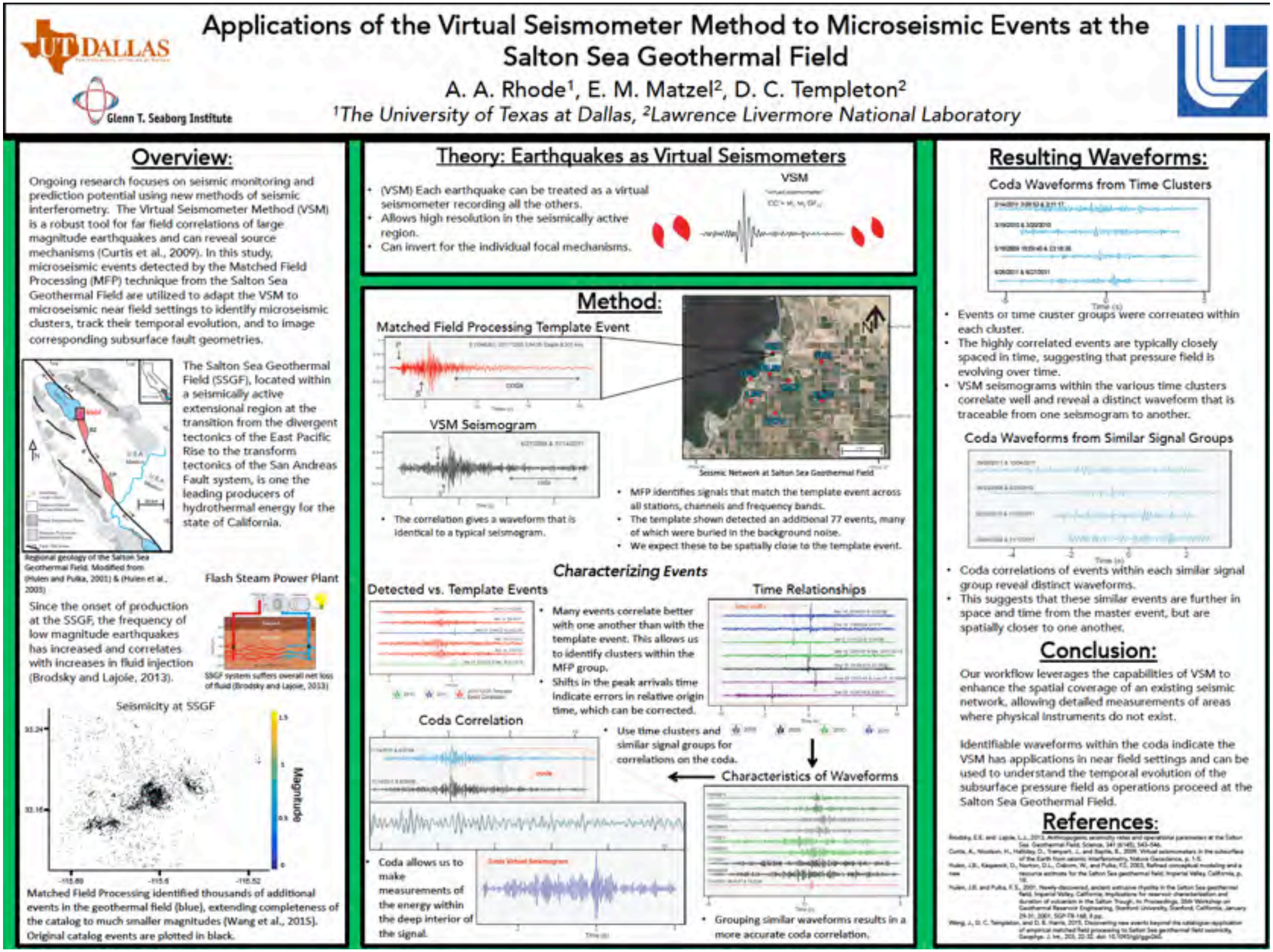
Significant variability is observed in chloride (0-50 mg/L), sulfate (0-4 mg/L) and sulfate to chloride anion ratio. Most samples have low chloride (<15 mg/L) and low sulfate (<2 mg/L). Snow has the lowest concentration, and springs have low concentrations. Wells (especially domestic wells) have the highest concentrations and the most variability. This may be a result of mixing of older groundwater with spring water and/or snowmelt, or may be due to localized contamination. Three domestic wells appear to represent end-member signatures of water sources on Mt Shasta. Multivariate analysis will aid in the attribution of samples to specific water sources.

