

RIMS 2024

resonance ionization mass spectrometry instruments workshop

Book of Abstracts

Klaus Wendt

Fundamental laser spectroscopy and laser ion source development at the LARISSA laboratory of the University of Mainz –from 6-Lithium to 255-Fermium

The LARISSA laboratory at the Institute of Physics of Johannes Gutenberg University was founded in 1988 shortly after the Chornobyl nuclear reactor accident to develop laser mass spectrometric techniques for the sensitive and selective determination of lowest-level contaminations of specific radiotoxic isotopes of relevance, as e.g. 41-Ca, 90-Sr, 236-U. In the past 35 years, R&D activities have been widely broadened by addressing the advancement of multi-step resonance ionization mass spectrometry (RIMS) and its application to numerous exotic elements and isotopes. For this purpose, the 30 keV RISIKO off-line radioactive ion beam (RIB) facility and the MABU quadrupole mass spectrometer were equipped with dedicated laser ion sources in combination with highly specialized solid-state lasers.

A multitude of applications aside from the original goal of ultra-trace analytics, cover direct laser spectroscopic studies on the atomic and nuclear structures of rare isotopes complementing the identification of efficient and selective laser ionization schemes for use at on-line RIB production plants and in analytics. On top of this, ion beam purification and isotope selection for distinct fundamental studies are performed. This wide spectrum of applications addresses species from almost the entire periodic table of elements, for which two basic prerequisites are imperative: (1) the access to and the handling permission for altogether about 100 radioisotopes up to the German exemption limit including 47 isotopes out of 12 actinide elements and (2) the steadily ongoing refinement and adaptation of the laser systems. Optimized laser systems at present allow for (1) maintenance-free, stable long-term utilization, (2) fast automated access as well as wide-range continuous tuning of wavelengths or, alternatively, (3) narrow bandwidth operation for high-resolution spectroscopy.

Today, more than 100 of these dedicated Ti:Sa laser types are in use worldwide, predominantly at large-scale research centers. A presentation of the Larissa lab together with recent results shall be given, highlighting the relevance of the work for the sensitive and selective ultra-trace analysis of radioisotopes by using conventional RIMS as well as resonant laser secondary neutrals mass spectrometry.

Thursday 28 March

8:50 Clemens Walther (intro)
9:00 Klaus Wendt
9:30 Tetsuo Sakamoto
10:00 Brett Isselhardt
10:30 Break
11:00 Yoshikazu Hirayama
11:30 Darcy van Eerten
12:00 Chao Zhang
12:30 Lunch
13:30 Matou Stemmler
14:00 Naoki Matsumoto
14:30 Kenji Nanba
15:00 Karin Hain

Tetsuo Sakamoto

History of the Development of a High Spatial Resolution TOF-SIMS/SNMS Apparatus

In 2004, I started to develop a new TOF-SIMS/SNMS apparatus aiming at individual particle analysis of aerosols such as PM2.5. Since collected aerosols are a mixture of particles with different origin and histories during drifting in air, bulk analysis like ICP-MS and GC-MS is limited to reveal the details of each particles. Traditionally, SEM-EDS or SEM-WDS was used for individual particle analysis. But such method has insufficient sensitivity and lateral resolution because of low emission probability of characteristic X-ray and scattering of electron beam in the solid, respectively.

Imaging SIMS was developed in early 1980s using Focused Ion Beam (FIB) coupled with QMS or Magnetic sector MS. For a long time, FIB-SIMS was known as "high-lateral resolution" SIMS, and its lateral resolution was around 100 nm. But FIB-SIMS has some problems for aerosol analysis. One is lack of sensitivity and simultaneous detection of many species (both elements and compounds).

I designed a TOF-SIMS/SNMS with high lateral resolution and simultaneous detection ability. First of all, the FIB was carefully designed for chopping the DC beam while maintain a small beam spot. [cont. on following page]

[cont. from previous page] And a TOF-MS was also designed aiming for both SIMS and SNMS by considering deep depth of field of input lens system. As a result, ultimate resolution of 40 nm and high transmission of TOF optics were realized.

The TOF-SIMS/SNMS apparatus was adopted to many kinds of small samples, aerosols, cells, steels, all-solid-state batteries. After the accident of 1F, I focused on resonance SNMS for precise isotope analysis and imaging. I and my colleagues are now challenging the analysis of small dusts collected in 1F and fuel debris in the future.

