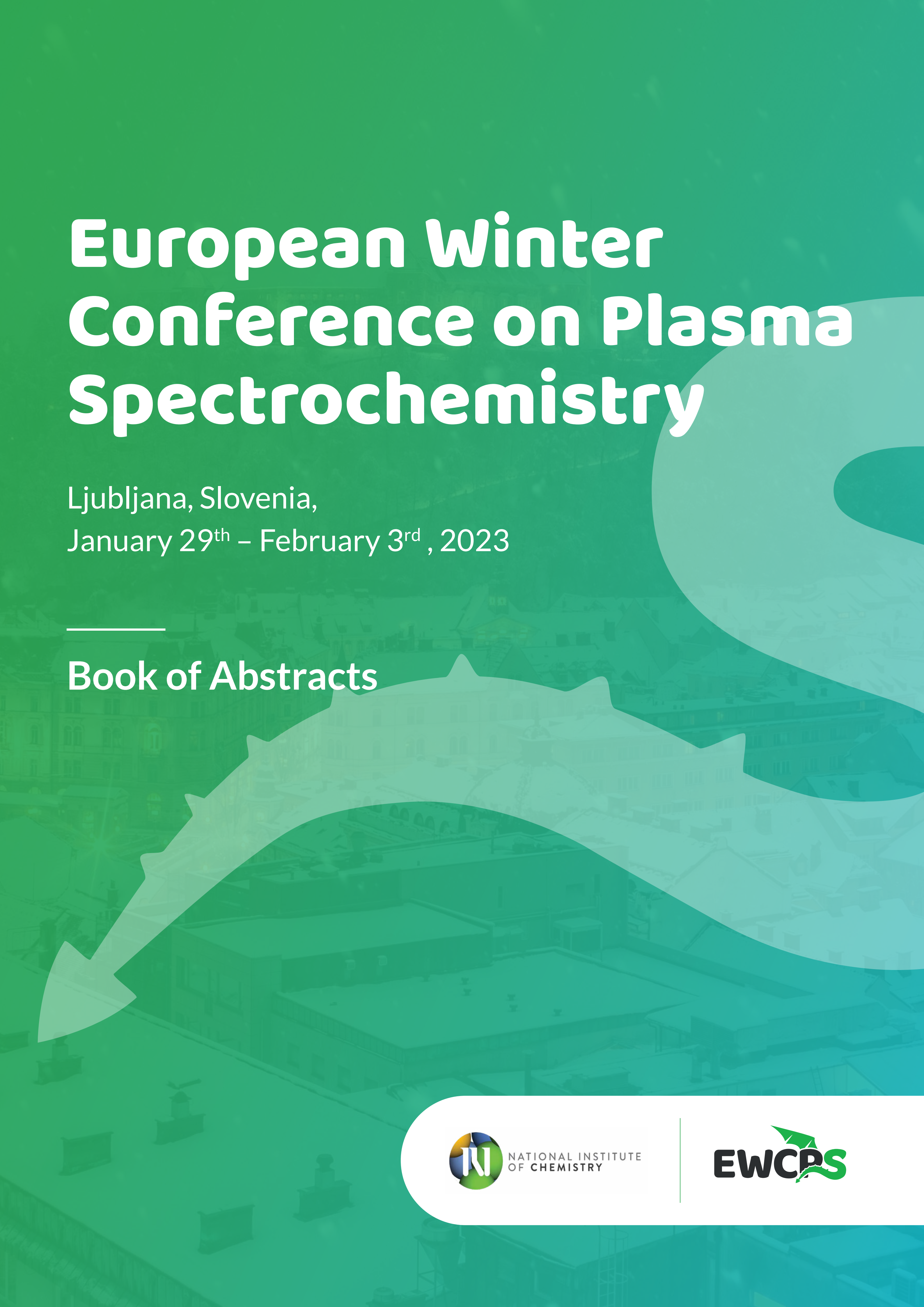

European Winter Conference on Plasma Spectrochemistry

Ljubljana, Slovenia,
January 29th – February 3rd , 2023

Book of Abstracts

NATIONAL INSTITUTE OF CHEMISTRY

EWCPS

Book of abstracts of the 19th European Winter Conference on Plasma Spectrochemistry

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Introduction

Dear Colleagues and friends,
Dear Plasma Spectrochemists,

It is our great honor and pleasure to welcome you to the European Winter Conference on Plasma Spectrochemistry, held from January 29th to February 3rd, 2023 in beautiful Ljubljana, capital of Slovenia and organized by the National Institute of Chemistry, Slovenia. Unfortunately, at the end of 2019 and beginning of 2020, the whole world was thrown off-axis by the Corona pandemic and lately by grave happenings in Ukraine. This influenced and influences each and every one of us in most unexpected ways. One of it - the continuity of the European Winterplasma conference series was broken for the first time, offsetting it for two years. However, finally here we are and we can meet and enjoy the conference as we are used to.

Ljubljana EWCPS will be the 19th time this event is organized as a continuation of the well-established and successful conference series that started way back in 1985. These biennial conferences, organized by European research groups in uneven years and alternating with the US Winterplasmas have become recognized and valuable platforms to exchange experience and share progress in the development and use of analytical plasma spectrochemical techniques.

This year the European Winter Conference on Plasma Spectrochemistry hosts over 500 delegates from more than 30 countries. We find this quite a success with the echo of the Corona pandemic still lingering and recent war in Ukraine.