Conclusion

Isotopic tracers provide insights into the sources and residence times of water in Mt Shasta aquifers. Tritium varied significantly in springs, domestic wells and public supply wells, indicating a range in the age of produced groundwater. Sulfur-35 also provides valuable constraints. Some springs had a detectable S-35 activity, indicating a component of very recently recharged water and potentially more rapid response to drought and climate change. The wells and other springs had no detectable S-35.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.
Funding was provided by the State Water Boards under the Groundwater Ambient Monitoring and Assessment program Special Studies.

LLNL-POST-675557



Applications of the Virtual Seismometer Method to Microseismic Events at the Salton Sea Geothermal Field

A. A. Rhode[1], E. M. Matzel[2], D. C. Templeton[2]
[1]*The University of Texas at Dallas*, [2]*Lawrence Livermore National Laboratory*

Overview:

Ongoing research focuses on seismic monitoring and prediction potential using new methods of seismic interferometry. The Virtual Seismometer Method (VSM) is a robust tool for far field correlations of large magnitude earthquakes and can reveal source mechanisms (Curtis et al., 2009). In this study, microseismic events detected by the Matched Field Processing (MFP) technique from the Salton Sea Geothermal Field are utilized to adapt the VSM to microseismic near field settings to identify microseismic clusters, track their temporal evolution, and to image corresponding subsurface fault geometries.

The Salton Sea Geothermal Field (SSGF), located within a seismically active extensional region at the transition from the divergent tectonics of the East Pacific Rise to the transform tectonics of the San Andreas Fault system, is one the leading producers of hydrothermal energy for the state of California.

Regional geology of the Salton Sea Geothermal Field. Modified from (Hulen and Pulka, 2001) & (Hulen et al., 2003)

Since the onset of production at the SSGF, the frequency of low magnitude earthquakes has increased and correlates with increases in fluid injection (Brodsky and Lajoie, 2013).

Flash Steam Power Plant

SSGF system suffers overall net loss of fluid (Brodsky and Lajoie, 2013)

Seismicity at SSGF

Matched Field Processing identified thousands of additional events in the geothermal field (blue), extending completeness of the catalog to much smaller magnitudes (Wang et al., 2015). Original catalog events are plotted in black.

Theory: Earthquakes as Virtual Seismometers

- (VSM) Each earthquake can be treated as a virtual seismometer recording all the others.
- Allows high resolution in the seismically active region.
- Can invert for the individual focal mechanisms.

Method:

Matched Field Processing Template Event

VSM Seismogram

- The correlation gives a waveform that is identical to a typical seismogram.

Seismic Network at Salton Sea Geothermal Field

- MFP identifies signals that match the template event across all stations, channels and frequency bands.
- The template shown detected an additional 77 events, many of which were buried in the background noise.
- We expect these to be spatially close to the template event.

Characterizing Events

Detected vs. Template Events

- Many events correlate better with one another than with the template event. This allows us to identify clusters within the MFP group.
- Shifts in the peak arrivals time indicate errors in relative origin time, which can be corrected.

Time Relationships

Coda Correlation

- Use time clusters and similar signal groups for correlations on the coda.

Characteristics of Waveforms

- Coda allows us to make measurements of the energy within the deep interior of the signal.

- Grouping similar waveforms results in a more accurate coda correlation.

Resulting Waveforms:

Coda Waveforms from Time Clusters

- Events of time cluster groups were correlated within each cluster.
- The highly correlated events are typically closely spaced in time, suggesting that pressure field is evolving over time.
- VSM seismograms within the various time clusters correlate well and reveal a distinct waveform that is traceable from one seismogram to another.

Coda Waveforms from Similar Signal Groups

- Coda correlations of events within each similar signal group reveal distinct waveforms.
- This suggests that these similar events are further in space and time from the master event, but are spatially closer to one another.