Brett Isselhardt

Co-authors: Andrew Conant, Manuel Raiwa, Michael Savina, Ziva Shulaker

Analysis of small samples of spent nuclear materials for interpreting reactor operating history

Interpreting the operating history of a nuclear reactor is a key question in safeguards, non-proliferation, and studies of environmental contamination. It can help answer questions related to the amount and quality of Pu or other radioactive materials that were produced during the irradiation. Traditional approaches to characterizing spent nuclear fuels rely either on radiometric counting and/or mass spectrometry, usually relying on chemical purification of the specific analyte to increase precision and accuracy. Here we present an approach using resonance ionization mass spectrometry (RIMS) to precisely analyze small, solid samples of spent nuclear materials to characterize isotope ratios of multiple elements simultaneously, without prior chemical separation. Dispensing with chemical separation avoids the addition of chemistry “blanks” (background), measuring multiple elements from the same volume allows the correlation of multiple irradiation characteristics, and working from small samples decreases the radioactive hazards in the laboratory.

We have applied Lawrence Livermore National Laboratory's Laser Ionization of Neutrals (LION) instrument [1] to several samples of spent nuclear material (see Figure 1). This presentation will explain how we can analyze nearly any combination of 3 elements including U, Pu, Am, Sr, Rb, Mo, Zr, Nd, Ba, Cs simultaneously [2], during a single measurement, usually with enough material remaining to analyze the others in a subsequent analysis. We will show how connecting multiple isotope ratios across elements and comparing those analytical results to computational models provide an improved understanding of the operating history of a nuclear reactor.

[1] Savina, M.R., Isselhardt, B.H., Trappitsch, R., Anal. Chem., (2021).

[2] Savina, M.R., Isselhardt, B.H., Shulaker, D.Z., Robel, M., Conant, A.J., and Ade, B.J., Sci. Rep., (2023).

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Yoshikazu Hirayama

Resonant laser ionization for nuclear spectroscopy at KISS

We have developed the KEK Isotope Separation System (KISS) [1] at RIKEN to study the nuclear structure of the nuclei in the vicinity of neutron magic number = 126 and 152 from the astrophysical interest. These neutron-rich nuclei have been produced by using multinucleon transfer reactions [2] with the combinations of the low-energy $^{136}\text{Xe}/^{238}\text{U}$ beams and the production targets of W, Ir, and Pt.

At the KISS facility, these radioisotopes are ionized by applying in-gas-cell resonant laser ionization technique. In the ionization process, we can perform laser ionization spectroscopy of the refractory elements with the atomic number = 72–78 such as Hf, Ta, W, Re, Os, Ir, and Pt, which can not be performed in other facilities. Laser spectroscopy can be used to effectively investigate the nuclear structure through the measured magnetic moments, isotope shifts (IS), changes in the mean-square charge radii $\delta\langle r^2 \rangle$, and quadrupole deformation parameters $|\langle \beta_2^2 \rangle|^{1/2}$.

We have studied the resonant ionization schemes of these elements by offline tests, and performed in-gas-cell resonant laser ionization spectroscopy of $^{199}\text{g}, ^{199}\text{m}, ^{200}, ^{201}\text{Pt}$ [3], $^{196}, ^{197}, ^{198}\text{Ir}$ [4], and $^{194}, ^{196}\text{Os}$ [5] produced at KISS. By using a multi-reflection time-of-flight mass-spectrograph (MRTOF-MS) combined with resonant laser ionization technique, we could discover the new neutron-rich ^{241}U isotope for the first time in 40 years [6].

In this workshop, we will report the results of resonant laser ionization spectroscopy at KISS, and the perspective of future plan at KISS.

[1] Y. Hirayama et al., Nucl. Inst. Meth. B353, 4 (2015), and B412, 11 (2017).

[2] Y.X. Watanabe et al., Phys. Rev. Lett. 172503, 1 (2015).

[3] Y. Hirayama et al., Phys. Rev. C 96, 014307 (2017), and 106, 034326 (2022).

[4] M. Mukai et al., Phys. Rev. C 102, 054307 (2020).

[5] H. Choi et al., Phys. Rev. C 102, 034309 (2020).

[6] T. Niwase et al., Phys. Rev. Lett. 130, 132502 (2023).