Over the course of five days a broad and attractive program will be offered, focusing on topics concerning mass and emission spectrometric techniques, including fundamentals and instrumentation, sample introduction techniques, glow discharge, laser ablation, laser induced breakdown spectroscopy, isotopic analysis, speciation and metallomics, quality control, and applications in disciplines such as geology, medicine, biology, forensics, materials science, archaeology, etc.

Our scientific programme features 125 oral talks in total, including an opening talk by Sir Alexander Norman Halliday, 7 plenary talks, 2 heritage talks,
2 new horizons talks (a new format for EWCPS), 8 plenum keynote talks and 14 section keynote talks. A substantial part of contributed talks will be dedicated to student participants. About 270 posters complement the oral programme. 6 short-courses, taught by renowned experts, are a great opportunity for novices to learn from experts and jump-start their venture in the fascinating world of Plasma Spectrochemistry. Another new format will take place at EWCPS2023 for the first time; "The focus group" which is an event hosted by moderators and welcomes all of the participants to contribute to the discussion of novel instrumentation, future of the field and emerging problems in the plasma spectrochemisty. The EWCPS2023 hosts also the exhibition where instrument and equipment manufacturers showcase and introduce their latest products. Be sure to stop by and chat about newest instrumental developments in the relaxed atmosphere of our exhibition.

Many of the exhibitors are also our sponsors. Without sponsors, EWCPS2023 would not be possible to organize on this level. A wholehearted thank you!

We are particularly happy to welcome this year's awardees for the European Award for Plasma Spectrochemistry and European Rising Star Award for Plasma Spectrochemistry, sponsored by Agilent Technologies. The awards will be presented to Heidi Goenaga-Infante (European Award for Plasma Spectrochemistry) and Thibaut Van Acker (European Rising Star Award for Plasma Spectrochemistry) at the beginning of their talks.

Two other awards will be presented also, the JAAS Emerging Investigator Award by Royal Society of Chemistry will be presented to Alexander Gundlach-Graham and the Emerging Leader in Atomic Spectroscopy Award by Spectroscopy magazine will be presented to Andreas Riedo. Congratulations Alex and Andreas!

A set of awards will also be presented to the best student poster and oral contributions, selected by the scientific panel and awarded by the organizers of EWCPS.

A major and unforgettable part of EWCPS are the social events. As tradition goes, no Winterplasma is complete without the very famous Hot Plasma Party, we will host it in the spectacular Rock Hall and Upper Lapidarium of Ljubljana Castle. The Gala Dinner will take place at the Grand Ballroom of Hotel Union in the heart of Ljubljana. Following the Gala Dinner, we will open the doors to all participants for the EWCPS Concert. Other social events here and there will complement the daily scientific programme to keep you entertained.

We wish you all a productive and successful conference and lots of fun in Ljubljana!

Vid Simon Šelih, conference chair
Martin Šala, programme chair

National Institute of Chemistry, Ljubljana, Slovenia

EWCPS Chairs

Vid Simon Šelih, National Institute of Chemistry, Slovenia - Conference Chair
Martin Šala, National Institute of Chemistry, Slovenia - Programme Chair

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Jorge Pisonero, University of Oviedo, Spain
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Michael Sperling, University of Münster, Germany, Münster - 2015
Joanna Szpunar, CNRS, Pau, France, Krakow - 2013
Juan R. Castillo †, Zaragoza, Spain, Zaragoza - 2011

Student Representatives

Monika Ogrizek, Kristina Mervič

Local Staff

Monika Ogrizek, Kristina Mervič, Antea Hrepić, Nina Valentič, Urša Skube, Dino Metarapi, Michaela Bahelková

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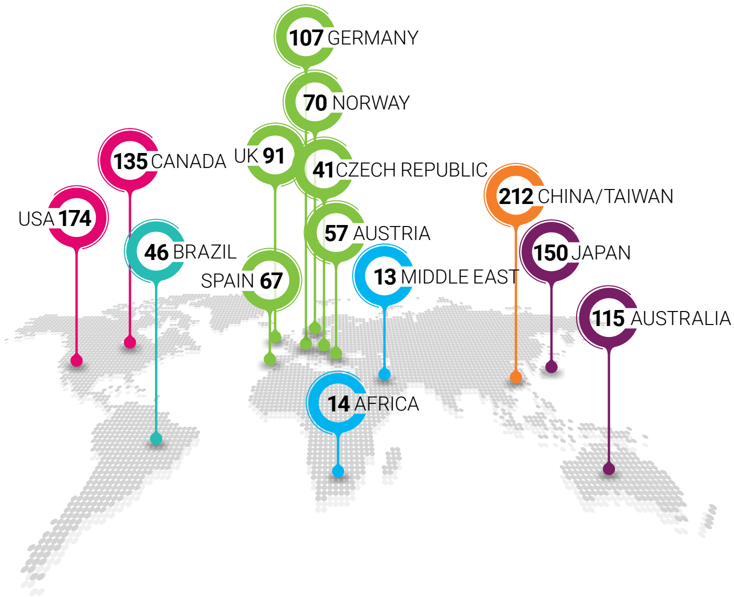