Conclusion:

Our workflow leverages the capabilities of VSM to enhance the spatial coverage of an existing seismic network, allowing detailed measurements of areas where physical instruments do not exist.

Identifiable waveforms within the coda indicate the VSM has applications in near field settings and can be used to understand the temporal evolution of the subsurface pressure field as operations proceed at the Salton Sea Geothermal Field.

References:

Brodsky, E.E. and Lajoie, L.J., 2013, Anthropogenic seismicity rates and operational parameters at the Salton Sea Geothermal Field, Science, 341 (6145), 543-546.
Curtis, A., Nicolson, H., Halliday, D., Trampert, J., and Baptie, B., 2009, Virtual seismometers in the subsurface of the Earth from seismic interferometry, Nature Geoscience, p. 1-5.
Hulen, J.B., Kaspereit, D., Norton, D.L., Osborn, W., and Pulka, F.S., 2003, Refined conceptual modeling and a new resource estimate for the Salton Sea geothermal field, Imperial Valley, California, p. 10.
Hulen, J.B. and Pulka, F.S., 2001, Newly-discovered, ancient extrusive rhyolite in the Salton Sea geothermal field, Imperial Valley, California: Implications for reservoir characterization and duration of volcanism in the Salton Trough, In: Proceedings, 26th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, California, January 29-31, 2001, SGP-TR-168, 8 pp.
Wang, J., D. C. Templeton, and D. B. Harris, 2015, Discovering new events beyond the catalogue: application of empirical matched field processing to Salton Sea geothermal field seismicity, Geophys. J. Int., 203, 22-32. doi: 10.1093/gji/ggv260.

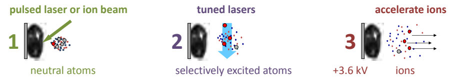
Modeling Tools for Resonance Ionization Mass Spectrometry

C.G. Thomas, B.H. Isselhardt, M.R. Savina

WHAT IS RIMS?

- Resonance Ionization Mass Spectrometry (RIMS) is useful for analyzing the chemical and isotopic makeup of solids
- The three basic steps in RIMS:

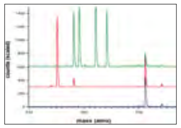
1. Generating a plume of neutral atoms from the sample through either ion sputtering or laser ablation
2. Resonantly ionizing only the atomic species of interest with lasers
3. Accelerating the photo-ions into a Time Of Flight (TOF) mass analyzer



The sample chamber has a (1) pulsed ion gun, (2) moveable sample stage, (3) numerous viewports for shining lasers, and (4) a 2 m flight tube

WHY DO WE USE RIMS?

- Because RIMS selectively ionizes atoms, it allows an accurate measure of isotopic ratios by limiting isobaric interferences
- RIMS requires very little sample prep and can be used on a sample with no "wet chemistry," leading to quicker measurement turnaround
- While RIMS is a destructive technique, it only requires sub-nanogram sample quantities to generate accurate mass spectra
- The above qualities make RIMS an excellent tool for nuclear forensics



RIMS spectra of a sample containing both U and Pu. RIMS can analyze samples like these without any preparation. (Measurement made with Chicago Argonne Resonance Ionization Spectrometer for Mass Analysis (CHARISMA))

HOW CAN WE IMPROVE RIMS?

- To accurately predict the measurement capabilities of a RIMS instrument, we need to
  - generate a representative sample of ions
  - understand laser ionization physics
  - realistically model flight paths
- Livermore has extensively studied laser ionization of isotopes interesting to nuclear analysts, and commercially available software models ion trajectories through electric and magnetic fields quite well
- **The purpose of this project is to simulate a representative "ion packet" and use it to predict the capabilities of the new Livermore Laser Ionization of Neutrals (LION) RIMS instrument**

HOW DO WE CREATE NEUTRAL ATOMS FOR ANALYSIS?