Darcy van Eerten

Co-authors: Paul Hanemann, Laura Leifermann, Tobias Weissenborn, Manuel Raiwa, and Clemens Walther

Spatially Resolved Multi-Element Analysis of Hot Particles in the SIRIUS RIMS instrument

So-called 'hot particles' are micrometre-scale fragments deriving from nuclear fuel. In the Chernobyl Exclusion Zone, these particles have contaminated the environment since the accident. They are composed of partially spent fuel fragments of mostly low-enriched U, and (ultra)-trace levels of other actinides and fission products.

Nuclear materials that contaminate the environment present an ongoing challenge to characterize due to their small size and diverse morphology. The SIRIUS RIMS instrument in Hannover, Germany, analyses isolated hot particles through resonance ionization mass spectrometry (RIMS). It is an adaptation of a commercial time-of-flight secondary ion mass spectrometry (ToF-SIMS) instrument (IONTOF.V), and five Ti:Sa lasers. With two frequency-doubled, fast-switching Ti:Sa lasers, it is capable of rapid element-selective analysis of U, Np, Pu, Am, Sr, Zr. Isotope ratio analysis of these elements in hot particles reveal the particle's origin, environmental sensitivity, and an estimation of the time spent in the environment.

Spatially resolved analysis can distinguish between fissionogenic and natural nuclides, which will be shown on a particle containing both natural Zr-cladding, and Zr fission products. In a second particle that has been bisected, environmentally-derived and fissionogenic Sr isotopes are homogenous over the cross-section, showing the particle's interaction with the environment is not limited to the particle's surface.

Chao Zhang

Co-authors: Shuichi Hasegawa, Ryohei Terabayashi

Research on Sr-RIMS under Triple Resonance Excitation

Resonance Ionization Mass Spectrometry (RIMS) leverages the energy differences in transition states between various elements and isotopes to achieve isobaric suppression and heightened isotopic selectivity. Furthermore, multi-step resonance ionization processes are capable of exciting atoms to specific Rydberg states, thus enhancing ionization efficiency. The focal point of this research is the three-step resonance ionization pathway involving the transition $5s^2 \ ^1S_0 \rightarrow 5s5p \ ^1P_1^o \rightarrow 4d^2 \ ^1D_2 \rightarrow 4dnf$ or $4dnp$. The measurement of the isotope shift (IS) among Sr natural isotopes, the evaluation of resonance ionization efficiency, and the observation and analysis for Stark shift in high Rydberg-state Sr atoms have been done in this study.

Matou Stemmler

Ionization scheme development for actinides at the LARISSA laboratory in Mainz

In order to perform ultra trace analysis of radionuclides in environmental samples based on resonance ionization mass spectrometry (RIMS), efficient and highly element-selective laser excitation schemes are required. To analyse different all-relevant actinides within a single sample during one measurement, simple and versatile two-step ionization schemes need to be developed. The use of fully automated grating Ti:sapphire lasers featuring intra-cavity second harmonic generation allows for an easy and instantaneous change of the ionization scheme and therefore element of interest during the measurement.

In the past few years, the RIMS method has been successfully used at the RISIKO mass separator in the Institute of Physics Johannes Gutenberg University Mainz for the development of highly efficient and selective ionization schemes and spectroscopic studies on various actinides. This presentation will focus on the development of ionization schemes and on atomic and nuclear studies of the minor actinides that are present in spent nuclear fuel, which comprises neptunium, americium, and curium. New two-step excitation schemes for the analysis of $^{237,239}\text{Np}$, $^{241,143}\text{Am}$ and $^{244-248}\text{Cm}$ were identified and investigated and will be discussed.

Naoki Matsumoto

Co-authors: Hiroki Miura, Takumi Mochizuki, Masato Morita, Tetsuo Sakamoto, Hideki TOMITA

Rapid Changeover of Target Element in Resonance Ionization Mass Spectrometry by switching fundamental/SHG Operation of Ti:Sapphire Laser

In the analysis of samples containing fission products, nuclear fuel materials, actinide nuclides, it is necessary to combine the fundamental and second harmonic generation (SHG) of Ti:Sapphire laser to achieve efficient resonant ionization for the target elements. We developed a modified grating-type Ti:Sapphire laser that can instantly switch between fundamental and SHG operation mode, named mode switching Ti:Sapphire laser. Rapid changeover of Cs/Sr resonant ionization using two set of the mode switching Ti:Sapphire laser was demonstrated.

This work was supported by JAEA Nuclear Energy S&T and Human Resource Development Project through concentrating wisdom Grant Number JPJA21P21465814.

Kenji Nanba, Yoshitaka Takagai

Introduction to Fukushima Institute for Environmental Radiation and trace analytical techniques.

Invited Speaker

Ass.-Prof Dr. Karin Hain
Isotope Physics Research Group
University of Vienna
Vienna, Austria

Abstract

Accelerator Mass Spectrometry (AMS) is the technique of choice for the detection of long-lived radionuclides with typical isotopic abundances of 10^{-12} to 10^{-16} (or 10^{-7} atoms per sample) in the environment. Interferences from stable isobars, however, can restrict the applicability of this method to selected nuclides. The novel Ion-Laser InterAction Mass Spectrometry (ILIAMS) technique at the Vienna Environmental Research Accelerator VERA can overcome this limitation in many cases by highly-efficient isobar removal at eV-energies. Nuclides can be measured for the first time with AMS while others become accessible also on low-energy AMS-systems. This opens up exciting possibilities e.g. in environmental radioactivity research (^{90}Sr , ^{99}Tc , ^{137}Cs) or Earth sciences (^{26}Al , ^{36}Cl , ^{41}Ca).

ILIAMS exploits differences in detachment energies (DE) within isobaric systems by neutralizing anions with DEs smaller than the photon energy via laser photodetachment. In addition, molecular interactions with the buffer gas can further enhance isobar suppression. Thereby, the VERA-facility has recently achieved the most sensitive detection of Sr at the 3 attogram level in mg of stable Sr from 300 mL of seawater and 1 g of coral aragonite. Furthermore, the laser-induced suppression of ^{236}U during measurements of ^{236}Np will considerably improve the characterisation of a spike material for the analysis of environmental ^{237}Np . During the last 4.5 years we have intensively studied possibilities of analyzing environmental concentrations of Tc with AMS. Complementary to ILIAMS, high-energy AMS was applied using the 14 MV tandem accelerator at the Australian National University (ANU, Canberra). With this method, we determined the Tc concentration in selected samples from different environmental reservoirs, including 1 g peat bog samples and 10 L water samples from the Pacific Ocean and European rivers.



Dr. Karin Hain

Dr. Karin Hain is a tenure-track assistant professor at the University of Vienna. She won the Austrian Physics Society (ÖPG) Fritz Kohlrausch Prize for Young Physicists in 2020, and was named Physicist of the month in Jan. 2024.

Co-authors

Martin Martschini, Stephanie Adler, L. Keith Fifield, Maki Honda, Oscar Marchhart, Merchel Silke, Stefan Pavetich, Aya Sakaguchi, Peter Steier, Stephen G. Tims, Andreas Wiederin, Alexander Wieser, Akihiko Yokoyama, Robin Golser

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Momo Mukai

Co-authors: Yoshikazu Hirayama, Takashi Hashimoto, Sun Chan Jeong, Hiroari Miyatake, Jun Young Moon, Toshitaka Niwase, Mikael Reponen, Marco Rosenbusch, Peter Schury, Hideki Ueno, Michiharu Wada, Yutaka Watanabe

Mass and isotope shift measurements of neutron-rich tungsten isotopes at KISS

The nuclei around $Z = 72 - 78$ are known as transitional nuclei, exhibiting a multitude of nuclear shapes depending on the neutron and proton numbers (N and Z) [1]. Around $N = 116$, various theoretical calculations predict prolate deformation for lighter isotopes, passing through γ -soft or triaxial shapes, and reaching oblate shapes in heavier isotopes [2,3]. The evolution of their nuclear structure has been investigated through the level structure and properties of β^- - and K -isomer decays obtained from γ -ray spectroscopy, nuclear electromagnetic moments, and charge radii obtained from laser spectroscopy, mainly for nuclei around the β^- -stability line and beyond $N = 116$ for osmium ($Z = 76$) and platinum ($Z = 78$). For neutron-rich nuclide around tungsten, fewer experimental results are known due to the difficulty of production.

The KEK Isotope Separation System (KISS) [4] was developed to perform nuclear spectroscopy of heavy neutron-rich isotopes produced by multi-nucleon transfer reactions. We conducted precise mass measurements using a multi-reflection time-of-flight mass spectrograph and isotope shift measurements of neutron-rich tungsten isotopes at KISS to study shape evolution. In this contribution the recent measurement results will be reported.

- [1] R. F. Casten, Nucl. Phys. A 443, 1 (1985).
- [2] L. M. Robledo et al., J. Phys. G 36, 115104 (2009).
- [3] K. Nomura et al., Phys. Rev. C 83, 054303 (2011).
- [4] Y. Hirayama et al., NIM Phys. Res. B 412, 11 (2017)

Tetsu Sonoda

Co-authors: PALIS, S104 Collaborators

The development of the gas cell-based laser ionization technique for low-energy RI beam

We have been developing a gas cell-based laser ionization technique for the production of low-energy Radioactive Isotope (RI)-beam in two application schemes.

One is to obtain a wide variety of the low-energy RI-beams from high-energy RI-beams provided by the BigRIPS fragment separator at RIKEN. And the other is ongoing phase -for the feasibility study of the production of medical radioisotope:astatine-211 that is one of remarkable advantage isotopes for targeted alpha-particle therapy. Both applications owe to the selectivity and sensitivity by a resonant laser ionization technique that gives an opportunity for performing the laser spectroscopy on nuclear physics.

Friday 29 March

9:00 Momo Mukai
9:30 Tetsu Sonoda
10:00 Mitzi Urquiza
10:30 Break
11:00 Felix Berg
11:30 Vadim Gadelshin
12:00 Paul Hanemann/Tobias Weissenborn
12:30 Lunch
13:30 Masato Morita
14:00 Ziva Shulaker
14:30 Michael Savina
15:00 Posters
16:30 Public Lecture

The presentation includes an overview and current status of our project.

- [1] T.Sonoda et al., Nucl.Inst.and Meth.B (2013).
- [2] T.Sonoda et al., Prog. Theor. Exp. Phys. (2019),
- [3] T.Sonoda et al., RIKEN Accelerator Progress Report, in printing.

Mitzi Urquiza

A cw-OPO seeded pulsed OPA system towards High-Resolution Laser Spectroscopy

Resonant laser excitation in atomic spectrum studies unveils nuclear structures. Interactions of the nuclear ground state with the electronic shell induce hyperfine structure (HFS) and isotope shift (IS), enabling precise measurement of nuclear properties such as spin (I), magnetic dipole moment (μ_s), electric quadrupole moment (Q_s), and changes in mean square charge radii ($\delta\langle r^2 \rangle$). Accessible with lasers, atomic transitions of valence electrons in the range of a few eV necessitate an optimal optical linewidth for high-resolution laser spectroscopy. Techniques like collinear resonance ionization spectroscopy employ a resonance peak linewidth of 40-70 MHz to resolve the HFS in most elements. Pulsed laser light with a full width at half maximum (FWHM) of less than 50 MHz has been achieved through various methods, including the seeding of a pulsed dye amplifier and injection-locking a titanium:sapphire (Ti:Sa) laser. As exotic nuclides demand hard to access wavelengths, new laser techniques are essential. While dye lasers and Ti:Sa-based systems prevail, an optical parametric oscillator (OPO) seeded dye amplifier system demonstrates comparable performance near 330 nm. This proposed setup aims to generate high-energy pulses (in the range of 1000 nm to 1530 nm) using a narrow-band cw-OPO seeded optical parametric amplifier (OPA) towards high-resolution spectroscopy of Actinides. Preliminary characterization of the pulse length and optical linewidth were done to meet specific experimental requirements, including mode-hop-free tuning suitability.

Felix Berg

Co-authors: Markus Breckheimer, Janik

Lohmann, Tobias Reich, Christopher Sirleaf

Application of TOF-SIMS and rL-SNMS for the investigation of geochemical interactions of plutonium with Opalinus Clay and hardened cement paste

The safety case of a deep geological repository (DGR) for long-term nuclear waste storage requires extensive knowledge about the interactions of the radioactive inventory with the (geo-)technical and geological barriers. Due to their long half-life, high radiotoxicity and complex aqueous chemistry, plutonium isotopes are of major interest as high-level radioactive waste (HLW) that needs to be stored safely for generations. To assess the capabilities as well as limitations of possible concepts for a DGR, the study of the geochemical interactions of plutonium with materials considered for a long-term nuclear waste repository is required. Therefore, to have a better and more in-depth understanding of the interactions between radionuclides and these materials, a spatially resolved approach would be favorable.

We will present the current development state of the combined approach of TOF-SIMS and rL-SNMS for the study of sorption and diffusion samples of HCP and OPA with plutonium on the micrometer scale and assess the capabilities and limitations of both methods. The rL-SNMS setup consists of a TOF-SIMS III (IONTOF, Germany) and three Ti:Sa lasers jointly pumped by a Nd:YAG laser [1]. The sensitivity of the setup has been systematically investigated via sorption samples of HCP placed in contact with 10 to 10 M Pu(IV) under anaerobic conditions in artificial cement pore water. To showcase the analysis of diffusion profiles, we used samples of OPA placed in contact with 10 M Pu(VI) in OPA pore water as mobile phase under aerobic conditions. The concentrations of Pu were in some cases deliberately set above the solubility limit to either ensure a constant equilibrium concentration in solution, or to assess the sensitivity of TOF-SIMS and rL-SNMS systematically. We will present a more method-oriented sample preparation as well as results concerning the oxidation state of plutonium in OPA pore water obtained via capillary-electrophoresis coupled to inductively coupled plasma mass spectrometry (CE-ICP-MS).

[1] Schönenbach et al., Anal. Bioanal. Chem., 2021

Vadim Gadelshin

Aerosol particle studies at rL-SNMS machine in Yekaterinburg: aspects and prospects

The Ural Mountains are a very interesting region for climate research on Earth. This mountain range runs north-south more than 2500 km from the Arctic Ocean to the Eurasian Steppe belt. Being the conventional boundary between Europe and Asia, the Urals are also the endpoint of climatic effects, caused by the Atlantic or Siberian air masses. Since Ancient times the region is world-known for its natural resources, mineral production, gold and gem mines, earned the «treasure box» fame. Today the biggest titanium and uranium production capacities are located here too. However, the large number of industrial facilities left their imprint on the regional ecology, with the Kyshtym disaster (1957) as the -

worse highlight, led to the formation of the East Ural Natural Reserve – the exclusion zone due to the radioactive contamination.

Anthropogenic aerosols are one of the main objects for ecological studies. Emitted by an industrial facility, they can be spread over a long distance, presenting a danger to the environment and to the population. To obtain the most realistic assessment of the associated health risks, it is promising to investigate the distribution of chemical composition over the surface and in the volume of aerosol particles. The new setup for laser resonance ionization secondary neutral mass spectrometry (rL-SNMS) at the Ural Federal University can be used for this purpose, and moreover, to compile an atlas of aerosol microparticles related to a specific regional production facility. To define a particular fingerprint of the aerosol origin, it is intended to focus on the content of rare-earth elements (REE) and their location in the structure of microparticles. For instance, the concentration ratio of light to heavy REEs is a good marker for anthropogenic sources, but, due to the trace amount of REEs in aerosol samples, this topic remains scarcely investigated. The recent developments in resonance ionization mass spectrometry can overcome this issue, providing a high sensitivity even to ultra-trace concentration of REEs. The status of the rL-SNMS machine in Yekaterinburg as well as the concept of the aerosol research program is going to be presented.

Paul Hanemann, Tobias

Weissenborn

Co-authors: Felix Brandt, Martina Klinkenberg,

Laura Leifermann, David Ohm, Clemens

Walther, Darcy van Eerten

Location, Isolation, RIMS and Dissolution of Hot Particles from the Chernobyl Exclusion Zone

Micron sized fragments of nuclear fuel, so called “hot particles” have been released during the Chernobyl nuclear accident in 1986 into the exclusion zone (CEZ). [cont. from prev. page] The combination of flotation with high-density-solutions, electron microscopy and a micromanipulator allow the isolation of single hot particles from soil samples of the CEZ [1]. Non-destructive mass spectrometry is performed on individual particles to characterize them. The RIMS-setup at the University of Hannover combines the spatial resolution of a commercially available IONTOF TOF.SIMS 5 with the elemental selectivity of resonant laser ionisation. The isotopic fingerprint of these particles allows to link them to the nuclear accident as well as identifying particles with unusual isotope ratios.

After the determination of the isotope ratios for different actinides, sequential leaching can be applied to the particles. Combined with non-destructive x-ray absorption spectroscopy at different beamlines the results of the sequential leaching give an insight on the chemical structure of the particles. Furthermore, a method to cut the particles in half was developed in cooperation with the Forschungszentrum Jülich. With that, it is possible to have a sample in reserve and study the inner core of the particle.

[1] DOI:10.1039/9781837670758-00001

Masato Morita

Co-authors:

Masato Morita, Shoki Yoshimura, Hideki Tomita, Tetsuo Sakamoto

Development of Practical Resonance Laser SNMS System for Decommissioning of Fukushima Daiichi Nuclear Power Plant

For taking out nuclear fuel debris safely, there is a strong need for analysis methods of debris precisely. The most important thing in the debris analysis is isotope ratio of a certain elements, because the ratio is closely related to both the accident progress and the state of debris. Secondary ion mass spectrometry (SIMS) is a candidate for the analysis. However, isobaric interferences often make it difficult to analyze precise isotope ratio analysis. We have been developed a resonance laser sputtered neutral mass spectrometer (R-SNMS) for element-selective ionization and detection by using a set of newly developed tunable Ti:Sapphire lasers. In R-SNMS, synchronization (alignment) between the SIMS device and the Ti:Sapphire laser requires specialist skill. By automation and remote, the R-SNMS improved to a practical and safe device.

This work was supported by JAEA Nuclear Energy S&T and Human Resource Development Project through concentrating wisdom Grant Number JPJA21P21465814.

Ziva Shulaker

Co-authors: Brett Isselhardt, Manuel Raiwa, Autumn Roberts, Michael Savina

Multielement Measurements Without Isobaric Interferences in Stardust Grains with application to Nuclear Fuel Analysis

Micrometer-sized particles condense in the atmosphere of exploding stars and their isotopic composition records the nucleosynthesis processes in the star. These particles, called stardust or presolar grains, formed before the formation of our sun and solar system. These stardust grains were ultimately incorporated in the cloud of matter that our solar system formed from. Because isotopic systems in stardust grains represent the ground truth values as inputs for nucleosynthesis models, studying isotopic systems in stardust is important for understanding the formation of p- and s-process nuclei. After separating stardust grains from their meteorite matrix, these grains are the only material older than the solar system that can be analyzed in a laboratory setting. However, stardust grains are difficult to analyze because the average grain size is ~1 μm diameter and analytes of interest (e.g., Ti, Sr, Zr, Mo, Ru, Ba, W) are atom limited. Resonance ionization mass spectrometry (RIMS) is ideal for analyzing stardust grains because of the high spatial resolution and sensitivity, low sample utilization, and the ability of RIMS to discriminate against isobaric interferences by selectively ionizing only the elements of interest. We present data from ~100 stardust (silicon carbide and graphite grains) using newly developed RIMS methods for simultaneously collecting multielement measurements (up to 19 isotopes of 3 elements, such as Zr, Mo, Ru) on the LION instrument at Lawrence Livermore National Laboratory. To achieve this, ionization lasers of elements with isobaric interferences (e.g., Mo, Zr) are offset by 200 ns to discriminate isobaric interferences. Ultimately, this method allows for elemental analysis, regardless of isobaric -

interferences, of micron-sized particles for isotopes without performing chemical separation. We apply these multielement analyses of stardust grains to analyzing spent fuel and intentionally tagged fuel elements.

Michael Savina

Co-authors: Brett Isselhardt, Manuel Raiwa

A new laser for ultra-trace RIMS

One of the strengths of Resonance Ionization Mass Spectrometry (RIMS) is its selectivity, that is the ability to ionize only one element in a sample containing many different elements and thereby eliminating the need for chemical purification prior to analysis. However, in cases where backgrounds are unavoidable, such as ultra-trace analysis or when overwhelming excesses of isobaric atoms are present, RIMS has the unique ability to quantitatively measure backgrounds by tuning the laser(s) off-resonance. The resonance signal of the analyte element disappears, leaving behind ions produced by other processes such as secondary ionization due to sputtering, off-resonance ionization of atoms and molecules, and photodissociation of molecules into fragments isobaric with the analyte. RIMS spectra generally take from several to several tens of minutes to collect. Provided that the sample does not change over that time under the influence of the ion beam or laser used to atomize it, off-resonance spectra collected later can be quantitatively subtracted to produce background-free results. However, ion sputtering during analysis can change the ratio of atoms to molecules in the sputtered flux over time, and hence change the contribution of non-resonant background ions caused by photodissociation. Further, in the case of ultra-trace analysis in which lasers are used to desorb material, the elemental composition of the sample changes over time as the more volatile components are preferentially removed in the early stages of the analysis. In these cases the off-resonance spectrum collected many minutes later is not a true representation of the background present in the resonance spectrum which was, in effect, collected on a different sample.

To address this issue we have developed a RIMS method known as blinking, in which the resonance signal is extinguished (or "blinked") by switching one of the lasers between on- and off-resonance every other (or every third, or fourth, etc.) pulse. In this way, perfect background subtraction is possible, since the on- and off-resonance spectra are interleaved rather than sequential, and both therefore sample the same time-dependent changes in the analyte. We first demonstrated this technique by alternating on- and off-resonance pulses from two lasers and achieved success in measuring ²³⁸Pu accurately at concentrations less than 1 ppb in a soil matrix containing a large (~30,000:1) excess of ²³⁸U. We later developed a Ti:Sapphire laser capable of self-blinking, such that a second laser is not needed, and measured ²³⁸Pu against an excess of ²³⁸U of ~50,000:1. The new laser has no moving parts, so there is no settling time after switching wavelengths, and can therefore blink at an arbitrary rate (we currently use 1500 Hz). In this talk, we demonstrate this laser for trace analysis of ²³⁸Pu, as well direct analysis of ultra-trace fission products in irradiated uranium. LLNL-ABS-858820

Posters

Paul Hanemann

Co-authors: Laura Leifermann, Clemens Walther, Tobias Weissenborn, Darcy van Eerten

Spatially resolved trace analysis of radionuclides with laser ionization mass spectrometry

The RIMS-setup at the University of Hannover uses multiple grating-tuned Ti:Sa lasers to access a range of resonant ionization schemes. Combined with mass spectrometry, the method can detect actinides in single radioactive particles from the environment, down to 10⁷ atoms of a single isotope [1]. In micron-sized particles from the Chernobyl exclusion zone, the relative ²³⁸Pu content can be determined by suppressing the dominant ²³⁸U in spent fuel. This is achieved quasi non-destructively without chemical preparation of the sample. The current capabilities of the RIMS-system are presented in this poster, with an outlook on further developments of the method and application to ultra-trace analysis.

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Production and characterisation of synthetic homogenous multi-element actinides samples via sol-gel as standards for mass spectrometry

MetroPOEM [1] is committed to developing SI-traceable mixed element reference materials for the calibration of mass spectrometric devices. In nuclear forensics, elemental selectivity and precise spatially resolved mass spectrometry is essential for ultra-trace analysis of environmental samples. Resonant laser secondary neutral mass spectrometry (rL-SNMS) combines both element selective isotope ratio measurements and spatial resolution on the micrometre scale. Multi-element reference materials are needed to investigate different ionisation efficiencies for the elements important for environmental analytics.

In this work we present a production method of mixed actinide samples such as U, Pu and Am via sol-gel. These samples consist exclusively of the respective metal and fulfil the conditions for homogeneity confirmed by EDX and SIMS. The spatially resolved element distribution was determined using rL-SNMS. ICP-MS is also used to determine the element composition.

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Spatially resolved trace analysis of radionuclides with laser ionization mass spectrometry

In radioecological studies, the plant uptake and distribution of radionuclides are of major interest for risk assessment. In the present work, the elemental distribution within the tissue of plants is imaged by resonant laser secondary neutral mass spectrometry (rL-SNMS). This technique combines a commercially available time-of-flight secondary ion mass spectrometry (IONTOF TOF.SIMS 5) with a laser system for ionization of sputtered neutrals. Due to the excellent suppression of molecular isobaric interferences by rL-SNMS, about 10¹⁰ atoms of technetium suffice to image the Tc-99 distribution inside plant cells with a spatial resolution of approximately 300 nm. The distribution of technetium in the two plant species *Daucus carota* and *Pisum sativum* was determined. For reasons of radiation protection, the plants were labelled with Tc-99 at a concentration of 0.1 mM. Such a low concentration renders measurements by conventional SIMS impossible. [1]

[1] DOI: 10.1016/j.jhazmat.2021.127143