

EWLA BERN2022
EUROPEAN WORKSHOP ON LASER ABLATION 12.07 - 15.07.2022



© Bern Welcome

Conference Booklet



www.ewla2022.ch

ESLumen

FULL ELEMENTAL COVERAGE

LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

FEATURES

- DETECTION OF EVERY ELEMENT ON THE PERIODIC TABLE
- DETECTION OF DIFFICULT ELEMENTS
 - INCLUDING H, O AND F
- MULTIPLE CONFIGURATIONS AVAILABLE DEPENDING UPON APPLICATION NEED
 - MULTI-CHANNEL CCD BASED DETECTOR
 - FULL SPECTRA FROM 190-1100 NANOMETER



Complementary technique for LA-ICP-MS, especially when performing imaging experiments on a quadrupole ICPMS

Expands elemental coverage – high ionization potential elements such as F and atmospheric elements such as H, N and O.

Increases the dynamic range of laser ablation experiments to cover sub-ppb (LA) to % range (LIBS)

- Requirements to add LIBS: TwoVol3 laser ablation chamber and iolite software



Image courtesy of Oak Ridge National Laboratory

Image of the fiber optics from a CCD (ESLumen) and ICCD detector connected to the TwoVol3

Welcome

Dear Colleagues,

It is a great pleasure to welcome you to the 2022 edition of the European Workshop on Laser Ablation in Bern, Switzerland. While initially planned for 2020, we are very proud to be able to organise this in-person event this year and hope you will enjoy it.

As we gather here, we bring together a diverse community unified by one objective: to learn more about laser ablation. Over the next few days, we will discuss the fundamental aspects of ablation, hear about the progress in elemental mapping, and see the latest data analysis tools to visualise the complex data and simulations. At the same time, we will celebrate the big impact that laser ablation makes on research and see the latest highlights in fields ranging from geology and archaeology to material and life sciences.

We are highly grateful for the support and generosity of our sponsors, who are pivotal in the successful organisation of this years EWLA. It goes without saying that without them our event would not be possible.

While the keynotes, talks, and poster sessions are the driver of this workshop, let's not forget about the social programme. There will be many opportunities to enjoy and explore the historic city of Bern with our colleagues and friends, and strengthen the bonds in our community.

On behalf of the EWLA2022 LOC and SOC, I wish you a warm welcome to Bern and look forward to an engaging workshop.

Andreas Riedo
Conference Chair

Scientific Organising Committee

Detlef Günther, ETH Zürich, Switzerland

Jhanis J. Gonzalez, Lawrence Berkeley National Laboratory, USA

Christophe Pécheyran, University of Pau et des Pays de L'adour - CNRS, France

Jorge Pisonero, University of Oviedo, Spain

Wolfgang Müller, Goethe-Universität Frankfurt, Germany

Johannes T. van Elteren, National Institute of Chemistry, Ljubljana, Slovenia

Frank Vanhaecke, Ghent University, Belgium

Andreas Riedo, University of Bern, Switzerland

Peter Wurz, University of Bern, Switzerland

Marek Tulej, University of Bern, Switzerland

Local Organising Committee

Andreas Riedo (Chair)

Niels F.W. Ligterink (Technical organiser)

Valentine Grimaudo-Riedo (Technical organiser)

Nikita J. Boeren (Technical organiser)

Coenraad P. de Koning (Technical organiser)

Salome Gruchola (Technical organiser)

Kristina A. Kipfer (Technical organiser)

Peter Keresztes Schmidt (Technical organiser)

Luca N. Knecht (Technical organiser)

Peter Wurz (LOC advisor)

Marek Tulej (LOC advisor)

Partners

Platinum Partner



Gold Partners



Silver Partner



Partners



Norris
Scientific



SCS
Swiss Chemical
Society
Division of
Analytical Sciences

We thank all our partners for their support

Conference Venue

The venue for EWLA2022 is the University of Bern's vonRoll Auditorium located in the North-Western part of Bern. This former factory area was converted in 2013 to a new university campus. Many elements of their industrial origin can still be seen, both outside and inside these buildings.



Venue address: vonRoll Auditorium, Fabrikstrasse 6, 3012 Bern, Switzerland.

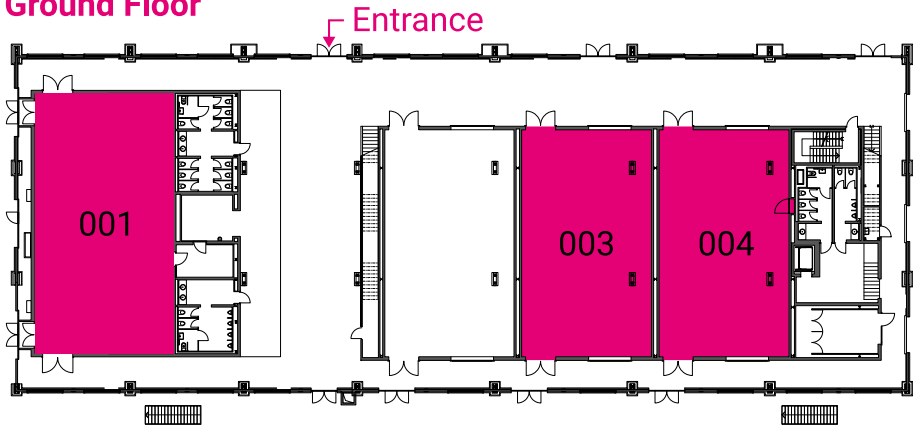
u^b

b
**UNIVERSITY
OF BERN**

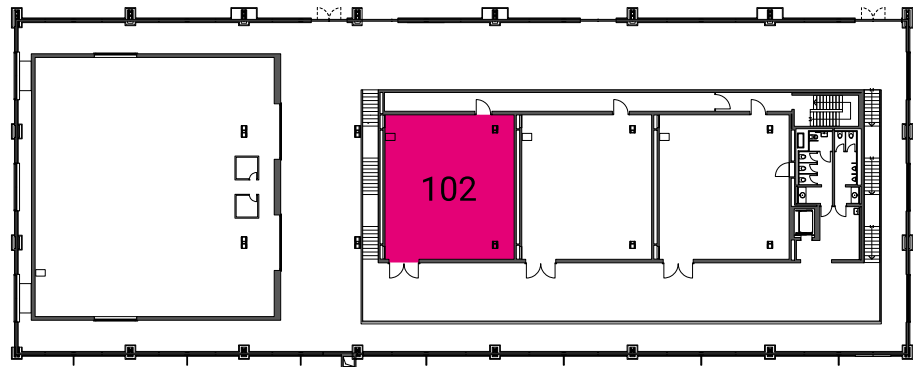
We thank the University of Bern for their support in organising EWLA2022

Floor Plan

Ground Floor



First Floor



Internet Access

eduroam is available in every building of UniBe. For guests with no access to eduroam, **public-unibe** WiFi network is available. Please contact the welcome desk to receive the access code for the public WiFi network.



HDIP 1.7

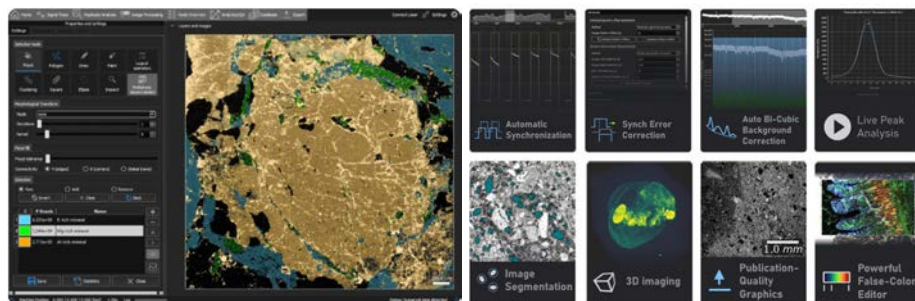
Mass Spectrometry Data Analysis



Accelerate Your Research

State-of-the-Art Software For LA-ICP-MS

HDIP® is a premiere, state-of-the-art data processing solution for LA-ICP-MS on Teledyne Photon Machines laser systems. It offers everything a lab needs to complete any laser ablation project and drastically reduces the time spent on data processing and analysis. The commercial license includes 5-year professional support and updates, to ensure that HDIP provides the best value to our customers.

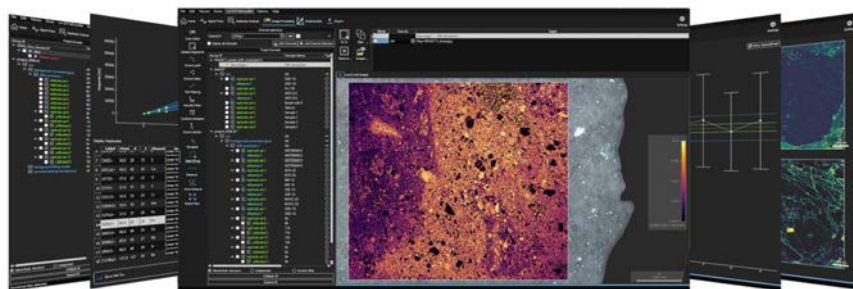


HDIP can generate fully calibrated multi-mega-pixel elemental/isotopic image maps and can produce images from any combination of laser pattern, with omnidirectional support, as well as arbitrary shapes of the ablation zone, using one of 5 advanced image reconstruction algorithms. With the advanced image analysis tools of HDIP, you can interrogate the elemental distribution in multi-mega-pixel images with hundreds of mass channels and gain deep insights in relational patterns between sub-domains in your multi-phase image. Automated segmentation and image feature recognition allow to dissect the image and extract particles, boundary mixing layers, cells, inclusions, ...

Superior Images Through Software Optimization

Accurate And Reliable Analysis

Whether you are interested in ultra-trace levels or major levels, HDIP offers a solution for a semi/fully quantitative elemental characterization for any matrix. The combination of multi-calibrant drift-corrected calibration curves, internal standardization, normalization, error propagation and limit of detection calculations within HDIP allow for complex experiments and batch runs of 1000's of samples.



Social Programme

Ice Breaker and Opening

When: Tuesday, 12 July 2022, 18:00 – 22:00

Where: vonRoll conference venue, Fabrikstrasse 6, 3012 Bern

Social Dinner

When: Wednesday, 13 July 2022, 18:00 – 00:00

Where: Restaurant Rosengarten, Alter Aargauerstalden 31B, 3006 Bern

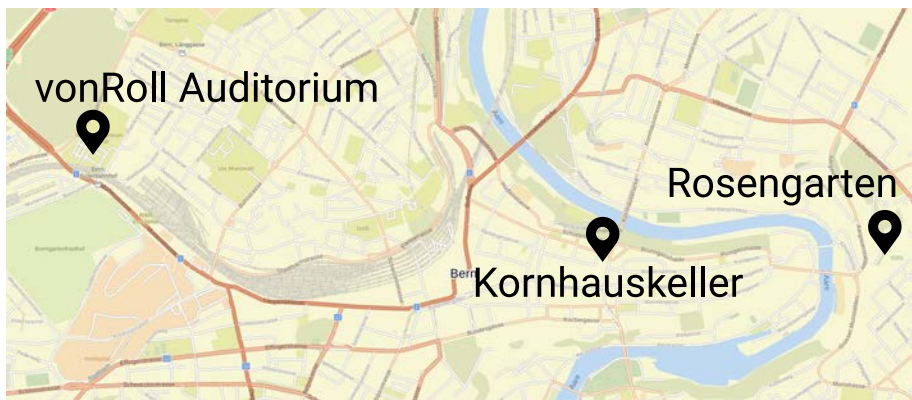
Info: From the venue, take the bus to the main station (**Bern, Hauptbahnhof**), and from there take the bus to station **Rosengarten**. Please check the website www.sbb.ch for further information.

Gala Dinner

When: Thursday, 14 July 2022, 18:00 – 00:00

Where: Restaurant Kornhauskeller, Kornhausplatz 18, 3011 Bern

Info: From the venue, take the bus to the main station (**Bern, Hauptbahnhof**), and take the tram or bus to the stop **Zytglogge**, which is in front of the restaurant.



All the elements.
All the time.

With high-speed, simultaneous analysis of all isotopes, the icpTOF is the ideal ICP-MS detector for fast laser ablation imaging in geological, biomedical, and environmental laboratories throughout the world.



icpTOF

**All the elements.
All the time.**

The icpTOF always records complete mass spectra, so you never miss an analyte or interference signal.

High mass resolution.

The icpTOF 2R has a mass resolving power of 6000 allowing you to separate interfering ions.

Precise isotope ratios.

The icpTOF simultaneously measures all isotopes, thus eliminating the susceptibility of your measurements to source and sample fluctuations. Precision approaches statistical limits.

High speed detection.

The icpTOF records a complete mass spectrum every 12-50 μ s making it the optimum detector for fluid inclusions and laser ablation pixels.

TOFWERK

icp.info@tofwerk.com
tofwerk.com

Scientific Programme

Registration

- Tuesday, 12 July 2022, 18:00 – 22:00
- Wednesday, 13 July 2022, 08:00 – 09:00
- Thursday, 14 July 2022, 08:00 – 08:30
- Friday, 15 July 2022, 08:00 – 08:30

Privacy Policy

Please, **DO NOT PHOTOGRAPH OR FILM** any presentation, person, or activity during the workshop without the explicit consent of the people involved.

Programme changes

Due to circumstances beyond the control of the organisation, last minute changes to the programme may be unavoidable. All information in this programme is on the basis of the information as at the day of printing (**6 July 2022**).

Lunch Seminars and Visit

Wednesday, 13 July 2022

12:30 - 13:15 in Room 003

Elemental Scientific Lasers

Expanding the capabilities of laser ablation imaging with the TwoVol3 (TV3) ablation chamber



12:30 - 13:15 in Room 004

TOFWERK/Photon Machines

Geo-applications of Laser Ablation – hardware and software updates



Thursday, 14 July 2022

12:30 - 13:15 in Room 003

Elemental Scientific Lasers

New features and capabilities of the *iolite* LA-ICP-MS (and beyond) Data Reduction Platform



12:30 - 13:15 in Room 004

TOFWERK/Photon Machines

Analysis of biological samples using LA-ICP-TOFMS – recent application highlights



12:30 - 13:15 in Room 102

Agilent

Recent development in ICP-MS/MS technology and laser ablation



For more details on the seminars please check the online schedule.



www.ewla2022.ch/programme

Wednesday, 13 July 2022

Start	End			Speaker	Page
09:00	09:10		Welcome session	A. Riedo	
09:10	09:40	PL01	Keynote: Laser ablation-ICP-mass spectrometry: from a micro-analytical tool for direct bulk analysis to a fast elemental mapping technique	T. van Acker	18
09:40	09:47		Partner talk: Elemental Scientific Lasers		
09:47	10:15		Coffee break		
Oral presentations					
10:15	10:32	C008	ICP-MS isotopic analysis using ns laser ablation for sample introduction	F. Vanhaecke	19
10:32	10:49	C004	Advanced technology for automated and high throughput LA-ICP-TOFMS element imaging	C. Neff	20
10:49	11:06	C005	Aligned LA-ICP-QMS Eliminates Aliasing From Images Collected With Fast-Washout Cells	A. Norris	22
11:06	11:23	C006	Single pulse, multiple dosage, and 2d oversampling / deconvolution imaging strategies compared and evaluated for best image quality	M. Šala	23
11:23	11:40	C007	The use of time of flight ICP-MS and very fast washout, high repetition rate laser ablation to image marine bio-carbonates. Insights into the growth processes and environmental contamination	P. Shaw	24
11:40	11:57	C002	Real matrix-matched calibration strategy for the quantification of neurodegeneration-related proteins in single human epithelial cells by LA-ICP-MS using specific metal-labelled antibodies	A. Lores Padin	26
11:57	12:04		Partner talk: TOFWERK		
Lunch					
12:04	13:30		12:30-13:15 Lunch Seminar by Elemental Scientific Lasers 12:30-13:15 Lunch Seminar by TOFWERK/Photon Machines		
13:30	14:00	PL02	Keynote: Automated, Three-dimensional and Sub-micron Accurate Ablation-volume Determination by Inverse Molding and X-ray Computed Tomography	E. Lörtscher	27
Oral presentations					
14:00	14:17	L002	Elemental composition of PM deposited on quartz fiber filter by LA-ICPMS	M. Orgizek	28
14:17	14:34	L001	Investigation of the Imidization Degree of Polyimides using Laser Induced Breakdown Spectroscopy (LIBS)	B. Achleitner	30
14:34	14:51	C003	Application of Diffusive Gradients in Thin Films (DGT) in Combination with LA-ICP-MS for the Spatial Investigation of Aluminium Corrosion	G. Mukhametzianova	31
14:51	15:08	L003	A multi-method approach for tracing non-metallic inclusions in steel	C. Walkner	32
15:08	15:40		Coffee break		
Oral presentations					
15:40	15:57	A001	Critical considerations in single particle analysis by laser ablation inductively coupled plasma mass spectrometry	D. Metarapi	34
15:57	16:14	B001	Impact of Ablation Cell Design in LA-ICP-MS on Elemental Fractionation	P. Becker	35
16:14	16:31	C001	Enhanced Detection Capabilities of a Novel Laboratory-Scale fs-LIMS Instrument through Mass-Selective Beam Blanking	C. de Koning	36
16:31	16:48	G001	Quantitative depth profiles in novel materials by combined consideration of online Laser Ablation of solids in liquids and LA-ICP-MS	M. Podsednik	38
16:48	17:05	H001	Investigation of Polymer ageing by combined LIBS and LA-ICP-MS analysis	J. Willner	39
17:05			End of scientific programme		
18:00	19:00		Aperitif Social Dinner, Restaurant Rosengarten		
19:00	00:00		Social Dinner, Restaurant Rosengarten		

Thursday, 14 July 2022

Start	End		Speaker	Page
08:30	09:00	PL03 Keynote: Laser Ablation / Ionisation Mass Spectrometry	P. Wurz	40
Oral presentations				
09:00	09:17	I006 LIMS: A novel measurement technique for the detection of life beyond Earth	A. Riedo	42
09:17	09:34	I001 Prototype Laser Desorption Ionization Mass Spectrometer for in situ lipid detection on Ocean Worlds	N. Boeren	43
09:34	09:51	I002 The breakthrough potential of LA-ICP-MS for understanding the chemical stratigraphy in deep polar ice cores	P. Bohleber	44
09:51	09:58	Partner talk: Teledyne		
09:58	10:30	Coffee break		
Oral presentations				
10:30	10:47	I005 ION4RAW: Inventory of by-products and critical raw materials in the El Porvenir Pb-Zn ore deposit through combined laser ablation ICP-MS, electron microprobe and micro-XRF mapping	C. Lerouge	46
10:47	11:04	I007 Comparison of the homogeneity of powdered geological materials prepared by four different methods for multi-elemental analysis by LA-ICP-MS	M. Susset	47
11:04	11:21	I008 Machine Learning Assisted Emerald Classification using 50+ Elements Analyzed by LA-ICP-TOF-MS	H. Wang	48
11:21	11:38	I004 I2DTool : U-Pb geochronology data treatment for dummies	P. Lach	50
11:38	11:55	I003 Rapid high-resolution Rb-Sr isotope mapping for geochronology	M. Kutzschbach	51
11:55	12:02	Partner talk: Agilent		
12:02	13:30	Lunch 12:30-13:15 Lunch Seminar by Elemental Scientific Lasers 12:30-13:15 Lunch Seminar by TOFWERK/Photon Machines 12:30-13:15 Lunch Seminar by Agilent		
13:30	14:00	PL04 Keynote: U/Th dating by fs-LA SF-ICP-MS isotope imaging: new perspectives for archeological biominerals	A. Galy	52
Oral presentations				
14:00	14:17	E001 Application of fs-LA-MC-ICP-MS for the simultaneous analysis of U and Pu isotope ratios in single particles of interest for IAEA safeguards	S. Konegger-Kappel	54
14:17	14:34	E002 In situ isotopic ^{238}U - ^{234}U - ^{232}Th - ^{230}Th dating analysis using LA-ICPMS	C. Wu	55
14:34	14:51	K001 Chemical heterogeneities documented in Iron Age glass artefacts from the Dacian fortress of Ardeu (Hunedoara County, Romania) – the case for using LA ICP MS elemental imaging	A.C. Casalean	56
14:51	16:30	Poster session		
16:30		End of scientific programme		
18:00	19:00	Aperitif Gala Dinner, Restaurant Kornhauskeller		
19:00	00:00	Gala Dinner, Restaurant Kornhauskeller		

Friday, 15 July 2022

Start	End			Speaker	Page
08:30	09:00	PL05	Keynote: The X-Factor in Laser-Assisted Solid Microanalysis	D. Bleiner	58
Oral presentations					
09:00	09:17	F001	Three Machine Learning Approaches for the Identification of Signatures of Life in Laser Ablation Ionization Mass Spectrometry	S. Gruchola	59
09:17	09:34	DO01	Micro-droplet-based calibration for quantitative elemental bioimaging by LA-ICPMS	A. Schweikert	60
09:34	09:51	JO04	Elemental distribution in shark teeth using high-speed LA-ICPMS imaging	D. Quarles	62
09:51	10:30	Coffee break			
Oral presentations					
10:30	10:47	JO03	Deciduous teeth as retrospective biomarkers of fetal metal exposure	T. Punshon	63
10:47	11:04	JO05	High-resolution LA-ICP-TOFMS imaging of asbestos fibers in human malignant mesothelioma tissue	S. Theiner	64
11:04	11:21	JO06	Unraveling the interaction of MRI contrast agents with tissue using LA-ICP-MS	H. Traub	66
11:21	11:38	JO02	Elemental and lipid bioimaging of atherosclerotic rabbit artery tissue by complementary use of LA-ICP-MS and MALDI-MSI	P. Niehaus	67
11:38	11:55	JO01	Application of multi-modal imaging to answer biological questions at the London Metallomics Facility	A. Morrell	68
11:55	12:15	Closing ceremony			
12:15	13:30	Lunch			
13:30		End of EWLA 2022			
13:30	18:00	Visit to TOFWERK Headquarters, Thun			

imageGEO 193

THE ULTIMATE PERFORMANCE FOR LASER ABLATION GEOIMAGING

THE ONLY LASER ABLATION SYSTEM DESIGNED
FOR MAXIMUM PERFORMANCE IN GEOIMAGING

FEATURES

- RAPID IMAGE PROCESSING
- 1 MS PEAK WIDTHS
- 1-220 μM SPOT SIZES
- 20X VIEWING OPTION

Water-cooled, 500 Hz
(or 1 kHz upgrade option)
laser frequency speeds up
the imaging process.

Equipped with ESL's TwoVol3
and DCI technology providing
1 ms peak widths for up to
1000 pixels per second.

"Imaging Mode" ensures control of
laser dosage and pixel overlap.

20x viewing (upgrade option)
provides ultimate clarity when
viewing geological specimens
with resolution $<0.55 \mu\text{m}$.



Abstracts

All oral presentation abstracts are given on the next pages.

The poster presentation abstracts can be found online by scanning the QR code below, or by visiting the web page listed below.



www.ewla2022.ch/poster-abstracts

Laser ablation-ICP-mass spectrometry: from a micro-analytical tool for direct bulk analysis to a fast elemental mapping technique

Thibaut Van Acker¹, Tom Van Helden¹, Stijn J.M. Van Malderen², Frank Vanhaecke¹

¹Atomic & Mass Spectrometry – A&MS Research Group, Department of Chemistry, Ghent University, Campus Sterre, Krijgslaan 281-S12, 9000 Ghent, Belgium.

²Teledyne Photon Machines, 384 Gallatin Park Dr., Bozeman, MT 59715, USA

Inductively coupled plasma-mass spectrometry (ICP-MS) is considered a well-established and robust analytical technique for trace elemental and isotopic analysis. It is characterized by its low limits of detection (down to the pg/L level), multi-elemental capabilities, a wide linear dynamic range and high sample throughput. The standard sample introduction system is composed of a peristaltic pump to transport the sample solution to the nebulizer and spray chamber, to generate a fine aerosol that can be introduced into the ICP ion source. When coupling a laser ablation (LA) unit to an ICP-mass spectrometer as alternative sample introduction system, direct solid sample analysis is enabled. A highly energetic pulsed laser beam is used to irradiate the solid sample surface and upon ablation, a dry aerosol (particle plume) is generated and transported away from the ablation chamber into the ICP ion source using a carrier gas. Apart from advantages such as low sample consumption and no requirement for sample dissolution, the main advantage is that spatially resolved information can be obtained.

Since the first application of LA-ICP-MS in 1985 by Gray et al. [1], many fundamental studies were focused on evaluating different types of lasers in terms of wavelength to improve the analytical performance, resulting in a clear shift towards deep-UV lasers [2]. In 2002, Russo et al. [3] demonstrated the first use of femtosecond lasers for LA-ICP-MS. After that, the main focus was on improving the aerosol transport by designing new ablation chambers of the 'two-volume type'. Since the introduction of 3rd generation low-dispersion ablation cells by Wang et al. [4] in 2013, many different ablation cell designs have been developed and elemental mapping via LA-ICP-MS has gained significant momentum and is being applied in many research fields ranging from geo- and cosmochemistry to biomedicine and the pharmaceutical sciences. Minimizing the aerosol dispersion maximizes the temporal analyte concentration spike in the ICP, which creates an enhancement of the signal-to-noise (S/N) ratios. Recent hardware developments are pushing the limits towards kHz pixel acquisition rates and time-of-flight (TOF) based ICP-mass spectrometers are considered the go-to instruments for dealing with these short transient signal profiles given their quasi-simultaneous monitoring capabilities across the entire elemental mass range.

[1] A.L. Gray, *Analyst*, 1985, 110, 551-556.

[2] D. Günther, R. Frischknecht, C.A. Heinrich, H.J. Kahlert, *J. Anal. At. Spectrom.*, 1997, 12, 939-944.

[3] R.E. Russo, X. Mao, J.J. Gonzalez, S.S. Mao, *J. Anal. At. Spectrom.*, 2002, 17, 1072-1075.

[4] H.A.O. Wang, D. Gromund, C. Giesen, C. N. Borca, J. R. H. Shaw-Stewart, B. Bodenmiller, D. Günther, *Anal. Chem.*, 85, 21, 10107-10116.

ICP-MS isotopic analysis using ns laser ablation for sample introduction

Frank Vanhaecke¹, Eduardo Bolea-Fernandez¹, Stepan Chernonozkin¹, Patrick Degryse², Steven Goderis³, Claudia Gonzalez-de Vega¹, Thibaut Van Acker¹, Alicia Van Ham-Meert², Stijn J.M. Van Malderen¹

1. Atomic & Mass Spectrometry – A&MS research group, Department of Chemistry, Ghent University, Campus Sterre, Krijgslaan 281-S12, 9000 Ghent, Belgium. E-mail : frank.vanhaecke@ugent.be

2. Earth and Environmental Science, Centre for Archaeological Science, KULeuven, Celestijnenlaan 200e, 3001 Heverlee, Belgium

3. Analytical-, Environmental-, and Geo-Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium

While LA-ICP-MS is considered a mature tool for bulk and spatially resolved (including depth profiling analysis and 2-D elemental mapping) elemental analysis, the use of LA as an introduction system in the context of isotopic analysis using ICP-MS (except for zircon dating) is more scarce. In this presentation, it will be shown that a commercially available ArF*excimer-based LA-system working in the nanosecond regime can be successfully used in this context by discussing applications from various research areas.

In ecotoxicology, *Daphnia* are often relied on for biomonitoring surface water quality. It has been shown that high levels of both waterborne and dietary Zn affect the well-being of these animals. Laser ablation ICP-MS and synchrotron radiation – X-ray fluorescence spectrometry (SR-XRF) revealed tissue-specific bioaccumulation and provided insight into the reproductive toxicity established. The kinetics of the assimilation of Zn could be demonstrated using a combination of LA-ICP-MS isotope ratio mapping with a tracer experiment with isotopically enriched Zn.

The ⁸⁷Sr/⁸⁶Sr isotope ratio needs to be determined in the contexts of Rb/Sr dating and provenance determination of, e.g., agricultural products of animal and plant origin and archaeological artifacts and typically requires chromatographic Rb-Sr separation to avoid isobaric overlap of the signals of parent (⁸⁷Rb) and daughter (⁸⁷Sr) nuclides at a mass-to-charge ratio m/z = 87. By pressurizing the collision/reaction cell of a tandem ICP-MS (ICP-MS/MS) instrument with CH₃F, Sr⁺ ions are converted efficiently into the corresponding SrF⁺ reaction product ions, the intensity of which can be measured free from spectral overlap. This enables the use of LA-ICP-MS/MS for direct (i.e. without dissolution) Sr isotopic analysis of natural and synthetic glassy materials.

Also in cosmochemistry, isotopic analysis is essential. We have developed a method based on the combination of LA and MC-ICP-MS for Fe isotopic analysis of glassy cosmic spherules (micrometeorites with a diameter of 400–800 μm). After method development, optimization and validation, it was deployed to obtain a more profound insight into the processes taking place during hypervelocity impacts.

Advanced technology for automated and high throughput LA-ICP-TOFMS element imaging

Christoph Neff¹, Pascal Becker¹, Peter Keresztes Schmidt¹, Gunnar Schwarz¹, Paolo S. Garofalo², Detlef Günther¹

¹ Laboratory of Inorganic Chemistry, ETH Zürich, 8093 Zurich, Switzerland

² Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Università di Bologna, 40126 Bologna, Italy

Laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOFMS) element imaging is a high resolution, high sensitivity and multi-element detection technique and provides valuable information of the distribution of major to trace elements within solid materials. We present an advanced LA-ICP-TOFMS element imaging setup for fast, robust and automated data acquisition. Further development of the tube ablation cell¹ leading to the parallel flow ablation cell (PFAC) allows for fast and reliable aerosol transport. The PFAC achieves shortest signal duration so far of 0.25 ms (full width at 10% of the maximum) for laser ablation sample introduction and ICP-MS detection.² The imaging control system (ICS) synchronizes the control of the translation stage, the laser and the TOFMS data acquisition and allows a virtually automated analysis.³ In addition, with the ICS multiple ablation modes can be applied according to the requirements of the application. For example, a single pulse mode allows the fast scanning of the area of interest or a hole-drilling mode to achieve lower limits of detection by a factor of 10-20. The triggered data acquisition for every ablation position leads to binned pixel data in relation to the sample position. This simplifies the data evaluation and allows for simplified quantification and image generation, and reduces the time for data evaluation. The figures of merit are demonstrated by the measurement of common reference materials for LA-ICP-MS and exemplified by quantitative element imaging of geological samples.

[1] H. A. Wang, D. Grolimund, C. Giesen, C. N. Borca, J. R. Shaw-Stewart, B. Bodenmiller and D. Günther, *Anal Chem*, **2013**, *85*, 10107-10116. Reference

[2] C. Neff, P. Becker and D. Günther, *Journal of Analytical Atomic Spectrometry*, **2022**, *37*, 677-683.

[3] C. Neff, P. Keresztes Schmidt, P. S. Garofalo, G. Schwarz and D. Günther, *Journal of Analytical Atomic Spectrometry*, **2020**, *35*, 2255-2266.

Aligned LA–ICP–QMS Eliminates Aliasing From Images Collected With Fast-Washout Cells

C A Norris¹, A Greig², B Paul^{2,3}, N West¹

¹Norris Scientific, Kingston, TAS, 7050, Australia

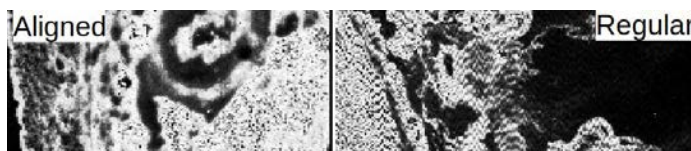
²University of Melbourne, Parkville, VIC, 3010, Australia

³Elemental Scientific Lasers, LLC., 685 Old Buffalo Trail, Bozeman, MT 59715, USA

Imaging by LA–ICP–MS is a powerful and useful technique with a wide range of applications in the earth, material, and biological sciences^{[1][2]}. When using a sequential mass spectrometer, such as a quadrupole, it is necessary to avoid certain conditions otherwise images will be marred by artefacts caused by aliasing. One way to eliminate aliasing is to lengthen the response time of the ablation cell, but since optimal imaging conditions couples acquisition time to response time, doing so is fundamentally at odds with the objective of collecting images that contain millions of pixels and require many days of ICP time^[3].

Our new approach^[4] is to align the firing of the pulsed laser with the sweep time of the quadrupole mass spectrometer. We call this *aligned* LA–ICP–QMS and the technique can be implemented by way of an external circuit that monitors the mass filter position of the mass spectrometer in real time and fires the laser as required.

We have collected a series of images (see example in the Figure below) from biological and mineral samples which demonstrate that aligned LA–ICP–QMS is an effective approach to imaging, that can eliminate aliasing, and by doing so makes it feasible to use fast-washout cells (e.g. washout time to 1% < 50 ms) for effective imaging using quadrupole mass spectrometers.



Laser ablation ICP–QMS image showing 66Zn intensity in a mouse embryo tissue section. The left half was acquired using aligned LA–ICP–QMS and the right half as regular LA–ICP–QMS, i.e. without the alignment device. The effect of the alignment is that all visible aliasing artefacts are entirely removed, while all other parameters remain unchanged on either side of the image. Width of image is 5.1 mm.

[1] Doble, Philip A., et al. *Chemical Reviews* 121.19 (2021): 11769-11822.

[2] Chew, David, et al. *Chemical Geology* 559 (2021): 119917.

[3] Marillo-Sialer, Estephany, et al. *Journal of Analytical Atomic Spectrometry* 35.4 (2020): 671-678.

[4] Norris, C. Ashley, et al. *Journal of Analytical Atomic Spectrometry* 36.4 (2021): 733-739.

Single pulse, multiple dosage, and 2d oversampling / deconvolution imaging strategies compared and evaluated for best image quality

Martin Šala¹, Johannes T. van Elteren¹, Dino Metarapi¹

¹Department of Analytical Chemistry, National Institute of Chemistry, SI-1000 Ljubljana, Slovenia.

Roughly in the last 10 years, elemental mapping by laser ablation - inductively coupled plasma mass spectrometry (LA-ICPMS) has seen enormous improvements in mapping speed as a result of the development of fast aerosol delivery systems [1]. Furthermore, fundamental studies on image quality as a function of the mapping parameters has led to higher quality images in the shortest possible analysis time by maximizing the signal-to-noise ratio and avoiding systematic errors such as aliasing [2]. In this presentation the imaging quality of several sampling strategies were compared for mapping of (ultra)low-concentration samples, both computationally and experimentally [3].

The imaging quality of several 0D, 1D, and 2D LA-ICPMS strategies were compared for mapping of (ultra)low-concentration samples, via computational modeling and confirmed by experimental work. Different beam sizes, dosages and oversamplings have been taken in account.

Acquisition of counts in LA-ICPMS mapping can be performed for each single laser pulse separately or by summing the counts of multiple laser pulses. Conventionally, pixels in an LA-ICPMS map are associated with spot-resolved single laser pulses (zero-dimensional, 0D), but also sub-pixel convolution strategies are in use, associated with one-dimensional (1D) or two-dimensional (2D) overlapping laser shots, and where possible followed by deblurring. Several combination of the parameters yielding described imaging strategies were modeled *in silico* and assessed by structural similarity (SSIM) index to identify the highest image quality between the tested parameter sets. Similar experiments were then executed in practice to confirm the modeling results.

[1] SJM Van Malderen, AJ Managh, BL Sharp and F Vanhaecke, *J. Anal. At. Spectrom.*, 2016, 31, 423-439.

[2] JT van Elteren, VS Šelih and M Šala, *J. Anal. At. Spectrom.*, 2019, 34, 1919-1931.

[3] JT van Elteren, M Šala and D Metarapi, *Talanta*, 2021, 235, 122785.

The use of time of flight ICP-MS and very fast washout, high repetition rate laser ablation to image marine bio-carbonates. Insights into the growth processes and environmental contamination.

Phil Shaw¹, Gavin Foster², James A. Milton²

¹Nu Instruments, Wrexham, UK,

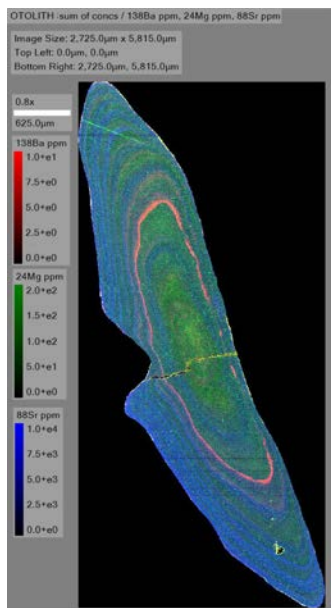
²University of Southampton, UK

The advent of time of flight ICP-MS where the ion beam from a laser ablation plume is sampled significantly faster than the ablation rate of the laser has dramatically improved the precision of measurements as the ion signals are available without aliasing effects between elements. As sample cells of laser ablation systems have developed, the single shot signal times have reduced to only a couple of milliseconds and even sub-millisecond for some minerals and ablation conditions. To fully utilise this performance and obtain the highest resolution images, it is necessary to collect data (store ICP-MS spectra to disk) faster than the single shot washout time and ideally faster than the laser repetition rate.

A Teledyne Cetac Iridia laser ablation system was used with 3-5 μ m spots, ablating at 200-1000Hz. NIST glass calibration standards along with mounted and polished samples were imaged using parallel lines with a spot spacings of 0.1-2.5 μ m so multiple laser shots could be combined to form one pixel with improved signal to background. The laser patterns were generated as free drawn irregular shapes around the minerals which saved 20 to 40% of the time that would have been taken for a rectangular block of ablation lines. The patterns included calibrations and bio-carbonates defined in one list and the running of the lines were then completely automated from the ICP-MS software.

A Nu Instruments Vitesse ICP-TOF-MS was used and this work will demonstrate a unique ability to store spectra to disk faster than the laser ablation rate, providing the ability to characterise each laser shot. The data integration and exact positioning of each pixel via hardware signals and software control of the laser patterns will be discussed along with the ability of the Vitesse's Nu Quant data reduction software to process the mass spectra in real time, displaying a live fully calibrated image to track the ablation whilst at the same time exporting data line by line for further reduction in the other 3rd party software packages software.

A range of marine bio-carbonates will be shown including tropical and cold-water corals, foraminifera and otoliths.



Real matrix-matched calibration strategy for the quantification of neurodegeneration-related proteins in single human epithelial cells by LA-ICP-MS using specific metal-labelled antibodies

Ana Lores-Padín¹, Montserrat García², Héctor González-Iglesias³, Beatriz Fernández¹, Rosario Pereiro¹

¹Department of Physical and Analytical Chemistry, University of Oviedo, Julian Clavería 8, 33006 Oviedo, Spain.

²Instituto Oftalmológico Fernández-Vega, Avda. Dres. Fernández-Vega, 34, 33012, Oviedo, Spain.

³Department of Technology and Biotechnology of Dairy Products, Instituto de Productos Lácteos de Asturias, Consejo Superior de Investigaciones Científicas (IPLA-CSIC), Villaviciosa, Spain.

Biological heterogeneity is a well-known fact that affects the study of biological processes, especially regarding cells. At present, there is a current need of developing new analytical methodologies allowing for the determination of elements and biomolecules in a cell-to-cell basis [1]. In this regard, laser ablation (LA) coupled to ICP-MS is a promising complementary alternative to liquid nebulization single cell (sc) ICP-MS for the characterization of individual cells. Furthermore, not only the analysis of elements naturally present in the cells can be tackled but also specific biomolecules through the combination of LA-ICP-MS with adequate metal-labelling strategies [2]. In this way, the qualitative 2D-mapping of target biomolecules with a subcellular resolution can be performed. However, the persistent lack of adequate matrix-matched reference materials still hinders the quantitative analysis of elements and biomolecules in biological samples by LA-ICP-MS, being especially critical in cell cultures due to their complex matrix.

In this work, we propose a novel matrix-matched calibration strategy, which fully mimics the matrix of cultured cells, by using the same cell line of the sample to create laboratory standards. As a case of study, the sequential quantification of two cytosolic proteins (MT2A and APOE) in individual human retinal pigment epithelial (HRPEsv) cells, both in cells subjected to inflammation with cytokine Interleukin-1 α and control, was carried out. For such purpose, a single biomarker strategy using well-characterized Au nanoclusters (AuNCs) as specific antibody labels was performed for the proteins tagging. The laboratory standards were created by supplementing HRPEsv cells with suspensions containing nude AuNCs (HRPEsv@AuNCs cells). The preparation and characterisation of the single-cell laboratory standards (by both ICP-MS and LA-ICP-MS) were optimised as well as the data treatment protocol required for obtaining the quantitative distribution of the proteins in individual cells. To corroborate the quantitative results obtained for the proteins determination by LA-ICP-MS in HRPEsv cells, sc-ICP-MS analysis and commercial ELISA kits were employed.

[1] P.E. Oomen, M.A. Aref, I. Kaya, N.T.N. Phan, A.G. Ewing, *Anal. Chem.* 91 (2019), 588-621.

[2] A. Lores-Padín, P. Menero-Valdés, B. Fernández, R. Pereiro. *Anal. Chim. Acta.* 1128 (2020) 251-268.

Acknowledgements. This work was financially supported through project PID2019-107838RB-I00 Agencia Estatal de Investigación (AEI)/10.13039/501100011033) and project AYUD/2021/51289 - FICYT. A. Lores-Padín acknowledges the FPU Grant (Ref. MECD-17-FPU16/01363; Ministry of Education).

Automated, Three-dimensional and Sub-micron Accurate Ablation-volume Determination by Inverse Molding and X-ray Computed Tomography

Monserrat Lopez, D.^{1,2}, Grimaudo, V.³, Prone, G.^{1,4}, Flisch, A.⁵, Zboray, R.⁵, Lüthi, T.⁵, Broekmann, P.⁶, Wurz, P.³, Lörtscher, E.¹

¹ IBM Research Europe – Zurich, Säumerstrasse 4, 8803 Rüschlikon, Switzerland.

² ETH Zürich, Department of Biosystems Science and Engineering, Mattenstrasse 26, 4058 Basel, Switzerland.

³ University of Bern, Physics Institute, Space Research & Planetary Sciences, Sidlerstrasse 5, CH-3012 Bern, Switzerland.

⁴ University of Basel, Department of Chemistry, St. Johanns-Ring 19, 4056 Basel, Switzerland.

⁵ EMPA, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland.

⁶ University of Bern, Department of Chemistry, Biochemistry and Pharmaceutical Science, Freiestrasse 3, 3012 Bern, Switzerland.

Ablation of materials in combination with element-specific analysis of the matter released is a widely used method to accurately determine a material's composition. With increasing depth of the volume ablated, however, secondary effects start to play an important role and the ablation geometry deviates substantially from the desired shape. Consequently, primarily conical but sometimes even more complex ablation craters are being created. Hence, the crater's dimensions need to be accurately analyzed to enable a direct correlation with the element-specific analytical signals. Existing metrology tools can either not determine all parameters in three dimensions, access deep craters or are simply very time- and labour-intensive to cover typical ablation studies.

In this contribution, we introduce a generic metrology and analysis method of ablation volumes that is based on first creating a polydimethylsiloxane-based molding of the craters to create a sample containing the ablation crater's inverse. Second, a volumetric reconstruction of the crater's inverse is done at scale using X-ray computed tomography to create a digital surface topography with sub-micron resolution.^[1] Automated algorithms enable the data to be processed further to e.g. identify the ablated region of interest, subtract the background and determine the full anatomy of the craters. We show exemplarily the entire process for silicon samples and present first a material-specific ablation study on Ru(0001) single crystals by correlating ablation volumes and ions generated and acquired by laser-ablation-ionization mass spectrometry.^[2]

The ablation volume determination approach is scalable and highly generic to various material classes. Due to large statistical analysis, it may lead to a better understanding of the fundamentals underlying laser ablation processes. Compared to existing methods, it enables a more accurate and comprehensive determination of heterogeneous material's composition applicable to a variety of applications without requiring time- and labor-intensive assessments of individual craters.

[1] D. Monserrat Lopez *et al.*, "Automated, 3-D and Sub-Micron Accurate Ablation-Volume Determination by Inverse Molding and X-Ray Computed Tomography", *Advanced Science*, 2022, <https://doi.org/10.1002/advs.202200136>.

[2] V. Grimaudo *et al.* "Quantitative laser-matter interaction: A 3D study of UV-fs-laser ablation on single crystalline Ru(0001)", to be submitted, 2022.

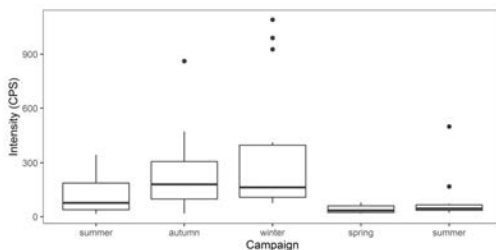
Elemental composition of PM deposited on quartz fiber filter by LA-ICPMS

Monika Ogrizek^{1,2}, Ana Kroflič¹, Martin Šala¹

¹Department of Analytical Chemistry, National Institute of Chemistry, Ljubljana, 1000, Slovenia

²Jožef Stefan International Postgraduate School, Ljubljana, 1000, Slovenia

Particulate matter (PM) is the sum of particles suspended in the atmosphere and is considered a harmful air pollutant. Its elemental composition is routinely monitored, traditionally by capturing PM on a quartz fiber filter and subsequent analysis by inductively coupled plasma mass spectrometry (ICPMS), demanding a pretreatment by acid microwave digestion (MW) [1]. Due to element toxic properties, monitoring of As, Cd, Ni, Pb, Cr, Cu, Se, Zn, Hg is required by European regulative, whereas only the first four elements have prescribed standard method for their determination. To overcome the current drawbacks of element determination in PM on quartz fiber filters originating mostly from microwave digestion, we developed a direct method using laser ablation (LA) coupled to ICPMS [2]. Within the method development, we optimized instrumental parameters (fluence, dosage, and dwell time), investigated the homogeneity of particles on a filter and determined the smallest representative sample size required for the analysis, resulting in a method where 20 elements were reliably measured in a single run. The calibration was an issue since no commercially available matrix-matched standard exists [3]. For the purpose of method development, in-house standards were made by characterizing a few real-life samples with instrumental neutron activation analysis (k_0 -INAA) to confirm the accuracy of the developed (LA-ICPMS) method. The method was later applied to a large number of samples collected in different seasons in Ljubljana, Slovenia.



Cd concentration in PM collected in the years 2020-2021 in Ljubljana. Shown typical trend with higher concentrations in the colder seasons and lower concentrations in the warmer seasons indicates that biomass burning, which is more extensive in winter due to heating purposes, is the major source of Cd in PM. The first summer had higher concentrations due to the fire episode near the sampling spot.

[1] M. Ogrizek, A. Kroflič, M. Šala, Critical review on the development of analytical techniques for the elemental analysis of airborne particulate matter, *Trends Environ. Anal. Chem.* 33 (2022) e00155.

[2] M. Ogrizek, R. Jačimović, M. Šala, A. Kroflič, No more waste at the elemental analysis of airborne particulate matter on quartz fibre filters, *Talanta* 226 (2021) 10.

[3] R.J.C. Brown, K.E. Jarvis, B.A. Disch, S.L. Goddard, An investigation of calibration materials for the measurement of metals in ambient particulate matter on filters by LA-ICP-MS, *Int. J. Environ. Anal. Chem.* 93(3) (2013) 335-348.

Investigation of the Imidization Degree of Polyimides using Laser Induced Breakdown Spectroscopy (LIBS)

Birgit Achleitner¹, Silvia Larissegger², Michael Nelhiebel², Patrick Knaack³, Andreas Limbeck¹

¹TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164, 1060 Vienna, Austria

²KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Technologiepark Villach Europastraße 8, 9524 Villach, Austria

³TU Wien, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163, 1060 Vienna, Austria

Polyimides (PI) are an important class of high-performance polymers. Due to their excellent chemical and physical properties, they are widely used in industrial applications including automotive, aerospace and electronics [1]. Polyimides are generally non-soluble and will degrade at high temperatures near their glass transition temperature. For this reason, the shaping of polyimides is done via a two-step process. The first step involves the synthesis of a soluble precursor, which is then cyclodehydrated in a thermal or chemical process called "imidization" to form the final product [2]. The degree of imidization represents the percent conversion of the amic acid group into imide and is closely related to the final properties of the polymer. Traditionally, IR is used to determine the degree of imidization of a polyimide [3]. This technique is well established but lacks the possibility of analyzing depth profiles and therefore only provides information about the sample surface. Hence, not completely cured or subsequently degraded polyimides cannot be analyzed thoroughly. The usage of LIBS for polymer analysis could be one strategy to overcome these shortcomings. LIBS allows the measurement of depth profiles and besides elemental analysis, characteristic regions in the spectrum can be used to gain molecular information.

In this work, we demonstrate the usage of LIBS for the investigation of the degree of imidization of poly(4,4'-oxydiphenylene-pyromellitimide) (PMDA-ODA). IR spectroscopy served as a reference method and a good accordance between those two measurement methods was found. Additionally, LIBS was applied for depth profiling of variably imidized samples.

[1] S. Diahm, "Polyimide in Electronics: Applications and Processability Overview", in *Polyimide for Electronic and Electrical Engineering Applications*. London, United Kingdom: IntechOpen, 2021 [Online]. Available: <https://www.intechopen.com/chapters/74939> doi: 10.5772/intechopen.92629

[2] C.E. Sroog, A.L. Endrey, S.V. Abramo, C.E. Berr, W.M. Edwards and K.L. Olivier, "Aromatic polypyromellitimides from aromatic polyamic acids", *J. Polym. Sci. A Gen. Pap.* Vol. 3, pp. 1373-1390, 1965

[3] W. Chen, W. Chen, B. Zhang, S. Yang and C.-Y. Liu, "Thermal imidization process of polyimide film: Interplay between solvent evaporation and imidization", *Polymer*, Vol. 109, pp. 205-215, 2017

Application of Diffusive Gradients in Thin Films (DGT) in Combination with LA-ICP-MS for the Spatial Investigation of Aluminium Corrosion

Gulnaz Mukhametzianova, Stefan Wagner, Masoud Moshtaghi, Magdalena Eskinja, Gregor Mori, Thomas Prohaska
Montanuniversität Leoben, Chair of General and Analytical Chemistry, Franz Josef-Straße 18, 8700 Leoben, Austria

Chemical imaging based on diffusive gradient in thin films (DGT) technique in combination with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) enables the visualization and quantification of chemical processes occurring at reactive interfaces *in situ*. Over the last 30 years, DGT has become a versatile tool for studying chemical concentration and bioavailability in the water–soil–sediment–biota systems [1]. The recent application of DGT LA-ICP-MS in materials science opened the door for studying metal corrosion processes at unprecedented spatiotemporal resolution.

In this study, we have developed and applied DGT LA-ICP-MS for the *in situ* investigation of pitting corrosion, a highly localised form of corrosion that initiates the formation of cavities in the metal, which is difficult to detect due to the small size of early pits. The 7075 aluminium (Al) alloy (AA7075), containing Zn ($w = 5.6\text{--}6.1\%$), Mg ($w = 2.1\text{--}2.5\%$), and Cu ($w = 1.2\text{--}1.6\%$), is used as sample material that is being widely applied in aircraft structural parts where susceptibility to pitting corrosion is critical because pits can act as starters for fatigue cracks. Advanced polyacrylamide-based DGT binding gels with a highly homogeneous distribution of Chelex (iminodiacetate) only, or both Chelex and Metsorb (TiO₂) binding phases are evaluated and applied for the simultaneous and quantitative sampling of corrosion products of Al, Mg, Zn, and Cu. The novel approach is combined with microscopic images to obtain detailed information on surface structural changes during AA7075 corrosion.

The study's results show that applying DGT LA-ICP-MS using Chelex gels enables accurate *in situ* visualization of corrosion reactions on AA7075 exposed to NaCl solution ($w = 1.5\%$) at pH 4.5 and room temperature with different exposure times. The development of the method for the analysis of highly localised pitting corrosion has also revealed less localised crevice corrosion resulting from stagnant solution flow. Thus, the presented results open up the prospect of applying the DGT method for the monitoring different corrosion processes.

[1] Wei T-J, Guan D-X, Li X-Y, *et al.* Analysis of studies on environmental measurements using diffusive gradients in thin-films (DGT) from 1994 to 2020. *J Soils Sediments* 2022

A multi-method approach for tracing non-metallic inclusions in steel

Christoph Walkner¹, Gulnaz Mukhametzianova¹, Stefan Wagner¹, Jörg Korp², Andreas Graf³, Johanna Irrgeher¹, Thomas C. Meisel¹, Thomas Prohaska¹

¹ Montanuniversität Leoben, Chair of General and Analytical Chemistry, Franz Josef-Straße 18, 8700 Leoben, Austria,

² Dr. Korp Technological-Consulting, Buchengasse 17, 8793 Trofaiach, Austria,

³ Breitenfeld Edelstahl AG, Breitenfeldstraße 22, 8662 St. Barbara im Mürztal, Austria

Steels for high-performance applications have to meet increasingly stringent criteria in terms of steel cleanliness. One of the parameters critical for steel quality is strict limitation of non-metallic inclusions in terms of size, composition and frequency. Non-metallic inclusions in steels negatively affect the performance of the finished product, lowering qualities such as fracture toughness, fatigue life, and corrosion resistance [1]. This applies particularly to macroscopic inclusions (larger than 100 µm), which rarely occur using state-of-the-art casting technologies, but which practically always result in rejection of the affected product. Therefore, even single large inclusions can cause major economic damage, especially in ingot casting [2].

In order to allow further improvements in the steel casting process, a better understanding of the sources and processes involved in inclusion formation is required. Within the present study, specimens of macroscopic non-metallic inclusions in steel ingots were investigated in detail using a combination of various analytical methods. SEM-EDX, LA-ICP-MS and LA-MC-ICP-MS allowed to extract detailed morphological and chemical information from individual inclusions. The inclusions were examined in terms of morphology, main constituents, and trace elements including the rare earth elements and ⁸⁷Sr/⁸⁶Sr ratios. For comparison, the same parameters were determined in materials constituting potential sources for inclusions, such as slag, refractory lining, and auxiliary materials used in the casting process.

Results show that entrained particles eroded from the refractory lining are likely primary source materials for inclusions. They also indicate that inclusions are altered by chemical reactions during the steel casting and refining process, which includes deoxidation and in the present case vacuum arc remelting, resulting in chemical modification of the initial materials. These findings were only made possible by the multi-method approach used and would not have been accessible by any single method.

[1] Zhang L, Thomas BG (2006) State of the art in the control of inclusions during steel ingot casting. *Metallurgical and Materials Transactions B* 37 (5):733–761.

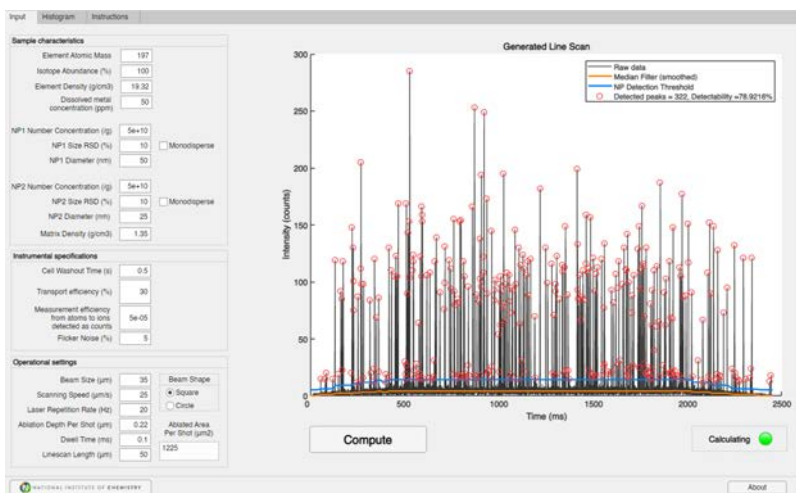
[2] Zhang L, Rietow B, Thomas BG, Eakin K (2006) Large Inclusions in Plain-carbon Steel Ingots Cast by Bottom Teeming. *ISIJ International* 46:670–679.

Critical considerations in single particle analysis by laser ablation inductively coupled plasma mass spectrometry

Dino Metarapi¹, Johannes T. van Elteren¹, Martin Šala¹

¹National Institute of Chemistry, Department of Analytical Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia, dino.metarapi@ki.si

Recent advancements in the ability to measure and visualize nanoparticles (NPs) in solid samples using single particle laser ablation inductively coupled plasma mass spectrometry (sp-LA-ICP-MS)[1,2] necessitated a thorough investigation into the operational settings imposed by the biomatrix characteristics and instrumental specifications of the LA-ICP-MS system lest erratic results may be produced. By deepening the fundamental understanding of the process of LA-sp-ICP-MS and by utilizing a simulation approach, we offer practical guidelines for the technique. Additionally, the critical parameter of laser fluence, which, if set improperly, has the potential to invalidate the results obtained by LA-sp-ICP-MS as a result of nanoparticle degradation was also explored in depth.



Web app for optimization of LA-sp-ICP-MS experimental conditions.

[1] Metarapi, D.; Šala, M.; Vogel-Mikuš, K.; Šelih, V. S.; van Elteren, J. T. Anal. Chem. 2019, 91 (9), 6200–6205.

[2] Metarapi, D.; van Elteren, J. T.; Šala, M.; Vogel-Mikuš, K.; Arčon, I.; Šelih, V. S.; Kolar, M.; Hočevar, S. B. Environ. Sci. Nano 2021, 8 (3), 647–656.

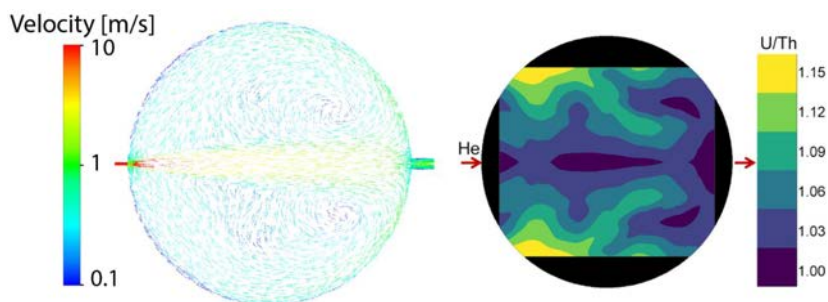
Impact of Ablation Cell Design in LA-ICP-MS on Elemental Fractionation

Pascal Becker¹, Joachim Koch¹, Detlef Günther¹

¹Laboratory of Inorganic Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been used routinely in the past few decades for the analysis of samples in geology, biology, material sciences, forensics and more. Large volume ablation cells are commonly used for the purposes of isotope and bulk analysis. The laser generated aerosol is highly dispersed, resulting in stable signals optimal for sequential mass analysers. For purposes that require spatial information, such as imaging and depth profiling, low dispersion laser ablation cells have been developed to resolve individual laser pulses. However, due to their fast aerosol washout nature, these ablation cells necessitate the use of simultaneous mass analysers, such as time of flight mass spectrometers, in order to perform multi-elemental analysis. The most common working principle makes use of a two volume approach, where samples are placed on a 3D-stage within a large volume, below a smaller volume with a narrow opening in-between.^[1,2]

This work focuses on the differences of the aerosol transport between these two types of ablation cells. Transport phenomena of the laser-generated aerosols were studied based on their particle size distributions, elemental ratios and gas simulations. The differences between low and high dispersion were investigated, as well as the effect of aerosol stretching after low dispersion ablation. The three setups were compared in regards to reproducibility and accuracy.



[1] A. Gundlach-Graham and D. Günther, *Anal. Bioanal. Chem.*, **2016**, 408, 2687–2695.

[2] S. J. M. Van Malderen, J. T. Van Elteren and F. Vanhaecke, *J. Anal. At. Spectrom.*, **2015**, 30, 119–125.

Enhanced Detection Capabilities of a Novel Laboratory-Scale fs-LIMS Instrument through Mass-Selective Beam Blanking

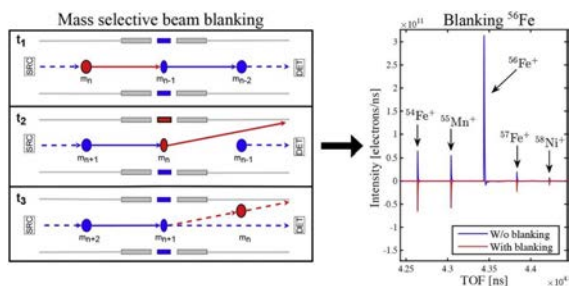
de Koning, C. P.¹, Gruchola, S.¹, Keresztes Schmidt, P.¹, Riedo, A.¹, Tulej, M.¹, Wurz, P.¹

¹Space Research and Planetary Science, University of Bern, Switzerland

Over the last few decades, the advent of commercially available ultrafast laser systems has fuelled rapid and significant progress in many laser-based solid-sampling techniques, including Laser Ablation Ionisation Mass Spectrometry (LIMS). The high stability and so-called cold ablation enabled LIMS systems to push performance characteristics further than ever before. One instrument taking advantage of these developments is the Laser Mass Spectrometer – Gran Turismo (LMS-GT) system, a fs-LIMS instrument built at the University of Bern.

With an achieved mass resolution of 20'000, a dynamic range of roughly 6–7 orders of magnitude, micrometre spatial resolution, quantitative detection, and simultaneous recording of every species up to uranium, LMS-GT has the potential to occupy an analytical niche not achievable by many other techniques [1]. However, current limits of detections (LoDs) achieved by LIMS instruments (including LMS-GT) are in the ppm to sub-ppm range (atomic fractions). In comparison, many other commonly used techniques for solid sample analysis reach LoDs at ppb levels or even below.

In the case of LMS-GT, the currently achieved LoD is mostly constrained by detector saturation caused by the major species present in the spectrum. To mitigate this behaviour, a mass-selective beam blanking device, comprising a fast high voltage switch connected to a split Einzel-lens, was developed in-house (see Fig. above) [2]. In this contribution, we will discuss the implementation of this device in LMS-GT, with a specific focus on the observed improvements in the instruments' detection limit. The obtained results show that fs-LIMS is a powerful quantitative technique for the chemical analysis of solids at μm spatial scales, with the potential to reach performance levels achievable by more established mass spectrometric techniques, such as SIMS and LA-ICP-MS.



[1] C.P. de Koning, S. Gruchola, A. Riedo, R. Wiesendanger, V. Grimaudo, R. Lukmanov, N.F.W. Ligterink, M. Tulej and P. Wurz, "Quantitative elemental analysis with the LMS-GT; a next-generation LIMS-TOF instrument", *Int. J. Mass Spectrom.*, 470, 2021, 116662, 1-11, doi:10.1016/j.ijms.2021.116662.

[2] S. Gruchola, C.P. de Koning, R. Wiesendanger, P. Keresztes Schmidt, A. Riedo, V. Grimaudo, R.A. Lukmanov, N.F.W. Ligterink, M. Tulej and P. Wurz, "Improved limit of detection of a high-resolution fs-LIMS instrument through mass-selective beam blanking", *Int. J. Mass Spectrom.*, 474, 2022, 116803, 1-13, doi:10.1016/j.ijms.2022.116803.

Quantitative depth profiles in novel materials by combined consideration of online Laser Ablation of solids in liquids and LA-ICP-MS

Maximilian Podsednik^{1*}, Maximilian Weiss², Silvia Larisegger¹, Michael Nelhiebel¹, Andreas Limbeck²

1. KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Technologiepark Villach Europastraße 8, 9524 Villach, Austria

2. TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-I2AC, 1060 Vienna, Austria

Today's society is confronted with challenges like climate change and environmental pollution, thereby technological progress became crucial for a sustainable future. The main part of this progress is achieved by novel high-performance materials enabling new technologies. Since crucial material properties are determined by the elemental composition from the bulk stoichiometry down to dopant levels or ultra-trace impurities, a precise analytical characterization is inevitable to push those novel materials to the edge of their capabilities. One method that would be ideal for the characterization of novel materials is the recently presented online laser ablation of solids in liquids (online LASIL) [1]. In online LASIL a solid sample is ablated under a continuous stream of a liquid carrier medium, which is then introduced into the plasma of an ICP-MS. This approach circumvents the laborious sample digestion step required for conventional ICP-MS analysis but enables in contrast to other solid sampling techniques the use of liquid standards for quantification [2,3].

In this work, the LASIL setup was further optimized by the introduction of segmented gas bubbles, that trap the generated nanoparticles in a single liquid segment. In this way, the washout behavior and the transport efficiency of the particles from the LASIL cell to the detection system could be improved drastically, enabling accurate quantification of trace elements. To demonstrate the capabilities of this improved method trace elements of the certified reference material NIST612 were analyzed quantitatively, derived findings were in good agreement with the certified values. Moreover, to show the applicability of this method the aluminum content of the hard to digest material silicon carbide was quantified. Those quantitative results can further be combined with qualitative LA-ICP-MS data of the same material, resulting in quantitative depth profiles with increased depth resolution.

[1] M. Bonta, J. Frank, S. Taibl, J. Fleig, A. Limbeck, *Anal Chim Acta* 1000 (2018) 93–99.

[2] M. Weiss, C. Riedl, J. Frank, J. Fleig, A. Limbeck, *Microchemical Journal* 166 (2021) 106236.

[3] Herzig C., J. Frank, A. Nening, M. Gerstl, A.K. Opitz, J. Fleig and A. Limbeck, *Journal of Materials Chemistry A* 2022 (10), 1840 – 1851, DOI: 10.1039/D1TA06873C.

Investigation of Polymer ageing by combined LIBS and LA-ICP-MS analysis

Jakob Willner¹, Lukas Brunnbauer², Michael Nelhiebel¹, Silvia Larissegger¹ and Andreas Limbeck²

¹KAI Kompetenzzentrum Automobil- und Industrieelektronik GmbH, Technologiepark Villach - Europastraße 8, 8524 Villach, Austria

²TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-1²AC, 1060 Vienna, Austria

Polymers are applied in many different industries because of their wide range of mechanical, physical, and chemical properties. One major application field is their utilization as protective anti-corrosion coatings. This is not only relevant for well-known macroscopic applications like painting and coating of construction materials, but also in high-tech applications like the semiconductor industry, where polymer layers in the low micrometer scale are used to protect devices from environmental influences such as high temperatures, humidity, and corrosive gases. As those coatings are, especially in harsh environments, subject to aging and degradation, at some point, the required protection capability is compromised. Hence, research is ongoing to further improve the quality and lifetime of the coating itself and thus the protected material.

This work aims to investigate the degradation of polymer films by oxidative reagents, UV radiation, and the resulting influence regarding the uptake of corrosive gases caused by subsequent weathering experiments. Recently we have shown that LA-ICP-MS is suitable technique to determine the sulfur uptake in weathered samples, giving insight into the uptake behavior in different environmental conditions. While this technique allows sensitive and depth-resolved analysis of the element sulfur, information about polymer degradation is not accessible with this approach. Using LIBS, additional specially resolved information about polymer degradation can be gained, i.e. by measurement of the oxygen signal to indicate oxidation of the polymer.

In this work the development of a tandem LA-ICP-MS/LIBS approach is presented, where polymer specific LIBS signals as well as signals from inorganic species via LA-ICP-MS are acquired simultaneously. LIBS is applied for the determination of the mentioned polymer oxidation, while LA-ICP-MS is used for measurement of Sulfur. Performing depth-resolved analysis of those elements simultaneously allows the investigation of possible correlations and dependences. The conjoint information of LIBS and LA-ICP-MS measurements is used to get additional insight into the synergistic effects of polymer degradation with the impairment of its protection capability by the uptake of corrosive gases.

Laser Ablation / Ionisation Mass Spectrometry

Peter Wurz¹, Marek Tulej¹, Valentine Grimaudo¹, Andreas Riedo¹

¹ Physics Institute, University of Bern, Switzerland

In this review we will address the use of pulsed lasers to ablate material from solid samples, forming an ablation plume that affords some ionisation of sample material, and the subsequent mass spectrometric analysis of the produced ions. This is known as Laser Ablation / Ionisation Mass Spectrometry (LIMS). Soon after the invention of the laser, especially the pulsed laser, it was used in mass spectrometry for the analysis of solid surfaces because of its high power density during a short time. First LIMS instruments became available in the early 1970'ies, and even commercial instruments became available in the early 1980'ies. However, the laser systems of the time limited the performance of these instruments, in particular the capability for reproducible quantitative measurements. In the following other laser-based mass spectrometric systems were preferred by many.

Thanks to the development of better, i.e., more stable pulsed laser systems (typically, Nd:YAG pulsed laser between 1064 nm and 212 nm, with nano-second pulses) and novel electronics, the LIMS instruments became attractive analytical instruments again, in part because of their simple setup and easy operation compared to other systems. Typically, LIMS systems consist of two parts, a laser ionisation ion source and a time-of-flight mass spectrometer (TOF-MS). TOF-MS are a natural choice with pulsed lasers, with the additional advantage that all masses are recorded at the same time, for each laser shot. No mass scanning is necessary, which results in much higher sensitivity for complete chemical analysis compared to scanning instruments. Most recently, the availability of commercial femto-second laser systems, ideally operating UV wavelengths, allows for highly reproducible quantitative measurements of the chemical composition of solid samples. Modern LIMS instruments allow for the quantitative chemical analysis of samples at the micrometer scale, range from 1D (depth profiles), 2D (surface chemical maps), and 3D (full 3D chemical analysis), providing chemical analysis within seconds, without or minimal sample preparation, with element abundances ranging from major species all the way to trace elements at the level of ppm and below, and isotope studies. Optimised LIMS instruments demonstrated a dynamic range of 8 decades, which allows for quantitative measurements of almost all elements. Laboratory class LIMS instruments using fs-lasers found applications in the semiconductor industry, in material science, mineralogy, geology, and other fields wherever the combination of high spatial resolution, quantitative measurements, and trace element sensitivity is a requirement. The combination of LIMS with a microscope observation of the sample surface at the investigated area at the same time increases the analytical capabilities tremendously.

Because of the large potential for substantial miniaturisation of LIMS instruments, basically to overall dimensions of a shoebox, without giving up too much on the various performance parameters, LIMS is also a very promising analytical technique to be used in space science, to be employed on planetary landers and rovers for in situ research of planetary material on the surface or sub-surface.

LIMS: A novel measurement technique for the detection of life beyond Earth

Riedo A.^{1,2}, Boeren N.J.^{1,2}, Kipfer K.A., Ligterink N.F.W., de Koning C.P.¹, Grimaudo V., Gruchola, S.¹, Keresztes Schmidt, P.¹, Tulej, M.¹, Wurz, P.^{1,2}

¹Space Research and Planetary Science, University of Bern, Switzerland

²NCCR PlanetS, University of Bern, Switzerland.

Ever since the Viking mission on Mars in the 1970s, humankind has been seeking indicators of life, past or present, in our Solar System. Unfortunately, so far without success. The identification of signatures of life is extremely challenging in space exploration missions and depends on a variety of parameters, ranging from field site selection to the application of appropriate systems providing sufficient detection sensitivity and wide-ranging capabilities. Six groups of life signatures are of high interest to the big space agencies, including e.g., organic molecules related to life as we know it, isotope patterns indicative of life, and/or morphological features of micrometer dimensions such as micrometer sized fossils.

In this contribution, the current measurement capabilities of our miniature LIMS system for the detection of three out of the six major classes of signatures of life are presented. First, studies conducted on Mars analogue material that contains artificially inoculated microbes are presented. The measurements will show that single cell detection in a complex host is possible using LIMS through the identification of the major biologically relevant elements [1,2]. The second study is devoted to life detection via Sulphur isotopes [3]. The study was conducted on five Sulphur containing samples that mimic some parameters of past and current Mars and are differentiating in their Sulphur abundance (96.5 % - 5.7 %) and fractionation level ($\delta^{34}\text{S}$ ranging from - 7.12 ‰ to + 8.63 ‰). The measurement methodology presented will show that $\delta^{34}\text{S}$ was measured with an absolute accuracy of $\delta^{34}\text{S} \sim 2$ ‰. The third study will show that LIMS operated in desorption mode has the capability of the identification of organic molecules, such as amino acids and lipids, simply and robustly, through the observed parent peak and the fragmentation pattern [4, 5].

With the recently elaborated measurement methodologies, LIMS advanced to a truly promising measurement technique for future space exploration missions devoted to life detection. One single instrument can be applied to several groups of life signatures while so far typically one instrument for one class of signature was applied in current missions.

[1] A. Riedo et al., "Laser Ablation Ionization Mass Spectrometry: A space prototype system for in situ Sulphur isotope fractionation analysis on planetary surfaces", *Front. Astron. Space Sci.*, 8, 2021, 726373, 1-12.

[2] A. Riedo et al., "The detection of elemental signatures of microbes in Martian mudstone analogues using high-spatial resolution laser ablation ionization mass spectrometry", *Astrobiol.*, 20, 2020, 1224 - 1235.

[3] A.H. Stevens et al., "Detectability of biosignatures in a low-biomass simulation of martian sediments", *Nature Sci. Rep.*, 9, 2019, 9706.

[4] N.F.W. Ligterink et al., "ORIGIN: a novel and compact Laser Desorption – Mass Spectrometry system for sensitive in situ detection of amino acids on extraterrestrial surfaces", *Nature Sci. Rep.*, 10, 2020, 9641.

[5] N.J. Boeren et al., 2022, to be submitted.

Prototype Laser Desorption Ionization Mass Spectrometer for *in situ* lipid detection on Ocean Worlds

Boeren, N.J.^{1,2}, Kipfer, K.A.¹, Ligterink, N.F.W.¹, de Koning, C.P.¹, Keresztes Schmidt, P.¹, Gruchola, S.¹, Tulej, M.¹, Wurz, P.^{1,2}, Riedo, A.^{1,2}

¹Space Research and Planetary Sciences, Physics Institute, University of Bern, Switzerland,

²NCCR PlanetS, University of Bern, Switzerland.

A high priority topic for future space exploration missions is the detection of extant or extinct life on extraterrestrial Solar System bodies. Therefore, reliable detection of signatures of life is necessary. However, this is a highly challenging task, posing severe requirements to instrumentation. The capability for the detection of signatures of life should ideally not be limited to one compound, but more broadly applicable for the detection of several different compounds at the same time. Furthermore, highly sensitive instrumentation is required to detect biosignatures with trace abundances, while, simultaneously, a broad dynamic range should be covered as to not exclude highly abundant compounds.

The NASA Europa Lander Report [1] marks several groups of compounds as potential targets in the search for signs of life, including lipids. Lipids show high stability and, on Earth, play a major role in various processes imperative for the formation of life. Detection and identification of lipids on future space exploration missions, specifically the Europa Lander mission, is therefore of high interest in the search for signs of life.

ORIGIN (ORganics Information Gathering INstrument) is a novel prototype Laser Ionization Mass Spectrometer (LIMS) operated in desorption mode. ORIGIN was designed for *in situ* detection of biomolecules on future space exploration missions, and subsequently constructed at the University of Bern, Switzerland [2]. The design is simple and compact and complies with the requirements for space instrumentation. The current setup of ORIGIN comprises a nanosecond pulsed laser system ($\lambda = 266$ nm, 20 Hz, $\tau \sim 3$ ns) for desorption and ionization of analytes, and a miniature reflectron-type time-of-flight mass analyzer (160 mm x \varnothing 60 mm) [3].

The capabilities of ORIGIN were recently demonstrated by measurements of amino acids and polycyclic aromatic hydrocarbon standards and are now extended to lipids [2,4,5]. Six different lipids were investigated, with four being prenol and two being sterol lipids [5]. Studies were conducted to investigate the limits of detection, optimal laser desorption conditions, and influence of the sample substrate. We will discuss the instrument setup, measurement procedures, as well as the latest findings regarding lipid detection using the ORIGIN prototype. The implications of the results will be discussed, with a focus on the suitability of the presented technique for future space missions to explore Ocean Worlds in the search for signatures of life.

References:

- [1] K.P. Hand, *et al.*, Report of the Europa Lander Science Definition Team. Posted February 2017.
- [2] N.F.W. Ligterink, *et al.*, *Sci. Rep.*, 2020, 10, 9641.
- [3] A. Riedo, *et al.*, *J. Mass Spectrom.*, 2013, 48, 1-15.
- [4] K. A. Kipfer, *et al.*, *Planet. Sci. J.*, 2022, 3, 43.
- [5] N.J. Boeren *et al.*, 2022, to be submitted.

The breakthrough potential of LA-ICP-MS for understanding the chemical stratigraphy in deep polar ice cores

Pascal Bohleber¹, Remi Dallmayr², Martin Rittner³, Marco Roman¹, Nicolas Stoll², Frank Wilhelms² and Carlo Barbante^{1,4}

¹Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Venice, Italy,

²Alfred-Wegener-Institute Helmholtz Zentrum für Polar- und Meeresforschung, Bremerhaven, Germany,

³TOFWERK AG, Thun, Switzerland

⁴Institute of Polar Sciences, CNR, Venice, Italy

State-of-the-art ice core research calls for understanding the deepest and oldest ice sections at unprecedented resolution, not least for retrieving a 1.5 million-year “Oldest Ice Core” record from Antarctica. Mastering this frontier demands high-resolution analysis due to layer thinning and accounting for post-depositional changes to the stratigraphy. Its micron-scale resolution and micro-destructiveness make laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) especially suited for the analysis of chemical impurities in ice cores [1]. If employed for 2D imaging, LA-ICP-MS allows to map the spatial impurity distribution in ice. This already shows great potential for assessing the interplay of impurities and the ice matrix [2]. However, deep ice features ice crystals larger than a few cm and can alter the composition of its impurities by chemical reactions. To succeed further, LA-ICP-MS ice core analysis needs to cover a broad spectrum of elements while avoiding cutting ice cores into small-sized samples. Aiming to engage with the broad laser ablation community we present our latest developments and some initial steps in tackling this challenge. In a recently conducted pilot experiment we explored “time of flight” mass spectrometry for a range of elements, including Antarctic ice with very low concentrations [3]. Multi-elemental images at 20 microns resolution allow the geochemical characterization of impurities localized at crystal boundaries as well as clustered dust particles. Aiming to increase physical image dimensions and to avoid destructive sample preparation, we present first progress in developing a large cryocell housing up to 55 cm long ice core rods. Here, the main challenge is to expand on pioneering solutions [4] by integrating 2D imaging capabilities. When combined with a modern high-repetition rate laser system, a large imaging-capable cryocell would bring into reach the recording of centimeter or even decimeter-sized images along a broad range of analytes – ultimately making LA-ICP-MS a true breakthrough technology for the “Oldest Ice” quest.

[1] W. Müller, J. M. G. Shelley, and S. O. Rasmussen, “Direct chemical analysis of frozen ice cores by UV-laser ablation ICPMS,” *J. Anal. At. Spectrom.*, vol. 26, no. 12, pp. 2391–2395, 2011.

[2] P. Bohleber, M. Roman, M. Šála, and C. Barbante, “Imaging the impurity distribution in glacier ice cores with LA-ICP-MS,” *J. Anal. At. Spectrom.*, vol. 35, no. 10, pp. 2204–2212, 2020.

[3] P. Bohleber, M. Roman, N. Stoll, Y. Bussweiler, and M. Rittner, “Imaging the Distribution of Elements in Antarctic Ice Cores with LA-ICP- TOFMS,” *TOFWERK Application Note*, 2021. <https://www.tofwerk.com/imaging-ice-cores-la-icp-tofms/>.

[4] S. B. Sneed *et al.*, “New LA-ICP-MS cryocell and calibration technique for sub-millimeter analysis of ice cores,” *J. Glaciol.*, vol. 61, no. 226, pp. 233–242, 2015.

ION4RAW: Inventory of by-products and critical raw materials in the El Porvenir Pb-Zn ore deposit through combined laser ablation ICP-MS, electron microprobe and micro-XRF mapping

Lerouge Catherine¹, Lach Philippe¹, Wille Guillaume¹, Duhamel-Achin Isabelle¹, Gourcerol Blandine¹, Moreau Pauline¹, Warscheid Werner², Negrel Philippe¹

¹BRGM, 3 Avenue Claude Guillemin, 45060, Orléans Cédex 2, France

²Cumbrex S.A.C, Cl. Nicolo Paganini AK 16, Los Alamos, Santiago de Surco (Lima 33), Lima, Peru

Long-term management of mineral resource supply, incorporating anthropogenic environmental impacts, is crucial for sustaining human society. As part of the European H2020 research and innovation program, the ION4RAW project aims at obtaining reliable assessment of by-products and critical raw materials (CRM) and at developing ionometallurgy processes to improve their extraction from primary resources.

For the inventory of by-products and CRM, we currently develop the analyse of trace elements by laser ablation-ICP-MS on ore and gangue, combined with electron microprobe and μ X-ray fluorescence mapping. The final objectives of this study are to determine the carrier minerals, to define the variability of their chemistry, to characterize their distribution and related quantification, in order to improve the CRM and by-products recovery during the ore treatment processes.

We present here the preliminary mineralogical and chemical characterization of a skarn mineralization from the El Porvenir Zn-Ag-Pb-(Au-Cu) ore deposit (owned by Nexa Resources) located in the Western Cordillera of the Andes mountain range, central Peru.

Mineralogical investigations, including μ -XRF mapping, indicate that the ore consists of sphalerite, galena, chalcopyrite, pyrite with minor tennantite-tetrahedrite-series minerals, pyrrhotite, tellurides, molybdenite, gold in a gangue composed of garnet, clinopyroxene, amphibole, micas, carbonate, quartz and K-feldspar with minor minerals such as titanite, apatite and fluorite.

The electron microprobe allows analyzing micron-sized metal-carrier minerals, including electrum, Bi-Pb sulfosalts, hessite [Ag₂Te], determining the composition of tennantite-tetrahedrite-series minerals (from argentotennantite containing up to 12 wt.% Ag and 5 wt.% Bi to tetrahedrite) and detecting traces in major ore at detection limits of 200-1000 ppm (for example, galena significantly contains Ag, Bi, Sb and Te). Analyses of silicates allow precisising the compositions of garnet, clinopyroxene, micas and minor minerals, as exemplified by grandite solid solution (from pure andradite to andradite 15-grossular 85), diopside, F-bearing phlogopite, Ba-muscovite present in different zones of the skarn.

The laser ablation-ICP-MS is applied on sulfide minerals and in-house developed sulfide standards at maximum power of the laser and at various beam diameters adapted to the grain sizes (from 85 to 10 μ m). Laser ablation-ICP-MS analyses confirm electron microprobe data and allows detecting lower metal contents, such as Ag, Bi, Se, Rh, Pd, In, Te, in major ore at detection limits of the ppm with a beam diameter of 10 μ m and at detection limits of 10 ppb with a beam diameter of 85 μ m.

Comparison of the homogeneity of powdered geological materials prepared by four different methods for multi-elemental analysis by LA-ICP-MS

Michaël Susset¹, Axelle Leduc--Gauthier, Anne-Claire Humbert¹, Fabien Pointurier¹, Christophe Pécheyran²

¹ CEA, DAM, DIF, F-91297, Arpajon, France.

² Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, IPREM UMR 5254, CNRS, Université de Pau et des Pays de l'Adour, 2 Avenue du Président Angot, 64053, Pau Cedex 9, France.

Sample preparation is a crucial point for quantitative multi-elemental analyses by LA-ICP-MS of powdered materials.

Four different methods are compared in this study: preparation of glass beads by the alkaline fusion method and three grinding and pelletizing methods (two milling protocols for each) after mixing with an organic binder [1], mixing with an adhesive [2] and glass formation by a sol-gel process [3], respectively. These methods were applied to three geological standard materials. The following criteria were used for method comparison: (1) percentage of outliers, i.e., measurement cycles for which count rates are outside of statistical uncertainty range (above or below the average count rate $\pm 3 \times SD$) and are not considered for calculation of RSDs, (2) levels of homogeneity of the samples (relative standard deviations over raw count rates for 60 analyzed nuclides), (3) level of homogeneity of liquid internal standards incorporated into the materials before the preparation step, (4) reproducibility of the preparation method (reproducibility of the normalized count rates and of the RSDs of the normalized count rate).

Thanks to the suppression of grain effects by alkaline melting, the glass bead method provides RSDs and percentages of outliers close to the one of the NIST glasses in contrast to the pelletizing methods.

Finally, the use of tungsten carbide as grinding material brings some metallic contamination (W and Co) but produces more homogenous pellets for the sol-gel and mixing with glue protocols than grinding with PTFE material. Specific contaminations in one or several elements (Cr, Fe, Co, Ni, Cu, Mo, W, Au and Bi) have been observed for one or the other methods.

[1] C. O'Connor, M. R. Landon, and B. L. Sharp, « Absorption coefficient modified pressed powders for calibration of laser ablation inductively coupled plasma mass spectrometry », *J. Anal. At. Spectrom.*, vol. 22, no 3, p. 273-282, 2007.

[2] W. Klemm and G. Bombach, « A simple method of target preparation for the bulk analysis of powder samples by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) », *Fresenius' Journal of Analytical Chemistry*, vol. 370, no 5, p. 641-646, 2001.

[3] I. Hubová, M. Holá, J. Pinkas, and V. Kanický, « Examination of sol-gel technique applicability for preparation of pellets for soil analysis by laser ablation inductively coupled plasma optical emission spectrometry », *J. Anal. At. Spectrom.*, vol. 22, no 10, p. 1238-1243, 2007.

Machine Learning Assisted Emerald Classification using 50+ Elements Analyzed by LA-ICP-TOF-MS

Hao A.O. Wang¹, Michael S. Krzemnicki^{1,2}

¹Swiss Gemmological Institute SSEF, CH-4051, Basel, Switzerland. (hao.wang@ssef.ch)

²Depart. of Environmental Sciences, Mineralogy and Petrology, University Basel, Switzerland

Mineral classification is an effective approach to distinguish different types of mineral deposits and contribute in studying their formation. Several methods have been developed, based on either geological formation environment or elemental composition.[1] Due to complexity and variability in formation processes, finer and flexible classification of deposits is often desired. Minerals commonly allow chemical substitution by trace elements in their crystal structure. Often, various trace elements may be incorporated on the same site in the crystal, because of similar chemical properties and/or ionic radii. In the case of emerald (green Cr-bearing variety of beryl, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$), its composition may include more than 50 elements, which is potentially helpful in terms of fine classification, thanks to the large number of elemental parameters. In addition, by considering different number of elements, it is possible to provide a flexible classification scheme for various degree of fineness (a bottom-up approach).

In this contribution, we focus on multi-element analysis of emerald, using a 193nm excimer laser from ESI coupled to an icpTOF R from TOFWERK, and a protocol described recently.[2] Conventionally, trace element results of minerals are shown in bivariate plots, tri-plots, and 3D scatter plots to separate and classify them into different groups or to visualize their elemental similarities with reference samples from a database. However, LA-ICP-TOF-MS intrinsically produces multi-element results (high dimensional dataset), therefore one would need to compare multiple bivariate-plots for a comprehensive data analysis, because direct visualization of the high dimensional dataset is challenging. Alternatively, statistical dimension reduction can be applied on the original multi-element result. Using unsupervised machine learning algorithms - t-SNE, the high dimensional dataset of 50+ element concentrations of thousands of emerald samples is projected to a 3D space. In the reduced t-SNE plot, data points are grouped solely dependent on their elemental similarities among the analyzed samples. In this way, emeralds from different deposits can be separated from each other based on their chemical composition. Our approach not only is in accordance with more conventional mineral classification schemes, but also may provide finer classification even within a local region or a single emerald deposit. This may indicate local and small-scale differences in formation conditions within a region or deposit. In this presentation, we will also discuss the robustness of this machine learning assisted mineral classification approach using synthetic data.

[1] Groat, L.A., et al., *Ore Geol. Rev.*, **2008**, *34*, 87–112.

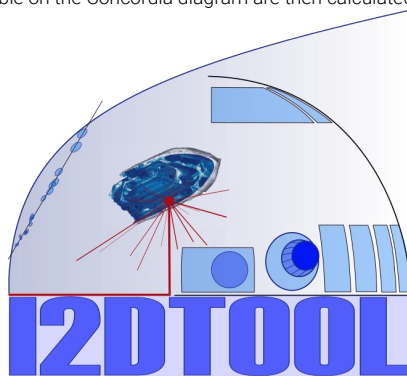
[2] Wang, H.A.O., Krzemnicki, M.S., *J. Anal. At. Spectrom.*, **2021**, *36*, 518-527.

I2DTool : U-Pb geochronology data treatment for dummies

Lach P.¹, Morel O.¹, Laurencelle M.¹, Padel M.¹,

¹BRGM, 3 Avenue Claude Guillemin, 45060, Orléans Cédex 2, France

I2DTool (Intuitive and Interactive Dating Tool) is a free, flexible, and upgradeable software package designed to significantly reduce the time required to process conventional U-Pb geochronology data performed with LA-ICP-MS. I2DTool is written in a non-proprietary language (Python 3). The program is built with a graphical user interface designed to be as intuitive as possible. It allows importing raw LA-ICP-MS files, as well as the image and laser shot coordinates corresponding to the ICP-MS file. An automatic selection of the standard/sample is performed followed by a classification by family. The effective signal is already automatically selected and a first estimate of the age of the population is automatically computed and shown on the Wetherill diagram. The strength of I2DTool is the interactivity of all windows. A click can be made on the sample list or on the Concordia window to automatically update the laser position on the SEM image and the corresponding ICPMS analysis. Subfamilies can be created within an existing family to clearly separate generations of different ages (core-rim, two distinct populations etc...). The calculation of isotope ratios from the raw data (and the necessary corrections) is done directly in I2DTool according to Fischer et al 2010. These ratios are provided to Isoplot R [1]. The age and corresponding values (error, MSWD, probability etc...) visible on the Concordia diagram are then calculated directly in Isoplot R.



[1] Fischer C. M., Longerich H. P., Jackson S. E., Hancher J. M. (2010): Data acquisition and calculation of U-Pb isotopic analyses using laser ablation (single collector) inductively coupled plasma mass spectrometry. *JAAS*, DOI: 10.1039/c004955g.

[2] Vermeesch P., (2018): IsoplotR: A free and open toolbox for geochronology. *Geoscience Frontiers*, 9, 1479-1493.

Rapid high-resolution Rb-Sr isotope mapping for geochronology

Martin Kutzschbach¹, Johannes Glodny²

¹Technische Universität Berlin, Chair of Applied Geochemistry, 10587 Berlin, Germany

²GFZ, German Research Centre for Geosciences, 14473 Potsdam, Germany

With advances in triple quadrupole plasma mass spectrometry, in situ Rb-Sr dating of rocks and minerals by LA-ICP-MS has become an established technique in recent years^{[1], [2]} However, the potential of age mapping similar to those in the U-Pb system^{[3], [4]} has remained unexplored.

Now we present the first high resolution Rb-Sr isotope map of a mica aggregate in a metamorphic rock, acquired with an Agilent 8900 MS/MS and a Teledyne Analyte Excite equipped with the Aerosol rapid introduction system (ARIS) and a low volume adapter from Glass Expansion. The mapping shown in the Figure covers an area of 800 x 300 μm and was recorded in about 90 minutes using a 3 μm laser beam. NIST610 was used as a calibration standard and phlogopite from the Phalaborwa complex with a homogenous age distribution was used as secondary standard.

Such mappings enable dating of very fine-grained rocks such as strongly deformed ultra-mylonites and allow detailed thermochronological studies and visualization of the age resetting during dynamic recrystallization.

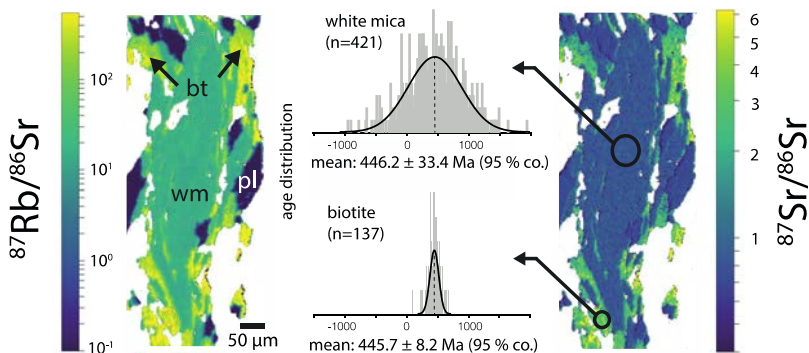


Fig.1: $^{87}\text{Rb}/^{86}\text{Sr}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio maps of mylonitic rock from Jämtland (Sweden) consisting mainly of biotite (bt), white mica (wm) and plagioclase (pl). Given the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7388[5] ages can be assigned to single pixels. However, sufficiently sized clusters are required for acceptable precision (e.g. $\sim 2\%$ @ 95% confidence level using a 30 μm circular spot). Expected age as derived by TIMS is $431.7 \pm 3.1\text{ Ma}$ [5] and hence accuracy is estimated with $\sim 3\%$.

References:

- [1] Zack, T., & Högalm, J. (2016). Chem. Geol. doi: 10.1016/j.chemgeo.2016.05.027
- [2] Rösel, D., & Zack, T. (2021). Geostand. Geoanal. Res. doi: 10.1111/ggr.12414
- [3] Chew, D.M., et al. (2017). J. Anal. Atom. Spectrom. doi: 10.1039/C6JA00404K
- [4] Drost, K., et al. (2018). Geochem. Geophys. Geosy. doi: 10.1029/2018GC007850
- [5] Bender, H., et al. (2019). Lithos. doi: 10.1016/j.lithos.2019.06.033

U/Th dating by fsLA SF-ICP-MS isotope imaging: new perspectives for archeological biominerals

Asmodée Galy ^{1,2}, Chantal Tribolo ², Norbert Mercier ², Christophe Pécheyran ¹

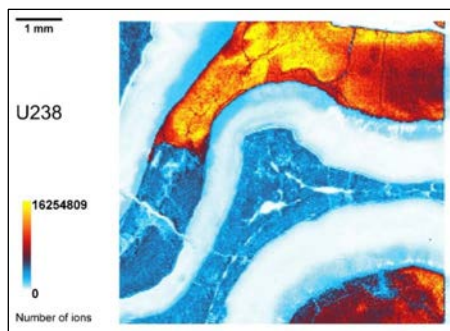
¹ IPREM, Université de Pau et des Pays de l'Adour [UPPA],

² Archéosciences-Bordeaux, Université Bordeaux Montaigne, CNRS : UMR6034

U-series datings are a method of choice for the chronological approach to archeological remains because of its large applicability (from a few thousand years to 600 ka), on a wide range of carbonate materials (from speleothems to biominerals). These advantages make it a particularly important tool for archaeology, especially for the investigation of the Middle and Upper Pleistocene, beyond the period of applicability of radiocarbon.

Currently, the common chemical protocol involves sample dissolution with spike addition and ion exchange chromatography. However, this approach is not suitable for small, valuable samples with very low uranium content (ultra-traces, <10ppb) and showing particularly complex diagenesis (open systems). These characteristics are specific to many samples, which are very abundant on most archeological sites (ostrich eggshells, teeth, snail shells, etc.). Therefore, these samples have a geochronological potential that has not yet been fully exploited.

We present an original approach for the dating of these neglected materials, taking advantage of the coupling of a femtosecond UV laser ablation system with a high sensitivity sectorial field ICP-MS. The methodology developed, using isotopic imaging, allows the direct measurement of ultra-traces of ²³⁸U and its descendants, with detection limits of the order of ag/mg. In addition, appropriate processing of these isotopic images of the analyzed materials allows the identification and selection (with a resolution of the order of a few μm) of the most suitable zones for U/Th dating, offering therefore a strong control of the data produced. Laser ablation sampling requires very little preparation of the material, preserving its integrity, since the masses collected are of the order of a mg or less. The ultra-trace isotope imaging thus developed is a particularly powerful tool for the study of incorporation and diagenetic processes within complex materials. In this presentation, we will discuss the possibilities offered by this new tool, particularly through its application to various biominerals from major Levantine prehistoric sites for the study of human evolution. These different examples will then lead us to consider new possibilities for uranium series dating.



²³⁸U distribution within an auroch tooth from Neshar Ramla, Israel (resolution: 30 μm).

Application of fs-LA-MC-ICP-MS for the simultaneous analysis of U and Pu isotope ratios in single particles of interest for IAEA safeguards

Stefanie Konegger-Kappel, Guillaume Stadelmann, Herbert Siegmund, Michael Minixhofer, Mathieu Rosenzweig, Andrew Bosko, Alex Venzin, and Sergei Boulyga

International Atomic Energy Agency, Department of Safeguards, Office of Safeguards Analytical Services, Seibersdorf, Austria

The International Atomic Energy Agency's (IAEA) environmental sampling program (ES) is used to detect possible evidence of undeclared nuclear material and activities, and is an effective tool that provides assurances that nuclear programs are only used for peaceful purposes. A crucial part of ES is the analysis of individual particles containing U and/or Pu. Such particles, which are typically in the micrometer size range, are collected by so-called swipe sampling in nuclear facilities. The power of swipe sampling comes from the fact that the isotopic and elemental compositions of the sampled particles reflect the entire history of the respective facility. Analyzing multiple particles by bulk analysis yields information about parameters of interest on the average, but individual particle analysis can provide a more in-depth summary of the past and present processes at a facility.

Highly sensitive analytical techniques are required to analyze the U and Pu isotopic compositions in single particles. We present the application of a Neptune Plus™ (Thermo Fisher Scientific, Bremen, Germany) multi-collector ICP-MS that is coupled to a J200 fs-laser ablation (LA) system (Applied Spectra, Inc., Sacramento, USA) for the analysis of mixed U/Pu particles containing less than 1 % of Pu that simulates typical spent fuel particles. The capability of simultaneously acquiring all U isotope ratios ($^{233}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{236}\text{U}/^{238}\text{U}$) together with Pu isotope ratios ($^{240}\text{Pu}/^{239}\text{Pu}$, $^{242}\text{Pu}/^{239}\text{Pu}$) was only possible by modifying the collector array of the "L5 ion counter package". While the major U (^{235}U and ^{238}U) and Pu isotopes (^{239}Pu) are measured with Faraday cups, the minor U (^{233}U , ^{234}U , and ^{236}U) and Pu (^{240}Pu and ^{242}Pu) isotopes are measured with ion counters because of the typically very low count rates of the minor isotopes.

The applicability of LA-ICP-MS was successfully demonstrated [1, 2, 3, 4] in the past for U isotope ratio analysis in single particles of interest for the IAEA. This presentation describes the first time that U and Pu isotope ratios have been measured simultaneously in single U/Pu particles by using LA-MC-ICP-MS after particle mapping by scanning electron microscopy (SEM). The merits and limitations of this currently developed method will be discussed.

[1] F. Claverie, A. Hubert, S. Beraïl, A. Donard, F. Pointurier and C. Péchéryan, *Anal. Chem.*, 2016, 88, 4375-4382.

[2] S. Kappel, S. Boulyga, L. Dorta, D. Günther, B. Hattendorf, D. Koffler, G. Laaha, F. Leisch and T. Prohaska, *Analytical and bioanalytical chemistry*, 2013, 405, 2943-2955.

[3] G. Craig, M. S. Horstwood, H. J. Reid and B. L. Sharp, *J. Anal. At. Spectrom.*, 2020, 35, 1011-1021.

[4] A. L. Ronzani, A. Hubert, F. Pointurier, O. Marie, N. Clavier, A. C. Humbert, J. Aupiais and N. Dacheux, *Rapid Commun. Mass Spectrom.*, 2019, 33, 419-428.

In situ isotopic ^{238}U – ^{234}U – ^{232}Th – ^{230}Th dating analysis using LA-ICPMS

C.-C. Wu¹, C.-C. Shen², D. Günther¹, B. Hattendorf¹

¹Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland

²Department of Geosciences, National Taiwan University, Taiwan ROC

U-Th (or ^{238}U – ^{234}U – ^{232}Th – ^{230}Th) dating is frequently used to determine the timing of Earth's geological, environmental, and biotic processes from materials formed a few years in the past to over 800 thousand years (ka). Here we present high sensitivity, *in situ* determinations of carbonate U and Th isotope ratios and ages using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Through the use of a "Jet" interface setup and the optimization of LA and ICP-MS conditions, the detection efficiency has been improved to a yield of 1-2%. A well characterized triple-spike (TS) ^{229}Th – ^{233}U – ^{236}U tracer was added to the laser generated aerosol by means of a desolvation nebulization system (DSN). The TS ($^{236}\text{U}/^{233}\text{U}$) and TS ($^{233}\text{U}/^{229}\text{Th}$) intensity ratios were used to monitor and correct for instrumental mass discrimination and U/Th elemental fractionation effects, respectively. The mass load was increased step by step using circular laser with spot diameters of 16, 24, 44, 60, and 90 μm , with constant repletion rates of 20 Hz and a scan speed of 5 $\mu\text{m}/\text{sec}$. Through the careful tuning and optimization by LA analyses on the standard of NIST SRM 612 with its $^{238}\text{U}/^{232}\text{Th}$ ratios approximately to 1, the mass discrimination for the measured TS ($^{236}\text{U}/^{233}\text{U}$) was slightly below the certificate ratios (0.9796), but in line with the $^{238}\text{U}/^{235}\text{U}$ ratio obtained by laser ablation for the NIST SRM 612 (0.9705). U/Th isotopic ratios for the TS ($^{233}\text{U}/^{229}\text{Th}$) were also close to the reference values (1.0150), while the laser generated aerosol exhibited a slightly lower ratio (0.9785) for NIST SRM 612 ($^{238}\text{U}/^{232}\text{Th}$). Yet, analysis of a flowstone sample in secular equilibrium, collected from Northern Calcareous Alps, resulted in activity ratios of 1.011 ± 0.066 ($2\sigma_m$) for $^{230}\text{Th}/^{238}\text{U}$, indicating that laser ablation data can be generated with good accuracy. A 2-sigma precision of $\pm 3\%$ from only 5 μg of carbonate mass (10 fg of ^{238}U) for a 190-ka stalagmite, could be achieved. This approach allows for the reconstruction of high spatial age profiles for young carbonates with age >5 ka, and could be applied for the better constrain the timing of past climatic events.

Chemical heterogeneities documented in Iron Age glass artefacts from the Dacian fortress of Ardeu (Hunedoara County, Romania) – the case for using LA ICP MS elemental imaging

Căsălean AC¹, Stremtan C², Barbula J³, Pușcaș CM⁴

¹Museum of Dacian and Roman Civilisation, Deva 330005, Romania

²Teledyne Photon Machines, Bozeman MT 59715, USA

³Quantel Lumibird, Bozeman MT 59718, USA

⁴Terra Analytic SRL, Alba Iulia 510095, Romania

The archaeological literature regarding Dacian sites has so far neglected the analysis of glass vessels due to their rarity and poor state of conservation. Whilst focusing mainly on the identifiable fragments of vessels with the help of well-known glass typology studies, most authors viewed glass vessels as imported luxury goods originating from the Mediterranean Basin, generally ranging from the 2nd century BC until the beginning of the 2nd century AD, when Dacia became a Roman province.

The primary goal of this contribution is to give new perspectives regarding 14 glass vessel fragments discovered in late Iron Age contexts at the Dacian fortress from Ardeu, Romania. We combine typological analysis of the archaeological artefacts with chemical analysis using laser ablation inductively coupled plasma mass spectrometry. The goal is to establish the origin of the raw materials from which the glass was made, as well as the area where these vessels were manufactured, and details regarding the production technique. We use LA ICP MS elemental imaging to document chemical heterogeneities in the analyzed samples, which we believe are closely linked to the manufacturing techniques. We also try and assess the usefulness of single spot bulk analysis in this type of assay and how representative this approach truly is for the overall chemical composition of the glass.

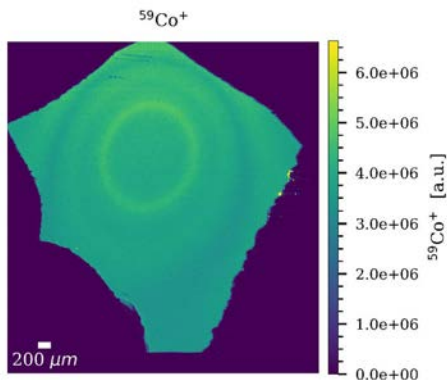


Figure 1. Spatial distribution of Co in an Iron Age glass sample from the Ardeu fortress.

The X-Factor in Laser-Assisted Solid Microanalysis

Davide Bleiner, Di Qu, Yousuf Hemani, Kevin Kraft, Mirushe Suloska, Claudia Masucci

¹ Swiss Federal Laboratories for Materials Science & Technology (Empa)

Among all techniques for microanalysis (Fig. 1) lasers have proven extremely effective for rapid sample introduction. Be it for optical emission analysis, e.g. LIBS, or mass spectrometry, e.g. LIMS, LA-ICP-MS, MALDI, laser-assisted microsampling is direct and flexible. Furthermore, it offers access to spatially resolved and/or time-resolved analysis.

Regardless the progress made so far, still a few challenges remain, such as:

- i how to make the laser-assisted solid microanalysis fully quantitative and sensitive, improving the precision to make sample heterogeneities always visible,
- ii how to make it free from matrix effects,
- iii how to make it nano-scale, and
- iv how to improve the sample utilization efficiency (SUE).

The extraction of compositional information comes from signals affected by flicker and shot noise, induced during the sampling, transport and excitation steps. This indicates the need to develop approaches to observe the very first instants of the laser-sample interaction. In the "big bang", laser plasmas are brighter, with consistent output from shot to shot. Being hotter and denser, their emission is however XUV-shifted.

The focusing to nano-scale spots requires lasers that operate in the short wavelength range. In fact, the diffraction limit is a linear function of the wavelength. Unfortunately, the reduction of the sampling volume causes a reduction of signal intensity and detection limit (Fig. 1), following counting statistics. Fortunately, there is a large room for improvement, because state-of-the-art solid microanalysis is far from a 100% sample utilization efficiency and the theoretical limit (Fig. 1). Thereafter, one may substantially reduce the spot size without degradation in sensitivity, if the SUE is comparably improved.

All these considerations indicate that the utilization of X-rays would bring about a substantial advantage in laser-assisted solid microanalysis. The discussion implies both the use of X-rays as probe photons (excitation pulses) as well as emitted photons (detected signals). In particular, extensions of LIBS into the X-rays, called LIXS, or an extension of LIMS called High Energy Laser Desorption Ionization (HELDI) are discussed.

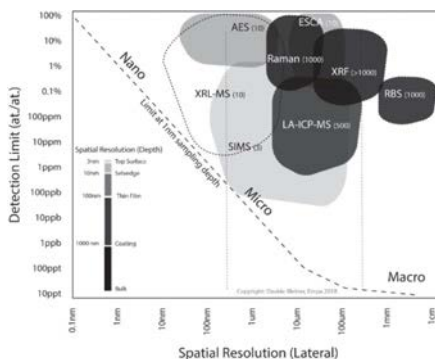


Fig. 1 Tradeoff between detection limit and spatial resolution. X-Ray Laser mass spectrometry (XRL-MS) fills the "nano-gap".

[1] Bleiner, D., Juha, L., & Qu, D. (2020). Soft X-ray laser ablation for nano-scale chemical mapping microanalysis. *Journal of Analytical Atomic Spectrometry*, 35(6), 1051-1070.

[2] Bleiner, D. (2021). Tabletop beams for short wavelength spectrochemistry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 181, 105978.

[3] Bleiner, D., Trottmann, M., Cabas-Vidani, A., Wichser, A., Romanyuk, Y. E., & Tiwari, A. N. (2020). XUV laser mass spectrometry for nano-scale 3D elemental profiling of functional thin films. *Applied Phys. A*, 126, 1-10.

Three Machine Learning Approaches for the Identification of Signatures of Life in Laser Ablation Ionization Mass Spectrometry

S. Gruchola¹, L. Schwander¹, R. Lukmanov¹, N.F.W Ligterink¹, C.P. de Koning¹, P. Keresztes Schmidt¹, V. Grimaudo¹, K.A. Kipfer¹, N.J. Boeren^{1,2}, A. Riedo^{1,2}, M. Tulej¹ and P. Wurz^{1,2}

¹Space Research and Planetary Sciences, Physics Institute, University of Bern, Switzerland,

²NCCR PlanetS, University of Bern, Switzerland

The identification of signatures of life, ranging from complex organic molecules to features of micrometre dimensions (i.e., microfossils) is a challenging task in space exploration. With the progressing search for life on different bodies of our Solar System, the question arises whether we will be able to find and identify the signatures of life as we know it. In this contribution we present three distinct machine learning (ML) models, which approach this task from different angles. The three models were applied to data collected with two space prototype laser ablation ionization mass spectrometric (LIMS) instruments, LMS and ORIGIN, with latter being operated in desorption mode [1,2]. The presented data analysis approach is of special interest to agnostic life detection.

One method applied to data collected with ORIGIN is mass correlation network analysis, which was used to identify single amino acids in extracts from permafrost samples [3]. The method compares the intensities of single masses between different mass spectra and determines the correlation coefficients. The correlations are then visualized in a mass correlation network that facilitates the identification of amino acids by analysing their fragmentation patterns in the mass spectra (Fig. 1A).

The second method was applied to data collected with LMS from the 1.88 Ga Gunflint sample, which hosts remnants of microfossils [4]. The method determines the similarity between spectra based on all masses present in the spectrum, and connects similar spectra (i.e., spectra collected from the same chemical compound) visually in a network (Fig. 1B), which allows for automated assignment of the spectra to chemically distinct phases of the sample.

Recently, we constructed a neural network to identify amino acids in mixtures from data obtained with ORIGIN, and the method shows promising first results. Neural networks are a powerful extension to the two methods discussed above, as they combine the advantages of mass correlation analysis (the ability to work with mixtures) and spectral similarity analysis (predictions for each spectrum). The presented models all have different applications and different outputs, yet they can all be used for the same task: Finding signatures of life.

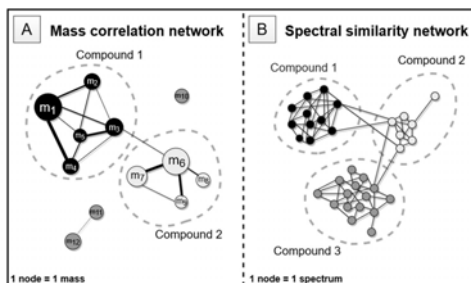


Figure 1: Example of a mass correlation network (A) and a spectral similarity network (B). A: Masses are connected if they correlate. B: Spectra are connected if they are similar.

[1] Ligterink, et al., Sci. Rep., 2020, 10, 9641.

[2] Riedo et al., (2013), Planet. Space Sci., 87, 1 – 1.

[3] Schwander et al., (2022), Front. Astr. & Space Sci. Accepted.

[4] Lukmanov R. et al., (2021a), Front. Artif. Intell., 4, 668163, 1-12.

Micro-droplet-based calibration for quantitative elemental bioimaging by LA-ICPMS

Andreas Schweikert^{1,2}, Sarah Theiner¹, Martin Šala³, Petra Vician⁴, Walter Berger⁴, Bernhard K. Keppler², Gunda Koellensperger¹

¹Institute of Analytical Chemistry, Faculty of Chemistry, University of Vienna, Waehringer Strasse 38, 1090, Vienna, Austria,

²Institute of Inorganic Chemistry, Faculty of Chemistry, University of Vienna, Waehringer Strasse 42, 1090, Vienna, Austria

³National Institute of Chemistry, Hajdrihova 19, 1000, Ljubljana, Slovenia

⁴Center of Cancer Research and Comprehensive Cancer Center, Department of Medicine I, Medical University of Vienna, Borschkegasse 8a, 1090 Vienna, Austria

A quantification strategy for elemental bioimaging by LA-ICPMS is presented.[1] Gelatin micro-droplet standards were produced by automated spotting of pL-volumes of gelatin solutions spiked with elemental standards onto glass slides. The small dimensions of the micro-droplets and the use of a low-dispersion laser ablation ICP-TOFMS setup enables measuring a set of calibration standards in less than 10 minutes. This allows setting up standardisation and control sample sequences comparable to solution-based quantification approaches by ICP-MS. This is necessary because no commercial standards are available for bioimaging applications and most standardisation methods are either sample specific, limited to a small number of analytes, often only one point calibrations and, laborious to produce.[2,3]

Due to the lack of appropriate reference materials for bioimaging applications by LA-ICPMS, the gelatin micro-droplets were compared to matrix-matched standards based on different tissue types using standard addition and isotope dilution approaches. Both quantification methods resulted in consistent results as external calibration using the developed gelatin micro-droplet standards. Overall, gelatin micro-droplets showed better reproducibility and lower elemental background and have proven to be a valid matrix mimic as external calibrant with the potential for multiplexing.

[1] A. Schweikert, S. Theiner, D. Wernitznig, A. Schoeberl, M. Schaier, S. Neumayer, B.K. Keppler, G. Koellensperger, Micro-droplet-based calibration for quantitative elemental bioimaging by LA-ICPMS, *Anal Bioanal Chem*, 414 (2022) 485–495.

[2] M.T. Westerhausen, T.E. Lockwood, R.G. de Vega, A. Röhnelt, D.P. Bishop, N. Cole, P.A. Doble, D. Clases, Low background mould-prepared gelatine standards for reproducible quantification in elemental bio-imaging, *Analyst*, 144 (2019) 6881–6888.

[3] M. Šala, V.S. Šelih, J.T. van Elteren, Gelatin gels as multi-element calibration standards in LA-ICP-MS bioimaging: fabrication of homogeneous standards and microhomogeneity testing, *The Analyst*, 142 (2017) 3356–3359.

Elemental distribution in shark teeth using high-speed LA-ICPMS imaging

C Derrick Quarles Jr.,¹ Benjamin T. Manard,² Christopher Hintz,³ Alicia M. Cruz-Uribe,⁴ Joseph A. Petrus,⁵ Cole R. Hexel²

¹ Elemental Scientific, Inc.

² Oak Ridge National Laboratory

³ Savannah State University

⁴ University of Maine

⁵ Elemental Scientific Lasers

Quantifying the chemical composition of fast-growing hard tissues in the environment can shed valuable information on ecosystem evolution both current and prehistoric. Changes in chemical composition can be correlated with environmental conditions and can provide information about the life history of organisms. Sharks can lose 0.1 to 1.1 teeth per day, depending on species, which offers a unique opportunity to record environmental changes over a short period of time.

In this work, high-speed imaging was performed using laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) utilizing a two-volume laser ablation chamber (TwoVol3). Three different shark species (tiger, sand tiger, and hammerhead) were investigated for elemental distribution changes across the dentine, enamel, and root regions of the teeth. Of particular interest is the distribution of Mg, Mn, Zn, and Sr, which helps researchers understand more about the environmental conditions endured by sharks. In the past these types of measurements have been performed by bulk acid digestion ICPMS, x-ray spectroscopy, or electron microprobe, which suffer from lack of spatial information or long analysis times. Utilizing the high-speed imaging capabilities of the imageGEO193 allows for high-resolution elemental mapping in a timely manner, making it possible to look at larger data sets.

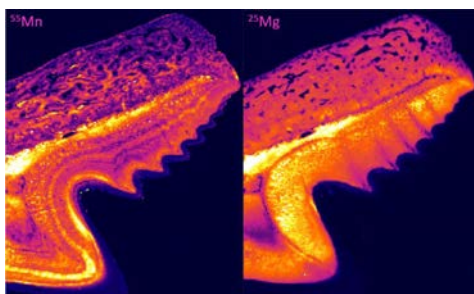


Figure 1. Elemental distribution of ^{55}Mn and ^{25}Mg in a tiger shark tooth.

Deciduous teeth as retrospective biomarkers of fetal metal exposure

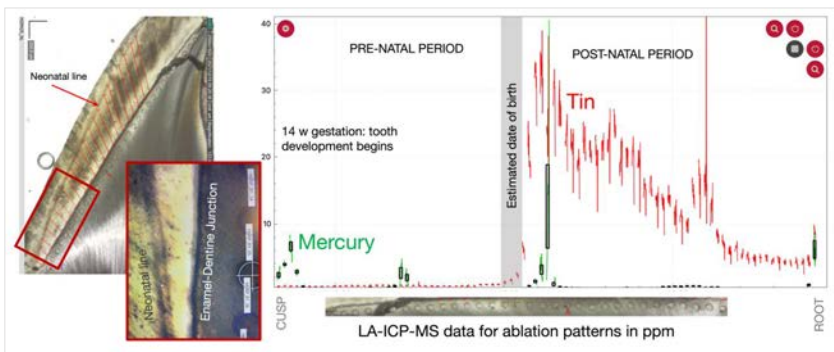
Punshon T¹, Jackson BP¹, Barr MN¹, Karagas MR², and Weisskopf M³

¹Dartmouth College, Hanover, NH, USA, 03755

²Geisel School of Medicine, Lebanon, NH, USA, 03756

³Harvard School of Public Health, Boston, MA, 02115

Fetal exposure to environmental contaminants during critical periods of development can have lifelong health consequences, a contributor to developmental origins of health and disease, or DOHAD. Examples include delays in cognitive development in children following fetal lead exposure. Typically, biomarkers of fetal exposure are rare and difficult to obtain. The accretionary growth form of teeth preserves an elemental signature of the blood during growth which can be used as a retrospective biomarker for metals that bind strongly to the hydroxyapatite matrix of teeth. Deciduous teeth begin to form at ≈ 14 weeks gestation and complete their growth at ≈ 1 year of age: a period encompassing development of the central nervous system. LA-ICP-MS analysis of sectioned deciduous teeth can provide a high-resolution (from days to weeks) historic record of metal exposure during this critical developmental period. Teeth can be dated relative to the day of birth using the neonatal line, a high-contrast growth line resulting from the temporary reduction in growth on the day of birth. We have applied LA-ICP-MS to the analysis of deciduous teeth from two epidemiological cohorts: the New Hampshire Birth Cohort (2009-present) and the St Louis Baby Tooth Study (1958-1970), completing analysis on 321 and 152 teeth respectively. We demonstrate that this technique can record early life exposures to numerous metals, notably manganese, lead, mercury and tin. Comparison between a modern-day and an historical cohort demonstrates the tangible reduction in environmental metal exposure, while allowing us to refine and standardize the appropriate analyte suite and methodology going forward.



Deciduous teeth preserve an elemental signature of the blood during growth that can be used as a retrospective biomarker of fetal and early life metal exposure.

High-resolution LA-ICP-TOFMS imaging of asbestos fibers in human malignant mesothelioma tissue

Sarah Theiner¹, Oana Voloaca², M. Clench², L. Cole², S. Haywood-Small², Gunda Koellensperger¹

¹ Institute of Analytical Chemistry, Faculty of Chemistry, University of Vienna, Vienna, Austria

² Biomolecular Sciences Research Centre, Sheffield Hallam University, S1 1WB Sheffield, U.K

Email: sarah.theiner@univie.ac.at

The potential of a low-dispersion laser ablation setup in combination with ICP-TOFMS detection will be highlighted for multi-element imaging of biological samples at the single-cell level. Examples of simultaneous mapping of endogenous elements with biological key functions together with exogenously introduced elements within different tissue samples will be presented.

In a clinical application, LA-ICP-TOFMS imaging was used to analyze human malignant pleural mesothelioma (MPM) samples at the cellular level [1]. MPM is an aggressive, incurable cancer associated with asbestos exposure, with a long latency and poor overall survival.

The low-dispersion LA setup employed, provided the high spatial resolution necessary to identify for the first time asbestos and other mineral fibers in lung and pleura tissue samples of MPM patients, based on their multi-element pattern (Si, Mg, Ca, Fe, and Sr) at a pixel size of 2 μm . The optimization of the laser fluence of the 193nm LA system proved to be the key parameter to simultaneously ablate soft, biological material and hard, mineral fibers without creating artefacts from co-ablation of the glass support.

Insights into the metallome of MPM patients with different pathologies were obtained and significant tissue inflammation was revealed around talc deposit regions in pleura samples. LA-ICP-TOFMS results correlated well with Perls' Prussian blue and histological staining of the corresponding serial sections.

References

[1] O. Voloaca, M. Clench, G. Koellensperger, L. Cole, S. Haywood-Small, S. Theiner, *Anal. Chem.*, 2022, 94(5), 2597-2606

Notes

Unraveling the interaction of MRI contrast agents with tissue using LA-ICP-MS

Traub H¹, Saatz J¹, Boyraz B², Tauber R²

¹ Bundesanstalt für Materialforschung und prüfung (BAM), Richard-Willstätter-Str. 11, 12489, Berlin, Germany

² Charité - Universitätsmedizin Berlin, Augustenburger Platz 1, 13353 Berlin, Germany

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is increasingly used to study the distribution of metal-containing drugs, imaging probes and nanomaterials in connection with disease related changes and therapy progress. Additionally, biomolecules can be detected indirectly by using metal-tagged antibodies.

The extracellular matrix (ECM) is, besides the cells, an important component of all body tissues. The macromolecular network of the ECM consists of structural proteins (e.g., collagen, elastin) and proteoglycans composed of highly negatively charged carbohydrates, the glycosaminoglycans (GAGs), which are covalently linked to a protein core. Many diseases, including inflammatory processes and tumors, are associated with characteristic ECM changes at an early stage. Recent studies have shown that contrast agents for magnetic resonance imaging (MRI), which are based on gadolinium containing chelate complexes or iron oxide nanoparticles, can bind themselves to ECM components.

To elucidate the role of GAGs like keratan sulfate (KS) and its modification state in disease, highly specific tools are necessary. As a complement to conventional immunohistochemistry LA-ICP-MS was applied to investigate the distribution of KS in tissue thin sections using a well characterized anti-KS antibody labelled with metal ions.[1] Furthermore, LA-ICP-MS was used for the detection of MRI contrast agents and the identification of their target cells and molecules in tissue samples from animal models, e.g. for cardiovascular diseases. The results show the possibilities of LA-ICP-MS for the elucidation of pathological tissue changes.

[1] B. Boyraz, J. Saatz, I.-M. Pompös, M. Gad, J. Dervedde, A.-K. B. Maier, O. Moscovitz, P. H. Seeberger, H. Traub, R. Tauber, *ACS Appl. Bio Mater.*, 2022, 5, 2, 853-861.

Elemental and lipid bioimaging of atherosclerotic rabbit artery tissue by complementary use of LA-ICP-MS and MALDI-MSI

Peter Niehaus¹, Esat Idi¹, Max L. A. Ebert², Melanie Kimm², Vanessa F. Schmidt², Moritz Wildgruber², Uwe Karst¹

¹Institute of Inorganic and Analytical Chemistry, University of Münster, Corrensstraße 48, 48149 Münster, Germany

²Department of Radiology, University Hospital, LMU Munich, Marchioninstraße 15, 81377 Munich, Germany

Laser ablation - inductively coupled plasma - mass spectrometry (LA-ICP-MS) has become an established tool for elemental bioimaging. In combination with matrix assisted laser desorption ionization mass spectrometric imaging (MALDI-MSI) used on parallel tissue sections, it is possible to obtain spatially resolved information of the elemental composition as well as the molecular distribution of biomolecules such as lipids.

The presented study makes use of these complimentary methods in order to identify changes in the permeability of atherosclerotic artery walls as well as their lipid distribution in different stages of disease progression. Artery samples of the aorta and the internal iliac artery were obtained from a rabbit study. Accelerated formation of atherosclerotic plaques were induced in the animals by cholesterol-rich diet and surgical injury of the endothelium over a period of 48 days. Sample arteries were harvested at different points throughout the study, with each of the animals being injected with gadolinium-labeled albumin prior to sacrificing.

Collected artery samples were cryosectioned and mounted to quartz and indium tin oxide coated glass slides, respectively, for investigation via LA-ICP-MS and MALDI-MSI. The embedding medium as well as the final sample preparation of the slices were optimized in order to allow sensitive and spatial resolved analysis for both utilized methods.

Matrix application via sublimation of 2,5- dihydroxybenzoic acid proved to be effective for lipid detection with MALDI-MS positive ionization mode and yielded bioimages of lipids with only minor wash-out effects. Using trapped ion mobility spectrometry (tims), ion mobilities for a number of analytes were obtained that, in combination with high resolution mass spectrometry allows for confident annotation of lipid species that can be confirmed via MS/MS experiments in future measurements.

For LA-ICP-MS, gadolinium, calcium and magnesium were quantified using an external calibration with matrix-matched gelatin standards for each element. Elemental bioimages were generated for all quantified elements as well as for phosphorus to depict the biological structure of the respective sample. Results were compared between different artery samples, suggesting a different gadolinium distribution for different stages of disease progression. Calcium and magnesium distributions were investigated in order to identify calcified plaques or other anomalies.

Application of multi-modal imaging to answer biological questions at the London Metallomics Facility

Alexander P Morrell¹, Alexander Griffiths¹, Madeline Parsons², Giovanni E Mann³, Nathan Siddall³, Theodora J Stewart⁴

¹London Metallomics Facility, King's College London, UK.

²Randall Centre of Cell & Molecular Biophysics, King's College London, UK.

³Vascular Biology & Inflammation, King's College London, UK.

⁴Research Management & Innovation Directorate, King's College London, UK.

The application of multiple analytical imaging modalities to investigate biological samples has become more routine in academic and clinical settings [1] due to advancing capabilities of newer instruments that have significantly increased sample throughput and improved resolution, allowing more comprehensive data sets to be acquired. The fundamental drive for such studies is the rich correlative data sets that can be generated to help answer complex biological questions. However, in practice these methods are confounded by many aspects from sample preparation to image analysis. The LMF is currently the only centre of its kind in the world, specifically dedicated to expanding frontiers in multidimensional analytics and correlative elemental bioimaging with a vision to provide and coordinate the most advanced combination of techniques for elemental analysis and correlative molecular imaging in biological samples, ranging from atomic to whole body scales. We routinely facilitate correlative projects requiring the comparison of multiple modalities. This includes comparing LA-ICP-MS, using the 193nm Iridia laser (Teledyne), for leading elemental imaging on biological samples with the cellular microanatomy (histology), and lipidomic and proteomic profiles (DESI-MS, raman, FTIR). Case studies will be presented where multi-modal imaging has been used including data from a murine ischemia stroke reperfusion model (Figure 1) and *ex-vivo* soft tissues sections from triple-negative breast cancers, from a \$55M Wellcome Leap funded project (DeltaTissue) for predicting changes in tissue states. These case studies will illustrate some of the advantages of combining techniques and highlight the practical challenges associated with acquiring such data. Key aspects including sample preparation, mounting substrates, instrumental parameters, pipeline orders, and correlative image analysis workflows will be discussed.

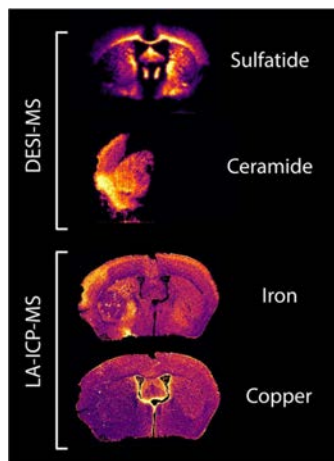


Figure 1. Lipidomic profile and metallic profile of murine stroke model using DESI-MS and LA-ICP-MS respectively.

[1] Stewart, T.J., 2019. Across the spectrum: integrating multidimensional metal analytics for in situ metallomic imaging. *Metallomics*, 11(1), pp.29-49.

Notes

Notes

IRIDIA Laser Ablation System

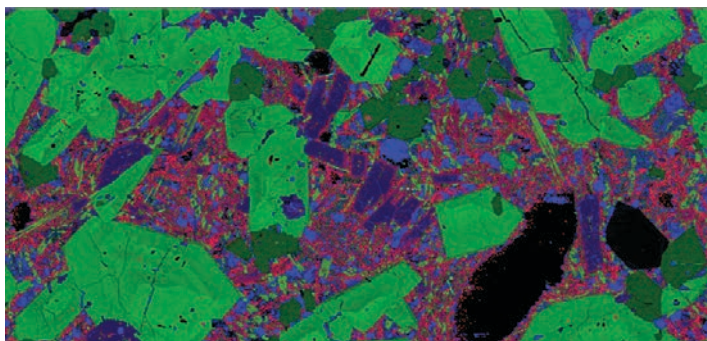
The Iridia laser ablation system exists to simplify what is normally a complicated and technically challenging process – proven to generate the highest quality data quickly and easily.



- The result of >5 years of collaborative academic research
- Quick, easy optimization for all types of solid sample analysis
 - HDIP software to automatically optimize the entire system, and to automatically process all resulting analytical data
 - » Able to produce fully quantified elemental image maps in minutes
 - » Publication quality images, plus high quality bulk analysis tools
 - » Can accept data from a wide variety of analytical instrumentation
- High resolution and high precision analytical data with rep rates from 1Hz to 1kHz
- Single Pulse Response (SPR) of <1ms to >1 second with simple configuration changes
- Eye-safe Class 1 laser operation, including alignment and maintenance
- Small footprint (600mm W, 888mm D, 1413mm H)
- Proprietary expanded objective array replacing the traditional style objective lenses
- Allows unrivalled video quality with compromising laser transmission

ENGINEERED BY SCIENCE

Fully field tested by globally renowned academic partners with analytical specification proven through peer reviewed and published data.



1kHz ablation of Basalt using Nu Vitesse ICP-TOF-MS

icpTOF

The TOFWERK icpTOF is the mass spectrometer of choice for biological and geological laser ablation imaging in leading laboratories throughout the world.

HIGH RESOLUTION ELEMENTAL IMAGING AT UNMATCHED SPEED



Sample courtesy of Dr. Hans-Eike Gäbler, BGR, Hannover, Germany.

Map of Ce intensity in a deep-sea polymetallic concretion sample. Laser ablation icpTOF intensity maps were simultaneously acquired for all elements with 5 μm spot size at a rate of 100 pixels per second.

TOFWERK
icp.info@tofwerk.com
tofwerk.com