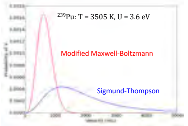
- Gas-phase neutral atoms are typically created by ion sputtering, where desorbed ion kinetic energies (E) follow the Sigmund-Thompson formula, and atom yield (Y) is described by [1]:

$$\frac{\partial^3 Y}{\partial E \partial^2 \Omega} \propto \frac{E \cdot \cos\theta}{[E+U]^3}$$

(U is surface binding energy
θ is spherical azimuthal angle)

- LION will also use laser ablation to create neutrals, a process that follows a modified Maxwell-Boltzmann distribution described by [2]:

$$P(v) = \frac{v^3}{2}\left[\frac{m}{kT}\right]^2 e^{-mv^2/2kT}$$

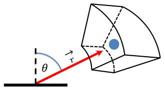


Laser-ablated neutrals desorb with lower velocity which makes them easier to focus once ionized, thereby improving mass spectrum peak shape

LET'S GENERATE SOME IONS!

1. Discretize hemisphere above sample into $\Delta r \Delta \theta \Delta \varphi$ "igloo bricks"
2. Compute charge weight factor (CWF), or relative fraction of desorbed particles in each cell

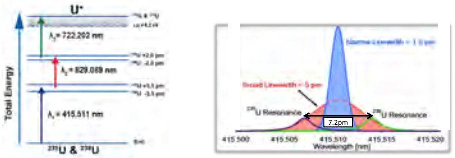
$$CWF_i = \int_{\varphi_{i-\frac{1}{2}}}^{\varphi_{i+\frac{1}{2}}} \int_{\theta_{i-\frac{1}{2}}}^{\theta_{i+\frac{1}{2}}} \int_{r_{i-\frac{1}{2}}}^{r_{i+\frac{1}{2}}} P(r,\theta,\varphi)\, dr\, d\theta\, d\varphi$$



3. Apply laser ionization probability on each cell to arrive at representative ion distribution

GET EXCITED WITH LASERS!

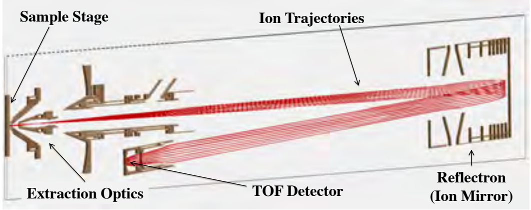
- To ionize neutrals in the desorbed plume, a broadband laser is tuned to resonantly excite the isotopes of interest and then shined into the sample chamber [3]



Three-laser resonance ionization scheme for uranium

LET 'EM FLY!

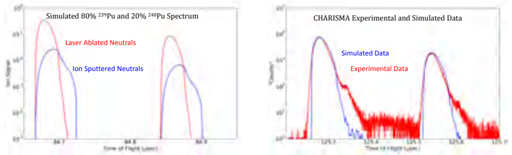
SIMION model of LION with predicted ion trajectories



- SIMION is a commercially available charged particle transport code that
  - models complex ion optic systems
  - calculates each cell's electrostatic potential using Laplace's equation
  - predicts ion flight paths and detector collision times

PUTTING IT ALL TOGETHER

- When all processes are simulated, we can predict mass peak shapes for different ionization schemes and compare LION's mass spectra with those from previous RIMS instruments



Left: LION simulation with laser ablated neutrals and sputtered neutrals
Right: CHARISMA simulated and experimental results with laser ablation

CONCLUSIONS AND FUTURE WORK

Conclusions

- RIMS is useful for isotope characterization of nuclear materials
- Laser desorbed ions generate sharper mass peaks
  - Ions have lower spread in velocity
  - For equal ionization delays, the ion packet is more tightly packed

Future Work

- Model pulsed extraction for simultaneous SIMS/RIMS experiment with high energy particle detector in reflectron
- Model delayed fragmentation/ionization of molecular species

[1] H. Gnaser, "Interactions of Low-Energy Ions with Solids" in *Low Energy Ion Irradiation of Solid Surfaces.* New York: Springer, 1999, pp 7-82.
[2] F. O. Goodman, "Elementary Kinetic Theory of Gases at Interfaces" in *Dynamics of Gas-Surface Scattering.* New York: Academic Press, 1976, pp 19-32.
[3] B. H. Isselhardt et al., "Improving Precision in Resonance Ionization Mass Spectrometry: Influence of Laser Bandwidth in Uranium Isotope Ratio Measurements" in *Anal. Chem.*, vol. 83, no. 7, pp 2469-2475, Mar, 2011.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC