PAPER
Benjamin T. Manard et al.
Laser ablation-inductively couple plasma-mass spectrometry/laser induced break down spectroscopy: a tandem technique for uranium particle characterization
Welcome to the fifth special issue dedicated to young analytical scientists in JAAS!

Jorge Pisonero

The aim of this issue is to highlight the contributions of outstanding young scientists in atomic spectroscopy and related areas, following the success of previous young analytical scientist (YAS) issues organized by Carsten Engelhard in 2014 and by Spiros A. Pergantis in 2010, 2006 and 2002. It should be remarked that the authors of this special issue are nominated by worldwide experts in the spectroscopy field, including members of the Editorial and Advisory Board of JAAS.

It is noted with great satisfaction that many contributors from previous YAS special issues were hired as new analytical faculty. This trend validates that nominated YAS authors show great potential to develop a successful career in analytical atomic spectrometry and related fields. In my case, I had the honour to participate as a contributing author in the 2006 YAS special issue of JAAS. I remember that by that time I was working at Prof. Günther’s Group at ETH, and I felt very proud to receive such a prestigious nomination. Eleven years later, back at my home University in Oviedo as an Associate Professor and with a bigger family (see Fig. 1), I have once more the honour of participating in this issue, this time as Guest Editor.

This YAS special issue contains 19 research articles dedicated to different atomic spectroscopy fields, related to fundamental studies, novel concepts and exciting applications using ICP-MS/OES, LA/LIBS, GD-MS/OES, atmospheric plasma sources or XRF:

State of the art ICP-MS based methods for trace elements and their species analysis in cells was reviewed by B. Chen et al.2 In this manuscript, hyphenated techniques with high potential for biomedical research and clinical applications, based on multi-dimensional chromatography, electrophoresis, chip-based microextraction or laser ablation, were discussed. In a tutorial, the operating principles of ICP-MS/MS and the new possibilities to deal with spectral overlaps, were described in detail by E. Bolea-Fernandez et al.3 Isotope fractionation, accompanying Fe uptake and transport mechanisms at a cellular level in an intestinal Caco-2 cell line in vitro model, was evaluated by M. R. Flórez et al.,4 using MC-ICP-MS. Both processes (absorption and transport) were found to produce Fe isotope fractionation in favour of the light isotopes, in agreement with previous conclusions from in vivo and ex vivo studies. Moreover, elemental mass spectrometry combined with bio-analytical methodologies was applied by H. González-Iglesias et al.,5 for the quantitative distribution of Zn, Cu and Fe in the human lens, and for the study of the Zn-metallothionein redox system in cultured lens epithelial cells.

In relation to new sample preparation methods, single digestion of polymeric waste electrical and electronic requirements, using microwave assisted ultraviolet wet digestion, was developed by P. A. Mello et al.,6 to determine Br, Cd, Cr, Hg and Sb by ICP-MS. Additionally, sample preparation of lipstick for further Cd and Pb determination using ICP-MS was carefully evaluated by M. Foster Mesko et al.7. The results indicate that complexing acids are not required for further determination of Cd, while only HCl combined with HNO3 was required for Pb detection. On the other hand, an analytical method for simultaneous speciation of As and Sb in water samples using TXRF was developed by V. Romero et al.8 This method was based on pre-concentration of inorganic As and Sb onto immobilized Pd NPs after selective hydride generation of arsine and stibine.

Mixed-gas plasma (combining argon, nitrogen and hydrogen) was evaluated by Y. Makonnen et al.,9 as a robust emission source for ICP-OES. Matrix effects were minimized and sensitivity was enhanced. Nevertheless, detection limits were not affected due to an increase in background. This methodology was shown to have great potential for accurate and precise multi-elemental analysis of a variety of environmental and geological matrices. Moreover, hydride generation combined with ICP-OES was investigated for non-chromatographic As speciation from solutions of As(III), As(V), dimethylarsinate (DMA) and monomethylarsonate (MMA) by M. Welna et al.10 In this work, several protocols for speciation of these species in one solution were proposed by combining the responses obtained under different pre-reduction and reaction conditions.

The laser ablation related papers include quantitative LA-ICP-MS Cu mapping of liver cryo-sections from mice by M. Costas Rodríguez et al.11 Calibration was performed either using thin sections of homogenate spiked liver tissue or spiked gelatine droplet...
standards. Results show inhomogeneous hepatic Cu distribution in mice with cholestatic liver disease, and increasing Cu levels with the progression of the disease. Mapping and characterization of uranium particles in a complex matrix of iron and nickel using tandem LA-ICP-MS/LIBS was investigated by B. T. Manard et al. Isotopic ratio measurements and quantification of uranium particles based on abundance was achieved using this innovative technology. LIBS technology was also investigated by J.-B. Sirven et al., for the assessment of exposure to airborne carbon nanotubes through the analysis of filter samples. Furthermore, the analytical capabilities of ArF laser ablation laser-excited atomic fluorescence (LA-LEAF) for rapid As quantification were evaluated by J. Merten et al. Measurements were carried out in copper and steel samples under He or Ar atmospheres, respectively. Arsenic LODs were slightly improved in comparison to standard LIBS. Additionally, optimum working conditions for laser ablation with accelerator mass spectrometry (LA-AMS), which enables spatially resolved analyses of radiocarbon in carbonates, were investigated by C. Welte et al. In this study, LA-ICP-MS was used to investigate laser sources that provide high $C_{\text{gas}}$ formation rates and $C_{\text{gas}}$ conversion efficiencies. Gas transport characteristics of the current LA-AMS were evaluated and the growth stop width of a natural stalagmite sample was characterized by a developed model. Based on these studies an improved LA-AMS setup is proposed.

Glow discharge spectroscopy papers are also included in this issue. For instance, GD-OES was evaluated for the characterization of oxidized Ni-based superalloys by W. J. Nowak. Fast depth resolved analysis of thick oxide layers and coatings (between 2 μm and 120 μm) was successfully achieved and validated using other analytical techniques such as light optical microscopy and scanning electron microscopy. Moreover, a setup based on differential interferometric profiling was developed by S. Gaiaschi et al., for real-time depth measurement in GD-OES. Measurement accuracy better than 5% was obtained for crater depth ranging from 100 nm to several μm, providing significant improvement to the quantification process in GD-OES. In relation to GD-MS, the production of doubly charged sample ions by charge transfer and ionization (CTI) was investigated by S. Mushtaq et al. This “non-selective” process was differentiated from the asymmetric charge transfer process that requires a close energy match. CTI was found to only occur for a limited number of elements, depending on the plasma gas used and the total energy required to doubly ionize the metallic atom.

In relation to atmospheric pressure plasma sources, a plasma assisted reaction chemical ionization source with liquid sample introduction was developed by K. Jorabchi et al. This source was found to provide high sensitivity detection of chlorine in liquid chromatography separated compounds. Moreover, a miniature microelectrolysis liquid electrode discharge optical emission spectrometer was developed and applied for potassium screening in human serum by Y.-L. Yu et al. Using this methodology, matrix interferences and sample consumption were reduced while sample throughput was increased.

Before signing off, I would like to thank all of the authors that submitted papers for this special YAS issue. I wish all of them success in their future industrial or academic careers. Moreover, I would like to acknowledge all referees for taking their time to review the submissions and all colleagues for taking their time to nominate this year’s YAS authors. Special thanks are due to Philippa Hughes, Rebeca Brodie and to the Editorial Board of JAAS for giving me the opportunity to organize this issue. Also, I would like to acknowledge the JAAS Editorial Staff for their hard work organising and publishing this year’s YAS issue.

References
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9 Y. Makonnen et al., DOI: 10.1039/C7JA00112F.
Contributors to the Young Analytical Scientists themed issue

C6JA00414H Beibei Chen is currently an Associate Professor at the College of Chemistry and Molecular Sciences, Wuhan University (China). She received her BSc degree in Chemistry (2005) and her PhD degree in Analytical Chemistry (2010) with Professor Bin Hu from Wuhan University (China). She worked as a Postdoctoral Fellow (2011–2014) at Wuhan University. She is was a Visiting Postdoctoral Fellow with Professors Xing-Fang Li and X. Chris Le at the University of Alberta in Nov. 2013–Nov. 2014. Her research focuses on the development of new hyphenated techniques, involving mass spectrometry and chromatography, for elemental speciation and metallomics.

C7JA00010C Eduardo Bolea Fernández obtained his degree in Chemistry at the University of Zaragoza (Spain) in 2012. Having obtained a Master degree in Analytical Chemistry from the same university, he is currently a PhD student at the Department of Analytical Chemistry, Ghent University (Belgium) in the “Atomic & Mass Spectrometry – A&MS research group”. His research has been focused on method development for ultra-trace elemental and isotopic analysis using tandem ICP-mass spectrometry (ICP-MS/MS). A second topic of interest is high-precision Hg isotopic analysis using multi-collector ICP-MS. The public defense of his PhD is planned for April 2017.

C7JA00092H Jonathan Merten received a B.Sc. in Chemistry from the University of Virginia in 1999. He subsequently taught chemistry at Musoma Day Secondary School in Musoma, Tanzania for two years, then worked as a chromatographer at the University of Florida, where he learned to hate sample prep. He eventually joined Nicolo Omenetto, Ben Smith and Jim Winefordner’s lab at the University of Florida, discovering the pleasure of building his own instruments while working in multiple (mostly) laser-related lines of research. While his primary interest is LIBS applications and diagnostics, he benefited from the long history of diverse spectroscopy in the Omenetto–Winefordner–Smith lab, as well as a brief
Benjamin Manard, born in Macon, Georgia, USA, completed his Bachelors of Science degree in Chemistry (2009) at Georgia Southern University while performing research in analytical chemistry under Dr. L. Shannon Davis.

He then entered the graduate school at Clemson University and studied analytical chemistry under the direction of Dr. R. Kenneth Marcus. He obtained his PhD in 2014 with a dissertation focused on two primary areas: (1) employing capillary channeled polymer (C-CP) fibers as an innovative stationary phase for solid phase extraction of proteins from bio-fluids prior to MALDI-MS detection, and (2) the development of a miniaturized plasma source, the liquid sampling atmospheric pressure glow discharge (LS-APGD), to be employed with OES and MS detection for elemental analysis. During his PhD studies, Benjamin obtained a position as a Visiting Scientist at the Lawrence Berkeley National Laboratory (LBNL) developing laser-based chemical analysis techniques under the guidance of Dr. Richard E. Russo. Additionally, Benjamin worked at the Pacific Northwest National Laboratory (PNNL) in collaboration with Dr. David W. Koppenaal coupling the LS-APGD as an ionization source on a high resolution Orbitrap mass spectrometer. In 2014, Benjamin was awarded a Glenn T. Seaborg postdoctoral fellow at the Los Alamos National Laboratory (LANL) under the mentorship of Dr. Ning Xu. Benjamin’s work was heavily directed towards using plasma-based techniques for trace elemental analysis in special nuclear materials including plutonium and uranium. After completion of his postdoctoral appointment (2016), Benjamin was promoted into a Staff Scientist position at LANL, which he currently holds. He continues his research on plasma-based techniques for trace elemental analyses. Benjamin currently serves on the Executive Committee (EC) of the Society for Applied Spectroscopy and has served on the EC for three years. His hobbies include playing basketball, skiing, camping, and traveling.

Dr. Ing. Wojciech Jerzy Nowak has been an Assistant Professor at Rzeszow University of Technology since February 2016. He received his BSc degree in Material Science [specialization: Organic Materials Engineering (2007)] at Rzeszow University of Technology, MSc degree in Material Science [specialization: Biomaterials and Composites (2010)] at AGH University of Science and Technology in Cracow and the PhD degree in Material Science [specialization: High Temperature Oxidation (2014)] under the supervision of Prof. Lorenz Singheiser from RWTH Aachen University. During PhD studies he worked as a PhD student in Forschungszentrum Juelich GmbH (2011-2014) in the Institute of Energy and Climate Research (IEK), department: Microstructure and Properties of Materials (IEK-2), Group of High Temperature Corrosion and Corrosion Protection with Prof. W. J. Quadakkers. After his PhD studies he continued working at FZJ as a post-doctoral researcher in the Group of High Temperature Corrosion and Corrosion Protection (2014–2016). Between 2011 and 2016 he participated in two EU-funded projects: “H2-IGCC” (FP7-239349) and “SAMBA” (FP7-309849). He was additionally responsible for performing all of the analyses using glow discharge optical emission spectroscopy (GD-OES). Since 2016 he has worked at Rzeszow University of Technology in the Faculty of Mechanical Engineering and Aeronautics, Department of Material Science as an assistant scientist in the Corrosion and Corrosion Protection group.
professor. Since 2016 he has been responsible for the Section of Chemical Composition Analysis (P2) which is a part of the Research and Development Laboratory for Aerospace Materials at Rzeszow University of Technology, therefore he continuously works with the GD-OES. His research is focused on materials for high temperature application and the processes in the materials during exposure at high temperature.

C6JA00415F Sohail Mushtaq is currently a Post Doctoral Research Associate in the School of Chemistry at the University of Bristol. He is exploring aspects of the gas phase chemistry that underpin the growth of diamond by microwave plasma enhanced chemical vapour deposition. He earned his M.Sc degree in 2005 and his M.Phil in 2007, both from the Government College University Lahore, Pakistan. After his M.Phil degree he was selected as the Marie Curie Early Stage Researcher at Imperial College (IC) London to work with Prof. J. C. Pickering in the EC Research Training Network on Analytical Glow Discharges (GLADNET). His PhD work was on the effects of traces of molecular gases in analytical glow discharge. For this work, he carried out the first multi-line study for oxygen as an impurity in glow discharges. After his PhD in 2011 at IC he took up a post-doctoral position with Prof. Edward Steers at London Metropolitan University. He has extensive experience of using the Imperial Fourier Transform spectrometer and glow discharge sources, and has carried out experimental work at EAG (Syracuse, USA), EMPA (Thun, Switzerland), BAM (Berlin) and IFW Dresden (Germany). He has made a significant impact in the field with 18 publications; this includes three papers with work featured on the front cover of JAAS and he is internationally known for his work on molecular gases in glow discharges. He was awarded the Payling prize for the best contribution by a young scientist at the 2nd IGDSS (Internl. GDS Symposium), Prague and also awarded JAAS Emerging Investigator Lectureship 2016. His main research interest is in the fundamental processes in glow discharges and their dependence on the plasma constituent.

C7JA00111H Yong-Liang Yu was born in 1981 in Dandong, China. He received his PhD degree in Analytical Chemistry (2010) from Northeastern University, China, under the supervision of Professor Jian-Hua Wang. His research interest focuses on the miniaturization of atomic spectrometric systems and their applications. In 2008–2009, he worked with Professor Manuel Miro as a visiting student at the University of the Balearic Islands, Spain, by developing analytical schemes for the hyphenation of microsolid phase extraction to liquid chromatography for automatic multiresidue analysis. In 2010, he joined the Department of Chemistry of Northeastern University as a lecturer, and since then he has devoted his time to the development of novel atomic emission spectrometric approaches based on low-temperature micro-plasma. He is currently a Professor in Analytical Chemistry in the Department of Chemistry of Northeastern University. He has published more than 30 papers in peer-reviewed international journals.

C7JA00090A María R. Florez was born in Gijón (Asturias, Spain) in 1984. She
studied Chemistry at the University of Oviedo and obtained her MSc diploma from the University of Zaragoza. She defended her PhD in October 2014 within a joint-PhD frame between the University of Zaragoza and Ghent University, under the supervision of Prof. Dr Martin Resano and Prof. Dr Frank Vanhaecke. Since 2015 she has held a post-doctoral position as part of the A&MS research group at Ghent University. Her current research is focused on the development of cell culture models to study biochemical processes leading to isotope fractionation.

Dr Yoseif Makonnen obtained his Ph.D. in Chemistry from Queen’s University, where he investigated mixed-gas plasmas and heated-sample introduction systems to enhance the analytical performance of inductively coupled plasma (ICP) spectrometry. He completed a Mitac’s Accelerate post-doctoral fellowship in collaboration with Burgener Research Inc. investigating enhanced sample introduction systems for ICP spectrometry. He is currently working as a post-doctoral fellow, with Dr Diane Beauchemin, in collaboration with Activation Laboratories in Ancaster, Canada. His current research focuses on the development of robust, high-throughput methods for the accurate multi-elemental analysis of geological and environmental samples by ICP mass spectrometry.

Hector Gonzalez Iglesias was born in 1979 in Pola de Lena, a small town in the mountains of Asturias, a beautiful region of the north of Spain. As a child he fell in love with “chemistry games”, so followed his passion and studied chemistry at the University of Oviedo. Upon graduation in 2005, he joined the research group of Prof. Alfredo Sanz-Medel and was also mentored by Prof. Marisa Fernández-Sánchez at the University of Oviedo. During the PhD program his research interest was in Bioinorganic Analytical Chemistry where he helped to develop methods for the accurate determination of isotopes in biological samples. He learned to use elemental mass spectrometry techniques, including ICP-MS instruments with different MS detectors such as single quadrupole, octopole reaction system, and sector field, as well as molecular ones including MALDI-MS and LC-MS/MS (ESI and APCI sources). In 2010, he started postdoctoral training at the Institute of Ophthalmology Fernández-Vega – Foundation of Ophthalmological Investigation (IOFV-FIO, Oviedo, Spain), under the supervision of Miguel Coca-Prados (Yale University, USA). He has worked on two main projects: “Genetic and Proteomic Biomarkers in Glaucoma”, and “Biometals in Age Related Macular Degeneration”. His current experience at IOFV-FIO has allowed him to learn many techniques in the field of cellular and molecular biology and the handling of animal models of eye diseases. Currently, he is Principal Investigator of the Unit of Neurodegenerative Eye Diseases at IOFV-FIO. He is a strong believer in the importance of a multidisciplinary approach in science and life.

Maja Welna was born in Poland, in 1980. She hopes to become a scientist, an ambition she has held since her early years. From 1999 she has fulfilled her fascination for chemistry at Wroclaw University of Science and Technology (Wroclaw, Poland), Faculty of Chemistry, where she received her MSc in Chemistry (2004) followed by a PhD in Analytical Chemistry (2008). After gaining her PhD she joined the Analytical Chemistry Group and at present works in the Division of Analytical Chemistry and Chemical Metallurgy, doing what she really wants to do. Being associated and inspired by energetic, dynamic and experiencing team she is able to continuously develop herself and her research career. Since 2012 she started her independent research (“habilitation”) focused on the area of analytical atomic spectrometry. Her current interests include: (1) the application of hydride generation techniques for atomic spectrometry (particularly in hyphenation with optical emission spectrometers) to single and simultaneous determinations of hydride-forming elements, (2) improvement in elemental speciation and fractionation without chromatography related to the evaluation of non-chromatographic approaches for species-selective As analysis directly by HG-ICP OES, and (3) the development of methodologies for the determination and non-chromatographic speciation of As using HG-ICP OES in food samples, especially in rice and rice products.
Marcia Foster Mesko concluded her PhD in 2008 and she has held a permanent position as Associate Professor at the Federal University of Pelotas, Brazil, since 2009. She has experience in analytical chemistry for the development of methods for sample preparation, atomic spectrometry, food and environmental analysis, speciation analysis and quality control of pharmaceuticals and other industrial products. She has authored more than 10 book chapters in these fields. She supervised eight Masters and one PhD student. She has presented at several conferences in national and international scientific meetings and has received more than 15 national and international awards, including the L’Oreal Brazil – Young Women in Science, Brazilian Academy of Sciences, UNESCO. She has reviewed for more than 15 international scientific journals and has published more 68 peer-reviewed international papers in high-impact journals such as Journal of Analytical Atomic Spectrometry, Analytical Chemistry, Talanta, Analytical and Bioanalytical Chemistry, among others. She was a staff member of the Brazilian Pharmacopoeia, for 4 years, responsible for the revision of monograph methods for the analysis of pharmaceutical products, and for the development of new methods for quality control of pharmaceutical products. She has worked as an invited researcher at Instituto Nacional de Metrologia, Qualidade e Tecnologia – INMETRO, Brazil (Laboratory of Inorganic Chemistry), for the development of certified reference materials of pharmaceutical products and a method for the direct determination of metals in bioethanol using ICP OES. She has cooperative works with many research groups in Brazil and other countries, such as Austria, Germany and Canada. Recently, she was elected as the vice-director of Analytical Chemistry Division of the Brazilian Chemical Society.

Dr Kaveh Jorabchi is currently an assistant professor of chemistry at Georgetown University in Washington, DC, USA. His research interests include the development of new elemental and molecular characterization techniques based on mass and ion mobility spectrometries. Dr Jorabchi’s interest in chemistry formed in high school in Iran under the influence of an excellent chemistry teacher and a group of talented friends. This led him to become one of the four members of the Iranian National Chemistry Olympiad team, winning a silver medal at the 1997 International Chemistry Olympiad in his senior year. He then pursued a BSc in chemistry at Tehran’s Sharif University of Technology and went on to receive a PhD in chemistry in 2006 under the direction of Prof. Akbar Montaser at the George Washington University, focusing on the fundamental investigations and development of plasma ion sources. Dr Jorabchi then completed postdoctoral training with Prof. Lloyd Smith’s group at the University of Wisconsin-Madison, conducting research on molecular ionization. Living in Madison brought him more than science by leading him to his life partner and wife who continually educates him about the arts. Prior to joining Georgetown University, Dr Jorabchi worked as an industrial R&D scientist for 2 years at Syagen Technologies, developing new ion sources for biological and homeland security applications. Dr Jorabchi incorporates elements of his experiences in his research and teaching at Georgetown University. Research in the Jorabchi group spans both elemental and molecular analyses and includes industrial and academic collaborations. His group frequently includes high school students who have received national recognition in science competitions such as Regeneron (former Intel) Science Talent Search.

C7JA00115K

Marta Costas Rodriguez obtained her Ph.D. from the University of Vigo (Spain) in 2011. Her work focused on the development and evaluation of analytical protocols for elemental determinations in biological samples by ICP-MS. Special attention has been paid to the introduction of miniaturized and green sample preparation procedures preceding different techniques. Since 2012, she has been
a postdoctoral researcher (currently with a postdoctoral fellowship from the Flemish Research Foundation FWO – Flanders) in the ‘Atomic and Mass Spectrometry’ research group at Ghent University (Belgium). Her research interest is the high-precision isotopic analysis by multi-collector ICP-MS and spatial resolution bio-imaging by laser-ablation (MC)-ICP-MS in a biomedical context.

Caroline Welte graduated in Environmental Physics from the University of Heidelberg (Germany) in 2010. During her diploma thesis “$^{36}$Cl in rain and cave drip water” she became involved with the use of radionuclides as tracers in environmental processes and paleoclimate research. She started her doctoral studies in a joint project of Analytical Chemistry and Ion Beam Physics at ETH Zurich. During her PhD her research focused on instrumental developments of spatially resolved radiocarbon ($^{14}$C) analyses of carbonate records combining Laser Ablation and Accelerator Mass Spectrometry. The main purpose was to optimize the $^{14}$C analysis of carbonates and to avoid the labor-intense sample preparation, to be able to acquire spatially resolved $^{14}$C measurements even at the μm scale. Under the title “Laser Ablation coupled with Accelerator Mass Spectrometry for online radiocarbon analysis”, she received her doctor of sciences in 2015. She continued her academic career enrolling in a postdoctoral position at the Laboratory of Ion Beam Physics, ETH Zurich (Switzerland) in 2016, and focused on $^{14}$C analyses of biomedical samples. This project brought her to her current postdoctoral position in the group of Biogeoscience at ETH Zurich (Switzerland). Her main interests are in the combination of instrumental developments of $^{14}$C gas measurements and their applications in order to push the analytical frontiers towards smaller sample sizes and a higher sample throughput.

Paola Mello is adjunct professor at the Chemistry Department, Universidade Federal de Santa Maria (UFSM), Brazil. She obtained her PhD in Chemistry in 2011, at UFSM. She has experience in Analytical Chemistry, focusing on the development of analytical methods and process intensification with ultrasound and/or microwaves. Research projects are devoted to the following subjects: sample preparation for elemental analysis, multielemental determination by ICP-based techniques, speciation analysis and coupled techniques (LC-MS, GC-MS, LC-ICP-MS, GC-ICP-MS). She is researcher at the Brazilian National Council for Scientific and Technological Development.
Laser ablation – inductively couple plasma – mass spectrometry/laser induced break down spectroscopy: a tandem technique for uranium particle characterization†

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Laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) in tandem with laser induced breakdown spectroscopy (LIBS) was employed to chemically map and characterize uranium particles. The uranium particles were doped in various concentrations (0.01, 0.1, 1.0, and 2.0%) to a 50 : 50 Ni : Fe mixture. There was an excellent correlation in regards to concentration and the LA-ICP-MS measurements. In addition, the isotopic composition of the uranium particles was determined within 10% measurement uncertainty. LIBS measurements also showed strong agreement in the particle mapping when compared to the LA-ICP-MS analysis. Moreover, the total analysis time for a 5 × 5 mm area was only 50 minutes. These data suggest that the tandem LA-ICP-MS/LIBS technique can provide rapid and valuable information for nuclear material safeguards and actinide material characterization.

Introduction

The development and application of analytical techniques for particle detection and characterization is increasingly important for nuclear material safeguards, nuclear forensics, and counter proliferation purposes. A primary goal of nuclear material safeguards is to detect sensitive nuclear activities such as uranium (U) enrichment or reprocessing and material movement to quickly and accurately determine the isotopic, elemental, and structural composition of mobile U and other actinide-containing particles. The isotopic composition of U particles is of particular concern to the safeguards community. Of the three naturally occurring U isotopes (234U, 235U, and 238U), only 235U is fissile with thermal neutrons. Small natural fluctuations in the 235U/238U ratio (0.0073) are insignificant compared to enrichment activities related to civilian (0.02–0.05) and military (>0.9) applications. As such, uranium isotopic measurements can provide detailed information about the enrichment activities of a particular installation (natural, enriched, depleted, etc.).

Generally, actinide particles are analyzed by direct non-destructive, minimally-destructive, and destructive methodologies using various instrumentation including scanning electron microscopy (SEM), fission-track-thermal ionization mass spectrometry (FT-TIMS), secondary ionization mass spectrometry (SIMS), laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS), and solution based ICP-MS. Due to the small size of particles (micrometer range) and inherently low mass of analyte, a very sensitive analytical technique is warranted. Methodologies that are typically employed include either bulk analysis of the entire sample or individual particle analysis to determine isotopic signatures. Advantages to individual particle analyses include selectivity and detection of variable isotopic compositions for a given location while bulk analyses provide only average isotopic composition information. The most widely utilized analytical techniques to determine single-particle isotopics are FT-TIMS and SIMS. Wide-range elemental composition is typically independently determined using either SEM with EDX (energy-dispersive X-ray spectroscopy) or micro-XRF (X-ray fluorescence spectroscopy). However, these techniques present limitations including low sample throughput and sensitivity (TIMS), subject to molecular interference bias for minor isotopes (SIMS), and lack of instrument robustness. As such, the viability of alternative techniques such as LA-ICP-MS has been explored for single particle analysis. Moreover, Kappel et al. expanded LA-ICP-MS to the arena of uranium particle analysis, primarily isotopic analysis. Studies by Kappel et al. included utilizing a ns-LA system coupled to a multi-collector ICP-MS for single uranium doped glass particles (10–20 μm) and data treatment strategies for the isotope ratio analysis.

Generally speaking, laser ablation based techniques, including laser induced breakdown spectroscopy (LIBS), are becoming powerful technologies for performing chemical analysis with direct solid sampling. During laser ablation, a pulsed laser beam is focused directly onto the sample surface...
forming a plasma and subsequently removing a finite amount of material. Photons emitted from the laser induced plasma can be detected spectrally (LIBS). The ablated material (particles) can be directed towards a secondary ionization source (e.g. ICP) in which mass spectrometric analysis can be performed. LA-ICP-MS has been reported for high sensitivity elemental analysis along with actinide isotopic determinations. However, a breadth of chemical information is still desirable for nuclear forensic fingerprint identification, and this can be accomplished by the LIBS technique. LIBS is capable of acquiring a wide-range of elemental information especially for low mass elements (e.g. H, C, N, O, and F). By coupling LIBS in tandem with LA-ICP-MS, both elemental and isotopic information can be obtained rapidly (<60 minutes per sample swipe, 5 × 5 mm). LIBS can be used for chemical fingerprinting and LA-ICP-MS employed to characterize the isotopic composition of the particles, greatly improving sample throughput.

To demonstrate the feasibility of this method, the current study utilized a femtosecond (fs) tandem LA-LIBS system coupled with a quadrupole ICP-MS to analyze uranium oxide particles in mixtures of iron and nickel particles. Method reproducibility, accuracy, and sensitivity were evaluated. Moreover, the uranium particles analyzed here were doped at very low concentrations, down to 0.01% in an iron/nickel matrix to demonstrate the ability to map, detect, and characterize single uranium particles in a complex matrix by LA-ICP-MS while analyzing its major constituents (Fe and Ni) by LIBS with just one single laser pulse per location. The capability demonstrated here, LA-ICP-MS/LIBS, has the potential to revolutionize particle analysis for nuclear forensics and materials safeguards.

**Experimental**

**Sample preparation/particle deposition**

Uranium oxide, U₃O₈ (New Brunswick Laboratory CRM 124-1, Lemont, IL, USA), nickel (100 mesh, MP Biomedicals, Solon, OH, USA), and iron powder (Los Alamos National Laboratory research sample, 100 mesh) were gravimetrically prepared such that the uranium composition was 0.01, 0.1, 1.0, and 2.0% in a 50 : 50 Ni : Fe mixture (w/w). A vacuum impactor (Sturmform Gramatneusiedl, Gramatneusiedl, Austria) was utilized with a Gillian 5000 air sampling pump (Sensidyne, St. Petersburg, FL, USA) at 3 L min⁻¹ to deposit the particle mixtures onto double-sided tape. This method has been highlighted in other manuscripts as the “Impaction method” for standard particle characterization by secondary ionization mass spectrometry (SIMS). For standardization on the LA-ICP-MS/LIBS instrumentation, National Institute of Standards and Technology (NIST) standard reference materials (NIST SRMs 610, 612, and 614) were employed.

**Instrumentation**

Here, an Applied Spectra (Fremont, CA, USA) J200 tandem laser ablation – laser induced breakdown spectroscopy (LA-LIBS) system equipped with a 343 nm femtosecond pulsed laser in junction with a Bruker Aurora Elite (Billerica, MA, USA) quadrupole inductively couple plasma – mass spectrometer (ICP-MS) was employed to analyze the deposited particles, illustrated in Fig. 1. The laser utilized here is an S-pulse laser (Amplitude Systemes, Pessac, France) that is directly pumped via laser diodes and employs <400 fs pulses at 1030 nm. The work here triples the frequency to 343 nm.

The LIBS system used a Czerny-turner spectrometer (resolution of 0.14 nm) equipped with an intensified charged coupled device (ICCD) detector. The spectrometer was set to a center wavelength of 215 nm using a 2400 grooves per mm grating. The spectrometer delay (or gate delay) was set to 0.1 μs, gate width set to 3.0 μs, and an intensifier gain of 25 (scale 1–100). A 50 μm laser spot size, determined with the Applied Spectra software, 100 μJ laser energy, and 5× objective lens was employed. For the particle mapping, 51 parallel lines were...
analyzed over a 5 × 5 mm area at 0.1 mm s⁻¹ at a 10 Hz laser repetition rate, resulting in 503 laser pulses per line. This scheme is employed to have overlapping ablation areas as an improvement in resolution can be seen. The total time required for the ablation was 3079 seconds (~51 minutes). The area determined for analysis was centered on the middle of the deposited particles. The vacuum impactor described above “sprays” particles and deposits the majority of them in a circular pattern near the center of the tape. Hence, the ablation region was positioned directly on the center of the deposited particles. Ablation of the sample material was performed in a gas purged chamber (0.9 L min⁻¹) which was successively mixed with argon gas after the plume leaves the ablation chamber. The ablation cell was in close proximity to the ICP-MS unit for optimal analysis. Here, the ICP-MS was set to detect 12C, 13C, 14N, 16O, 17O, 18O, 18Ar, 32S, 34S, 36Cl, 39K, 40K, 42Ca, 44Ti, 47Ti, 48Ca, 50Cr, 50V, 52Cr, 54Cr, 56Fe, 65Zn, 65Cu, 67Ga, 69Ga, 71As, 75As, 77As, 79Br, 81Br, 83Br, 85Br, 87Rb, 89Sr, 91Y, 93Nb, 95Mo, 97Mo, 99Mo, 107Cd, 109Cd, 111Cd, 115In, 117Sn, 113Cd, 115In, and 117Sn. The Ar flow rate for the ICP plasma, auxiliary, and sheath gasses were set to 18.0, 1.80, and 0.50 L min⁻¹, respectively, and the ICP was operated with an RF power of 1.40 kW. The analyses were performed in time resolved mode (55 minutes per sample) with a dwell time of 8 ms for each element and the triggering of the ICP-MS was synchronized by the LA system, meaning the ICP-MS was collecting data for the entirety of the sample analysis (55 minutes). Following the analysis, the time resolved data can be transcribed into the chemical maps depicted in the figures. The ICP-MS detector was optimized at 3160 volts. To account for the saturation of pure Fe, Ni, and U particles, the ICP-MS utilized the attenuation function so that saturation did not occur. The LA-ICP-MS/LIBS method employed for this manuscript was optimized utilizing the NIST glass multi-element standards described above. As seen in Fig. 2, there was excellent agreement when monitoring the 232Th, 235U, and 238U isotopes as a function of concentration. Additionally, the ICP-MS was tuned in order to accurately obtain precise ratio measurements (Th/U intensity = 1). It has been previously described that fs-LA demonstrates little to zero matrix effects; therefore, utilizing the NIST SRMs is efficient for the purpose of this study. The error on the isotope ratio measurements were all <12% (Table 1). While more fine tuning may have improved these measurements (e.g. particle introduction or laser energy), the optimized conditions were sufficient for the purpose of these experiments.

### Results

#### Uranium particle mapping

To investigate the ability to accurately quantify and characterize uranium particles, a matrix consisting of Fe and Ni particles (50:50 w/w) was doped with uranium particles at 0, 0.01, 0.1, 1, 2, and 100%. For all instances, a 5 × 5 mm area was analyzed utilizing laser ablation (fs-LA). fs-LA was selected as it allows for a more homogenous ablation scheme which leads to improved sensitivity, reduced matrix effects, better particle delivery to the ICP, and more precise isotope measurements. Advantageously, fs-LA at this energy/frequency (100 μJ/10 Hz) only ablates a minimal amount of the particle mass, thus leaving the majority of the particles bound to the tape. This is a beneficial facet as the remaining particles could be preserved for subsequent analysis or be used based on specific characteristics (particle sorting). Fig. 3 shows the analyzed area of 100% uranium particles (i.e., no Fe or Ni particles), with the line scanned area in the “after ablation” image and the pronounced appearance of the particles after the analysis was complete. All of the ablation imaging experiments in this manuscript follows the same 5 × 5 mm pattern and all areas show that particles remain bound to the tape. If there is a particular particle of interest, an analysis could be performed directly on that particle without rastering the entire substrate. Fig. 4 depicts a single uranium particle, 33.6 μm in size, before and after a single fs laser shot. The figure clearly illustrates that the particle remains intact, with a minute mass being ablated (fg to ng mass removal). Additionally, this figure depicts the ICP-
MS time-resolved intensity response acquired from a single fs laser shot. Here, $^{238}\text{U}$, $^{56}\text{Fe}$, and $^{60}\text{Ni}$ are monitored and the $^{238}\text{U}$ signals are clearly seen as the particles from the fs laser ablation process enter the ICP plasma. As previously mentioned, these uranium particles are mixed in different percentages of Fe and Ni particles; however, these isotopes are not observed as the laser was focused on a single uranium particle. Again, the ability to ablate and characterize a single uranium particle in a minimally-destructive manner plays a vital role in the detection of small amounts of material for recovery and cross-analysis using complimentary techniques. Traditional solution-based ICP-MS would require particle dissolution prior to introduction, resulting in the loss of the ability to further characterize the material. The retention of the particles could allow for further scrutiny to ensure confidence in nuclear forensic investigations.

Mapping of uranium particles in a nickel and iron matrix

After rastering the particle area, a 3D plot was constructed using the ICP-MS data (Fig. 5). The signal intensity from the ICP-MS is converted into an x–y–z matrix, with the x and y coordinates corresponding to the laser ablation event on each sample. The z direction corresponds to the signal intensity for each x–y position. The data analysis software from Applied Spectra, Inc. allows for simple transformations of large data sets to 2D and 3D elemental maps. This instance was from the sample containing 1.0% uranium by weight that, as the figure illustrates, represents approximately six uranium-rich areas (particles).

The $^{56}\text{Fe}$ and $^{60}\text{Ni}$ particles are seen in the top portion of the figure while the $^{235}\text{U}$ and $^{238}\text{U}$ isotopes are represented in the bottom. Even in the myriad of $^{56}\text{Fe}$ and $^{60}\text{Ni}$ particles, “the forest”, six isolated U regions, “trees”, can be identified and characterized. In addition to identifying uranium particles, their isotopic composition can be determined. Fig. 5 illustrates both $^{235}\text{U}$ and $^{238}\text{U}$ data, but this characterization tool will be described later. It should be noted, that this analysis and data processing, in its entirety, took less than 1 hour per sample.

Calibration of uranium particles in a nickel and iron matrix

The matrix consisting of nickel and iron particles was doped with uranium particles in varying concentrations including 0.01, 0.1, 1.0, and 2.0% in addition to a blank (no uranium) and 100% uranium particles. After analysis, 3D (Fig. 6a) and 2D (Fig. 6b) elemental images were constructed.

These data provide evidence that the technique was successful in mixing, depositing, and ablating the particles with a response that is quantitatively proportional to the uranium concentration in the covered area. Fig. 6a demonstrates an increasing number of spikes with the increase of uranium concentration as it relates to the increased probability of a uranium particle being deposited in the area analyzed. It should be noted that this method does not account for particle size. The laser spot size employed here was 50 µm and these particles may range in size (Fig. 4 describes a 33.6 µm particle). There is a realization that increased mass ablated would be correlated to particle size, if the assumption is made that the particle in its entirety was ablated. Additionally, the varying “particle size” seen in Fig. 6b could also be due to stacked or clumped particles in a specific area. With that said, the uranium was doped in the matrix by weight, not by the number of particles.

While indeed both Fig. 6a and b have very similar representations each plot could provide their own benefits. For

Fig. 3 Stitched image of uranium particles before and after fs-LA.

Fig. 4 fs-LA-ICP-MS on a single uranium particle (33.6 µm diameter).
example, if a particular particle was of interest and further analysis was warranted, the 2D plot in Fig. 6b would be valuable for determining particle location on the $x$-$y$ plane. The 3D plot, Fig. 6a, could be useful for visualizing abundance. The ability to visualize the counts on the $z$-axis could prove beneficial, particularly when isotopic determinations are required (i.e. for uranium enrichment detection).

Statistical analysis was performed on the uranium concentrations and the response curves are represented in Fig. 7. The first graph (a) monitors $^{238}\text{U}$ isotopic integrated intensity as
LA-ICP-MS particle analysis for uranium isotopics

Pertaining to the field of nuclear forensics and material safeguards, obtaining high-fidelity isotope ratios is warranted, especially in the realm of non-proliferation. During the analysis of the doped uranium particles, various isotopes of uranium were analyzed and summarized as a ratio of integrated counts in Table 2. The measured $^{235}\text{U}/^{238}\text{U}$ ratios were fairly close to the expected value, 0.0073 (±10% error). Obtaining this accuracy with no sample preparation and a relatively rapid analysis time could prove invaluable for nuclear forensic and safeguard applications. Attention should be brought to the fact this study was compared to the techniques of fs-LA-MC-ICP-MS, solution based MC-ICP-MS, and TIMS and had excellent correlation between the techniques and the values determined for a set of NIST glasses.

Particle mapping by laser induced breakdown spectroscopy (LIBS)

In addition to performing LA-ICP-MS analysis, this tandem LA-LIBS system from Applied Spectra, Inc., allows for obtaining LIBS measurements simultaneously. LIBS allows for the detection of low mass elements that are traditionally impossible to analyze using ICP-MS such as H, He, C, N, O, F, etc. LIBS can also measure major impurities that could be present in the percent level such as Fe, Ni, etc. In the event a MC-ICP-MS is employed, generally less than 10 isotopes can be monitored simultaneously (number of channels may range depending on MC model), making it impossible to detect other impurities in single U particles during one ablation event. Fig. 8 demonstrates the capabilities that LIBS can provide in single particle characterization. This figure depicts the analysis performed on the 1.0% uranium mixture. It should be noted that this one analysis was in situ with the LA-ICP-MS data previously described. The spectrometer was set to a center wavelength of 215 nm, such that the atomic lines of carbon (C 193 nm), iron (Fe 238 nm), and nickel (Ni 231 nm) were monitored in the same spectral window region. The corresponding elemental images were plotted in Fig. 8.

The carbon image in Fig. 8 shows where the double-sided tape (used to hold particles in place) was ablated with no particles present. A void in the C response corresponds to the laser ablating a particle only and none of the double sided tape. The Fe and Ni images correspond directly to the Fe and Ni particles present on the tape. The same correlation was achieved for the carbon images, especially when the fs-LA system is coupled with a multi-collector ICP-MS, more precise and accurate measurements is expected.

A separate method (LA-ICP-MS) devoted to isotope ratio measurements is applied to the specific particle itself (once located), then higher fidelity isotope ratios could be acquired. Especially, when the fs-LA system is coupled with a multi-collector ICP-MS, more precise and accurate measurements is expected.

Table 2. Uranium isotope ratio measurements from fs-LA-ICP-MS

<table>
<thead>
<tr>
<th>% of uranium</th>
<th>U-$^{235}\text{U}$/U-$^{238}\text{U}$</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.0064</td>
<td>−8.56</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0064</td>
<td>9.29</td>
</tr>
<tr>
<td>1</td>
<td>0.0072</td>
<td>2.28</td>
</tr>
<tr>
<td>2</td>
<td>0.0076</td>
<td>8.34</td>
</tr>
<tr>
<td>100</td>
<td>0.0068</td>
<td>−3.11</td>
</tr>
</tbody>
</table>

a function of total U particles. Here, the entire map was integrated and the $^{235}\text{U}$ was plotted (correlation coefficient = 0.9819). In the second instance (b), the integrated ratio is reported as $^{238}\text{U}/^{56}\text{Fe} + ^{60}\text{Ni}$ to account for the error in the particle deposition due to the variability of particle deposition using the impactation method. Here, it can be seen that after the normalization to the Fe and Ni particles, the correlation was indeed improved. The third plot (c) includes the 100% uranium particles to demonstrate the linear dynamic range of the method.

![Fig. 7 Calibration curves of uranium particle analysis by fs-LA-ICP-MS.](image-url)
observed with the LA-ICP-MS results in Fig. 6. An overlay of the emission spectra from the C, Fe, and Ni particles can be seen in Fig. 9. Moreover, the U emission lines (from LIBS) show similar plots as constructed to display LA-ICP-MS data (Fig. 6). However, for the sake of redundancy, these data were excluded from the manuscript.

As this work demonstrates, LIBS can provide excellent complimentary information to LA-ICP-MS. The use of this tandem system will be integral for performing rapid analysis especially when there are sample limitations (e.g. single particles). This will provide an invaluable tool for nuclear forensic studies and nuclear material safeguards that require rapid, high-fidelity isotopic information with simultaneous major-element data as a signature for material attribution and other applications.

Conclusions

LA-ICP-MS/LIBS methodology was employed to map and characterize uranium particles in a complex matrix of iron and nickel particles. It was determined that this technique is capable of not only obtaining isotope ratio measurements from the uranium particles, but also quantifying them based on abundance. Single uranium particles were located and characterized. Additionally, the particles were simultaneously scrutinized by LIBS which can be beneficial particularly when multi-collector ICPs are employed due to the limited number of isotopes that can be monitored simultaneously. Future studies will focus on using tandem configuration operated in conjunction with a MC-ICP-MS.

References