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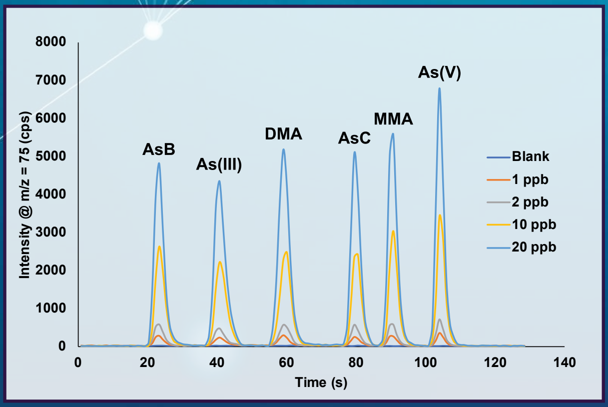
prep*FAST* IC



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Sunday

10:00
Short Courses
morning session

SC-1 ICP fundamentals
Thomas Prohaska
E1

SC-2 Speciation analysis strategies and applications
Jörg Feldmann
E2

SC-3 ICP QQQ and TOF-MS
Eduardo Bolea-Fernandez
E3

13:00

14:00
Short Courses
afternoon session

SC-4 Single particle analysis
Francisco Laborda
E1

SC-5 Laser ablation ICP-MS fundamentals and applications
Detlef Günther
E2

SC-6 Isotope analysis and MC-ICP-MS
Frank Vanhaecke
E3

16:50

17:00
OPENING CEREMONY

Welcome to EWCPS 2023

Opening lecture
Sir Alexander Norman Halliday

Linhart Hall

19:00
Plasma ON party

Get together event for all participants of EWCPS 2023

Grand Reception Hall

Sponsored by Ljubljana Tourism

21:00

Monday

8:30	**PLENARY** Carsten Engelhard **Fundamentals & Future Trends**	
9:15	**PLENARY** Joanna Szpunar **Speciation**	
10:00	**Coffee Break** sponsored by Slovenian Chemical Society	
	Fundamentals & Future Trends 1	**Speciation 1**
10:45	**KEYNOTE** Davide Bleiner	**KEYNOTE** Jörg Feldmann
11:10	**F&F 1** V. Karanassios	**SPEC 1** M.A. Subirana
11:25	**F&F 2** P.-E. Peyneau	**SPEC 2** D. Tukhmetova
11:40	**F&F 3** Shaun Lancaster	**SPEC 3** Michael Sperling
11:55	**F&F 4** Kaveh Jorabchi	**SPEC 4** Peter Heitland
12:10	**F&F 5** Franz Hallwirth	**SPEC 5** Zuzana Gajdosehova
12:25	**Lunch Break** sponsored by Mikro + Polo	
	Applications 1	**Nanomaterials 1**
13:35	**KEYNOTE** Carlo Barbante	**KEYNOTE** Bodo Hattendorf
14:00	**APP 1** M.I. Chronakis	**NANO 1** B. Moreira Álvarez
14:15	**APP 2** N. Giannakaris	**NANO 2** Eduardo Bolea
14:30	**APP 3** J.Jiménez-Lamana	**NANO 3** Tianyu Cen
14:45	**APP 4** Daniel Pröfrock	**NANO 4** Mathias Elinkmann
15:00	**APP 5** Ole Klein	**NANO 5** Laura Kronlachner
15:15	**Posters and Coffee** Session 1 - Monday	
16:15	**Heritage Lecture** Ralph Sturgeon	
17:00		

Tuesday

8:30	**PLENARY** Martín Resano **Applications**	
9:15	**KEYNOTE** María Montes-Bayón	
9:40	**KEYNOTE** Frank Vanhaecke	
10:05	**Coffee Break** sponsored by Omega	
	Applications 2	**Isotope ratio analysis 1**
10:45	**KEYNOTE** Pascal Bohleber	**KEYNOTE** Johanna Irrgeher
11:10	**APP 6** S.J. Abellán Martín	**IR 1** Michael Pribil
11:25	**APP 7** Kristina Brix	**IR 2** Kasper Hobin
11:40	**APP 8** B. Wiggershaus	**IR 3** J.I. García Alonso
11:55	**APP 9** Simone Trimmel	**IR 4** Emma Braysher
12:10	**APP 10** Thomas Vogt	**IR 5** Matthieu Boccas
12:25	**Lunch Break** sponsored by Chemass & Merel	
13:15	**After Lunch Coffee Seminars** Agilent - *Kosovel Hall* Shimadzu - *Linhart Hall*	
14:00		
	Speciation 2	**Applications 3**
14:15	**KEYNOTE** Katrin Löschner	**KEYNOTE** E. Bolea-Fernandez
14:40	**SPEC 6** Kelly LeBlanc	**APP 11** Koichi Chiba
14:55	**SPEC 7** J. García Bellido	**APP 12** Sarah Hill
15:10	**SPEC 8** S. Martínez	**APP 13** Ralf Kautenburger
15:25	**SPEC 9** T. Fernández-Bautista	**APP 14** Antonia Toska
15:40	**SPEC 10** Jelle Verdonck	**APP 15** Vishal Dwivedi
15:55	**Posters and Coffee** Session 2 - Tuesday	
17:00	**New Horizons Lecture** Denise Mitrano	
17:45	**Concert** organ concert at The Great Organ of *Gallus Hall*	**Focus Group** Spectrochemistry, Quo Vadis? *at Štih Hall*
18:30		
19:00		
20:00	**HOT PLASMA PARTY** *Ljubljana Castle*	
24:00		

Wednesday

8:30	**PLENARY** Detlef Günther **Laser & GD assisted analysis**	
9:15	**KEYNOTE** Andreas Riedo **Spectroscopy Magazine Award**	
9:40	**KEYNOTE** Vincent Motto-Ros	
10:05	**Coffee Break** sponsored by BIA	
	LA & GD assisted analysis	**Fundamentals & Future Trends 2**
10:45	**KEYNOTE** Beatriz Fernández	**KEYNOTE** Jake Shelley
11:10	**LA & GD 1** Andreas Limbeck	**F&F 6** Pierre Colleu
11:25	**LA & GD 2** Arne Bengtson	**F&F 7** Andrzej Bartnik
11:40	**LA & GD 3** Tom Van Helden	**F&F 8** Maximilian Heide
11:55	**LA & GD 4** Stefan Grünberger	**F&F 9** Zengchao You
12:10	**LA & GD 5** Jaime Orejas	**F&F 10** Helmar Wiltsche
12:25	**Lunch Break** sponsored by AnalysisAdria	
13:15	**After Lunch Coffee Seminars** Thermo Fisher - *Kosovel Hall* PerkinElmer - *Linhart Hall*	
14:00		
	Imaging 1	**Nanomaterials 2**
14:15	**KEYNOTE** Sarah Theiner	**KEYNOTE NANO** David Clases
14:40	**IMAG 1** Gabriel Braun	**NANO 6** G. Moreno-Martín
14:55	**IMAG 2** Asmodée Galy	**NANO 7** P. Menero-Valdés
15:10	**IMAG 3** Jan Preisler	**NANO 8** Faina Gelman
15:25	**IMAG 4** Katharina Kronenberg	**NANO 9** M. Jiménez-Moreno
15:40	**IMAG 5** Dirk Schaumlöffel	**NANO 10** Adam Sajnóg
15:55	**Posters and Coffee** Session 3 - Wednesday	
17:00	**New Horizons Lecture** Thibaut Van Acker **Rising Star in Plasma Spectroscopy Award**	
17:45		

Thursday

8:30	**PLENARY** Christophe Pécheyran **Isotope Ratio analysis**	
9:15	**PLENARY** Gunda Köllensperger **Metallomics**	
10:00	**Coffee Break**	
	Metallomics	**Isotope Ratio analysis 2**
10:40	**KEYNOTE** Uwe Karst	**KEYNOTE** Steven Goderis
11:05	**MET 1** Alexander Köhrer	**IR 6** Alicia Cruz-Uribe
11:20	**MET 2** Rinus Dejonghe	**IR 7** Jakub Karasiński
11:35	**MET 3** Alex Goupil	**IR 8** D. Malinovskiy
11:50	**MET 4** Markéta Vejvodová	**IR 9** Stefan Wagner
12:05	**MET 5** Simone Bräuer	**IR 10** Maria Alessia Vecchio
12:20	**Lunch Break**	
13:10	**After Lunch Coffee Seminar** Milestone - *Linhart Hall* Advion Interchim - *Kosovel Hall*	
13:55		
14:15	**KEYNOTE APP** Björn Meermann	
14:40	**KEYNOTE F&F** Thomas Zack	
15:05	**Heritage Lecture** Yngvar Thomassen	
15:50	**Posters and Coffee** Session 4 - Thursday	
16:50	**Young Scientists Focus Group** with guests from science, industry, publishing, etc. *at Štih Hall*	
18:10		
19:30	**Gala Dinner** *Hotel Union Grand Hall*	
22:00	**EWCPS Concert - Xequtifz** *Hotel Union Grand Hall* Free event for all participants Sponsored by ESI	

Friday

9:00	**PLENARY** Heidi Goenaga Infante **European Award for Plasma Spectrochemistry**	
9:45	**KEYNOTE** Takafumi Hirata	
10:05	**KEYNOTE** Alexander Grundlach Graham **JAAS Emerging Investigator Award**	
10:30	**Coffee Break**	
	Metrology and Appli 4	**Imaging 2**
11:15	**METRO 1** John Entwisle	**IMAG 6** Aristea Anna Leventi
11:30	**METRO 2** Are Bruvold	**IMAG 7** Karel Novotný
11:45	**METRO 3** Thomas C. Meisel	**IMAG 8** David Bishop
12:00	**APP 16** Daniel Torregrosa	**IMAG 9** Pavel Pořízka
12:15	**APP 17** C. Méndez-López	**IMAG 10** Tomáš Vaculovič
12:30	**Closing Ceremony**	
13:30	**SHUTDOWN Plasma** Farewell snacks and drinks *Grand Reception Hall*	

Lecture halls:

🟩 Linhart Hall 🟥 Kosovel Hall

except otherwise noted

Oral abstracts

Opening lecture

From planet formation to medicine – the impacts of multiple collector ICPMS

Alex N. Halliday[1], Heng Chen[1], Matthew Jerram[1], Emily Pringle[1], Naomi J. Saunders[1], Kathrin Schilling[2]

[1]Lamont-Doherty Earth Observatory, Columbia Climate School, Columbia University, New York, USA

[2]Environmental Health Sciences, Mailman School of Public Health, Columbia University, New York, USA

The ability to ionize efficiently most elements in the periodic table using an inductively coupled plasma, has led to many new techniques and applications in high precision isotope ratio mass spectrometry. This has been especially important for cosmochemistry for which improved chronology, especially using ^{182}Hf-^{182}W ($T_{½}$=8.9 Myr) and isotopic fingerprinting (e.g. of Mo or Ru) have been crucial. The ages of key early planetary objects for the first time have been reliably determined. Highly precise measurements of nucleosynthetic isotopic composition have facilitated fingerprints of the architecture of the circumstellar disk and the discovery that Earth derives from components not represented by any meteorites yet studied. Using such mapping, even the age of Jupiter has been determined indirectly from MC-ICPMS measurements. One of the biggest challenges remaining in planetary origins is the difficulty to model as a likely outcome, the identical isotopic compositions of refractory elements like Si, Ti and W in the Earth and Moon. This has forced a major rethink of models for the Giant Impact. The development of these and other high-fidelity isotopic methods for cosmochemistry, has naturally led to breakthroughs in other areas of science. Elements such as K, Zn and Ni for example, can be used to explore, not just the early Solar System, but also the solid Earth, the surface environment, biological processes, and even diseases. This is being taken even further with new developments in collision cell methodologies.

Back to the Future of Plasma-based Mass Spectrometry

Carsten Engelhard[1], George C.-Y. Chan[2], Cristian C. Escobar-Carranza[1], Maximilian Heide[1], Manuel Heinelt[1], Gary M. Hieftje[3], Petra Krystek[1,4], Darya Mozhayeva[1], Rob Ritsema[5], Annika Schardt[1], Johannes Schmitt[1], Désirée A.-M. Schütz[1], Jacob T. Shelley[6], Ingo H. Strenge[1], Joshua S. Wiley[7,8], Andreas Wimmer[9]

[1]University of Siegen, Germany, [2]Lawrence Berkeley National Laboratory, USA, [3]Indiana University, Bloomington, USA, [4]VU Amsterdam, The Netherlands, [5]RR Quality Consultancy, Utrecht, The Netherlands, [6]Rensselaer Polytechnic Institute, USA, [7]Purdue University, West Lafayette, USA, [8]Electrophoretic Mass Spectrometry Technology Corp., Auburn, USA, [9]Technical University of Munich, Garching, Germany

In this presentation, recent advances in plasma spectrochemistry for the detection of nanoparticles (NPs), microplastics (MPs), and other analytes will be reviewed and recent contributions from our laboratory to this field will be presented. Lessons that we have learned from the past helped us to develop improved instrumentation and methods.For example, the characterization of inorganic NPs is now feasible on the single-particle level in complex samples based on elemental mass spectrometry using high-speed data acquisition and a relatively hot argon plasma source. In the first part of the presentation, the current state-of-the-art in single-particle inductively coupled plasma mass spectrometry (spICP-MS) instrumentation for the detection and characterization of single NPs as well as remaining challenges will be discussed. While millisecond dwell times were used in the advent of spICP-MS, the use of microsecond dwell times helped to improve NP data quality and particle size detection limits. Further to this development, we could show that a custom-built high-speed data acquisition unit with microsecond time resolution (µsDAQ) can be used to successfully address issues of split-particle events and particle coincidence, to study the temporal profile of individual ion clouds, and to extend the linear dynamic range by compensating for dead time related count losses. Our next generation DAQ for spICP-MS features nanosecond time resolution. First results of a proof-of-concept study will be discussed. While instrumental parameters are important, appropriate sampling and pre-treatment protocols are of utmost importance because potential errors during these initial steps in the analytical workflow will influence the validity of final results.In the second part of the presentation, we turn to cooler plasma sources, which proved useful in ambient desorption/ionization MS. Specifically, the use of high-resolution MS with a home-built flowing atmospheric-pressure afterglow (FAPA) source (1-2) for the direct analysis of MPs will be discussed. In this work, the FAPA source was used to probe selected plastics directly on a sample target without a preceding separation step. Characteristic mass spectra from different MPs were obtained and multivariate statistical data analysis tools were used to process the raw data and to differentiate different types of MPs. Finally, spatially resolved optical emission images were obtained from the flowing afterglow of a helium-based low-temperature plasma (LTP) probe ionization source to better characterize plasma plume formation and propagation in the open air. Imaging made it possible to gain insights into important processes in the afterglow, which, in turn, will help to improve analyte ion formation and sampling in LTP-MS in the future.

fundamentals, instrumentation, nanoparticles, microplastics Andrade et al., Anal. Chem., 2008, 80, 2646-2653.

Molecules and atoms in elemental speciation analysis: the changing paradigms over the last three decades

Joannna Szpunar [1]

[1]Institute of Analytical and Physical Chemistry of the Environment and Materials, CNRS, Hélioparc, 64053 Pau, France

The understanding that the reactivity of trace elements is controlled by their chemical form has raised interest in analytical methods targeting the particular species of essential and toxic metals and metalloids. While the earlier approaches aimed at the isolation of a single metal-containing compound in amount sufficient for NMR characterization, the development of more sensitive and less time-consuming analytical techniques increased the number of metal species of interest and resulted in the emergence of a field in analytical chemistry, referred to as speciation analysis [1].

The advent of element specific detection in chromatography allowed an on-line detection of sub-picogram quantities of trace element and shifted the challenge from the NMR detection of the molecules to that of the metals it contained, while the molecular selectivity was attained by the separation of the target molecules by high resolution chromatography (2). However, while the resolution was sufficient to guarantee the species specificity in the case of anthropic contaminants or metallodrug metabolites, it was not for the analysis of naturally produced compounds.

The developments in electrospray ionization high resolution accurate mass (HRAM) mass spectrometry (MS) changed again the paradigm of analytical approach to speciation analysis. Instead of detecting atoms, it became possible to target the entire molecule on the basis of its accurate mass (3). Consequently, the challenge was shifted from the peak capacity in chromatography to that in a mass spectrum, from the atomic to the molecular signature. The latest developments in FT ICR and Orbitrap MS allow the separate detection of two ions differing by a mass of one electron (0.5 mDa) and the measurement of their masses with a sub-ppm accuracy, which opens the possibility to produce comprehensive lists of the element species present in a biological sample.

The lecture discusses the main steps of evolution of speciation analysis over the last three decades. A particular emphasis will be given to methods covering large populations of chemical species of one or several elements and their correlation with the biological role (metallomics). A novel high-throughput approach to quantification of element species based on isotope dilution electrospray HRAM MS will be presented. Perspectives of using the speciation information to the understanding of the molecular mechanisms of metal-dependent life processes will be highlighted.

speciation, metallomics, hyphenated techniques, mass spectrometry, high resolution, mass accuracy

Templeton, et al. Pure and Applied Chemistry, 2000, 72,1453-1470.

Szpunar, Lobinski, Hyphenated Techniques in Speciation Analysis, RSC, Cambridge, 2003.

Bierla, et al., Frontiers Chem. 2020, 8:612387

Targeting Materials Heterogeneities with Laser Induced XUV Spectrometry (LIXS)

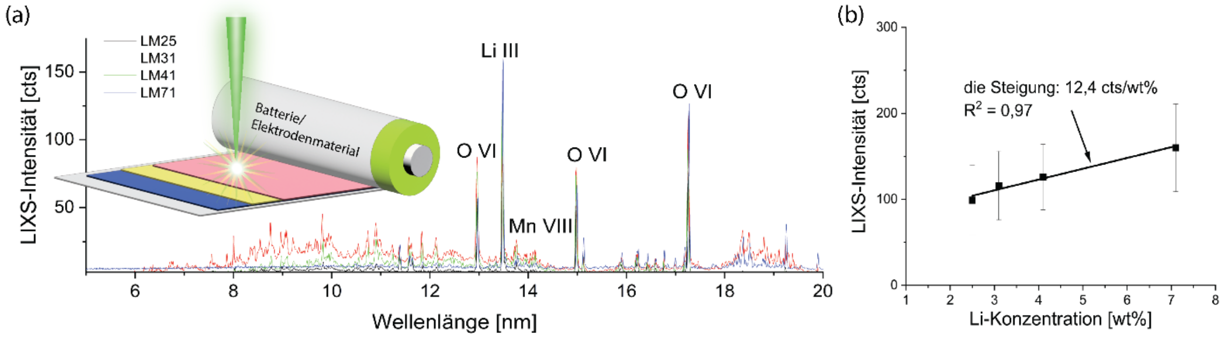
Davide Bleiner[1,2], Oksana Shlyakhtun[1,2] Di Qu[1,2], Adrian Wichser[1]

[1]Swiss Federal Laboratories for Materials & Technology (Empa), Dübendorf, Switzerland,
[2]University of Zurich, Zurich, Switzerland

Laser ablation (LA) is a spatially resolved technique enabling fast sampling of any kind of matrix without sample preparation. When coupled to an optical spectrometer, the laser-induced plasma provides spectral information on traces as well as major elements simultaneously. The ability to measure important elements such as H, C, N, O or Li, Be, B, F, P, Cl, makes laser-induced breakdown spectroscopy (LIBS) complementary to established laboratory techniques such as X-ray Fluorescence spectroscopy (XRF) or Laser Ablation ICP-MS (LA-ICP-MS).

LA-ICP-MS is very sensitive for quantitative analysis, while XRF is extremely specific and precise with calibration-free quantification. While poorer on the target analysis, LIBS offers a substantial potential for non-target qualitative analysis, if precision and specificity would improve consistency. Furthermore, although LIBS has the unique advantage to be operable *in situ*, i.e. in the field and/or in a low-pressure environment for space exploration, its susceptibility to the ambient conditions limits its impact for heterogeneous materials. Energy materials are often functionalized, implanted, or porous, which makes them heterogeneous. This puts a strict constraint for the spatially resolved analysis, especially if the measurement precision is worse than the material's heterogeneity.

Laser-Induced XUV Spectroscopy (LIXS) is similar to LIBS [1-2], but at a much shorter wavelength domain, the soft X-ray (10-100 nm) [3]. LIXS happens when the early laser-plasma is extremely hot and dense, giving selective prevalence to ion lines. These make the spectrum cleaner, stable and intense, with modest noise. The generation of a LIXS spectrum requires a high-fluence laser pulse, and a vacuum spectrometer for the short wavelength. The degraded resolving power (R=⍰⍰⍰⍰) at shorter wavelengths makes it generally difficult to collect a non-distorted (stigmatic) spectrum below 100 nm. We have addressed this technical challenge. The application of LIXS to characterize the heterogeneity of energy and valuable materials is discussed (see Fig.).



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Oral   Fundamentals & Future Trends 1

Battery-operated microplasmas for chemical analysis: Fundamental plasma diagnostics and selected applications

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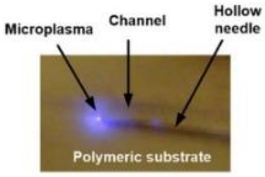
[1]University Of Waterloo, Waterloo, Canada

The Inductively Coupled Plasma (ICP) is widely used in elemental analysis.In a typical ICP, the plasma is formed on top of a quartz torch with the torch consuming about 20 L/min of Argon gas and requires about 1.25 kW of electrical power.We have been developing and characterizing miniaturized version of plasmas, called microplasmas (arbitrarily defined as those with one critical dimension, such as, depth or radius, in micrometer).In contrast to laboratory-scale ICPs, our microplasmas can be operated from a battery (requiring about 10 W of electrical power) and a flow-rate of about 250 mL/min of Argon gas, thus they can be used on-site (i.e., in the field). Microplasmas can also be fabricated using inexpensive technologies (e.g., 3D printing) using a variety of substrates (e.g., flexible polymeric materials).An example of a microplasma so fabricated is shown in the figure below.

In this presentation, microplasma instrumentation and fundamental diagnostics (required to enhance understanding and to provide improved analytical performance) will be discussed.Time permitting, applications such as Cr speciation, As determination, will be discussed.



Battery-operated, Microplasmas, Optical emission spectrometry (OES)

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Tormann, et. al., IEEE International Conference on Flexible and Printable Sensors

Towards pulse-overlapped single particle ICP-MS: a forward approach relying on a combination of theory, numerics and experiments

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[1]Université Gustave Eiffel, GERS-LEE, Bouguenais, France

The time-resolved signal measured when a dilute nanoparticle dispersion is analysed by ICP-MS in single particle mode (sp-ICP-MS) displays a succession of peaks. When the particle number concentration ρ of the dispersion is sufficiently low, each peak is associated with a single nanoparticle (i.e., is a particle event) with a probability close to one. However, when ρ increases, some particle events may overlap and give rise to composite peaks, resulting from the superposition of two or more particle events. This overlapping phenomenon causes a counting bias, i.e. a discrepancy between the number of particles entering the plasma of the instrument and the number of detectable peaks in the measured time signal. After showing that there is a one-to-one correspondence between the times at which particle events appear in an experimental time signal and the discontinuity points of a one-dimensional, homogeneous Poisson process [1], we build on this theoretical foundation to compute analytically this bias. The highly nonlinear relationship obtained depends on the flux λ of nanoparticles entering the plasma, the average duration of a particle event and the integration time of the measurement [2]. We also present some results regarding the statistical properties of the peaks. In particular, we calculate the average number of nanoparticles giving rise to a peak, the probability law of the number of nanoparticles per peak and the average duration of a peak. Monte Carlo simulations and sp-ICP-MS measurements performed with gold nanoparticle dispersions are in excellent agreement with the theory, over three orders of magnitude in λ. Finally, we show how to obtain the average nanoparticle mass of a potentially multimodal dispersion, even in the case of particle events pile-up in the sp-ICP-MS signal, and we study the impact of overlapping on the effective particle size distribution measured by sp-ICP-MS.

This work consolidates the theoretical basis of sp-ICP-MS and is a first step towards the analysis of real samples by pulse-overlapped sp-ICP-MS. Such an approach could indeed be useful to streamline the experimental workflow, or for unstable or specific samples for which dilution is not an option.

ICP-MS; nanoparticles; stochastic processes ; Monte Carlo simulations

Peyneau, 2021, Spectrochimica Acta Part B: Atomic Spectroscopy, 178, 106126.

Peyneau, Guillon, 2021, JAAS, 36(11), 2460-2466.

Characterisation of gas cell reactions for 73 elements with N_2O for tandem mass spectrometry measurements

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[1]Montanuniversität Leoben, Leoben, Austria, [2]University of Calgary, Calgary, Canada

One widely utilised method to overcome spectral interferences in ICP-MS is to employ the use of a reaction cell gas to mass-shift either the analyte or the interfering species to obtain interference free determinations at the shifted mass of the analyte or on-mass. Amongst others, ammonia (NH_3) and oxygen (O_2) have been used as reaction gas to resolve interferences via the formation of molecular species in the reaction cell. However, NH_3 is a corrosive and toxic gas that is not universally compatible with every gas cell and O_2 has a selective range of elements that react readily enough to benefit from mass-shift.

Nitrous oxide (N_2O) is an alternative reaction gas to form oxide species. N_2O has a higher reactivity than O_2 and leads to increased sensitivity when used in ICP-MS. However, due to its high reactivity, a tendency to form new spectral interferences from other matrix components historically rendered N_2O unfavourable for ICP-MS measurements. With the advent of tandem mass spectrometry (MS/MS), formations of new interferences are no longer as problematic, as the additional quadrupole provides a mass-filter that only allows the target mass-to-charge ratio enter the reaction cell. Thus, N_2O becomes a more viable option and is recently gaining traction within the community.

Here, the use of N_2O as a reaction gas for ICP-MS/MS measurements has been studied for 73 elements using a quadrupole-based reaction cell. Product ions formed within the reaction cell were monitored and their sensitivities (relative to no gas mode) were determined. Sensitivities from the formation of oxides using N_2O and O_2 were compared to highlight elements of particular sensitivity improvement. For example, the reaction of Ca^+ to CaO^+ was approximately 50 times more sensitive with N_2O than O_2. This, combined with no oxide formation for K or Ar, allowed for interference free determination of Ca on m/z 40 compared to standard (no cell gas) mode. This increased sensitivity of the method by 15 times, while lowering the background equivalence concentration by a factor of 44 and the detection limit by a factor of 10 (to 0.015 ng g^{-1}). Further trends found across the periodic table, as well as data for other selected elements of interest, will be discussed.

nitrous oxide, ICP-MS/MS, mass-shift, reaction cell

Post-plasma chemical ionization: a standalone ion source for nonmetal analysis

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[1]Georgetown University, WASHINGTON, United States

Nonmetal speciation has advanced substantially by LC-ICP-MS/MS. However, significant barriers remain for elemental detection to become a widely-used companion to LC-ESI-MS.In particular, simultaneous halogen, S and P detection offers quantitative nontargeted analyses in food, pharmaceutical and environmental applications.Yet such a capability is difficult to achieve using current ICP-MS/MS technologies because of challenges in ion generation for F and Cl and elusiveness of an effective isobaric interference reduction chemistry suitable for all nonmetals.

We have developed an alternative elemental-MS methodology to overcome these challenges. Rather than relying on plasma to generate ions, we use post-plasma chemical ionization. ICP is used as a reactive environment to convert nonmetals into polyatomic neutrals. These species are then ionized via interactions with reagent ions introduced downstream of plasma. The vast possibilities of reagent ions open myriad of avenues for enhancing ionization efficiencies. Here, we show that ionization using barium-based reagent ions supplied by a nanospray offers a universal approach for detection of halogens, S, and P. Moreover, ionization chemistry could be tuned for specificity and better matrix tolerance. We demonstrate that Sc-based ionization offers F-specific detection while a negative mode ionization using corona discharge enhances detection of S and P. To resolve isobaric interferences, the ion source is readily interfaced to molecular MS platforms that offer high resolution and MS/MS capabilities, thanks to the low-temperature chemical ionization. We show that coupling the ion source to an Orbitrap eliminates isobaric interferences, leaving background elemental contamination as the sole factor in determining LODs.

These attributes make the above-mentioned elemental ionization methodology a standalone ion source readily accessible on LC-ESI-MS instruments, complimenting molecular ionization for comprehensive speciation.

chemical ionization, high resolution, nonmetal, halogens, speciation

Redeker, et.al., Anal. Chem. 2022 (in press https://doi.org/10.1021/acs.analchem.2c02359)

White, et. al., JAAS. 2022, 37, 870-882

Microwave assisted, high-pressure, flow-digestion – a novel approach

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Reliable element analysis based on plasma or flames highly depends on efficient sample preparation since even clear and colorless solutions may obtain substantial amounts of residual organic compounds, that in turn can cause plasma interferences in subsequent quantification methods [1,2]. Most modern sample digestion techniques use microwave-assisted discontinuous closed vessel batch digestion as they are elaborated and show good digestion performances. However, these systems share a number of substantial drawbacks. It is hardly possible to fully automate the procedure which means the permanent need of trained technicians. The numerous manual work steps hold the risk of injuries and potential errors such as sample contamination or analyte loss. In contrast, the newly designed microwave assisted high-pressure flow-digestion system presented here drastically reduces the number of manual work steps and significantly increase safety and cost-effectiveness. The novel spatial arrangement of the perfluoralkoxy (PFA) digestion coil within the microwave cavity was optimized for effective microwave coupling.As a consequence, the heating rate as well as the digestion performance increase significantly. The compact design further allows for a potential application as built-in flow-digestion stage in analyte quantification instruments such as inductively coupled plasma mass spectrometry. The system was operated at 500 W microwave power and 5ml/min flow rate. The digestion performance was evaluated by quantifying the residual carbon content (RCC) of glucose, glycine, and phenylalanine via inductively coupled plasma optical emission spectroscopy. Phenylalanine is known to be extremely hard to digest due to the aromatic ring structures of the substance. Thus, the RCC was around 28% which is comparable to closed vessel batch systems. The accuracy and precision of the new setup was validated by the digestion of four certified reference materials. The achieved results were in good agreement with the certified values and are comparable to those attained by closed vessel microwave-assisted digestion systems. Blank digestions analysed by ICP-MS did not show any contamination by elements typical for the stainless-steel construction setup of the flow digestion system.

Microwave assisted high-pressure flow-digestion; elemental analysis; sample preparation; sample digestion

Allain et.al., Anal. Chem. 63, 1497–1498, 2002

Wiltsche et.al.,JAAS, 30, 2223–2234, 2015

Mass balance of elements: a tool for speciation the analysis of nanoparticles and organic pollutants

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Mass balance approaches of an element is always used in speciation analysis to determine extraction efficiency and column recovery[1]. This lecture will demonstrate who this aids the discovery of novel elemental arsenic species in biological samples such as the newly detected arsenic species in rice[2] and in whale brain using HPLC coupled to ESI-HRMS and ICPMS. The mass balance of mercury in whale liver and brain and oil and gas condensates indicated that methylmercury is not the predominate mercury species, but other species which are hidden and not amenable to derivatization of mercury speciation analysis. The mass balance made it possible to quantify the amount of mercury nanoparticles (NPs) in the samples. In whale tissues mercury-selenium aggregates could be determined while in oil and gas condensates meta cinnabar NPs were identified[3].

In the field of persistent organic pollutants (POPs) the mass balance approach is not used. ICPMS among other techniques could be used for mass balances when POPs contain a hetero-element such as P, S, Cl, Br or F. Here this lecture will show examples of total fluorine and PFAS speciation in biological samples and total phosphorous and P-speciation in petrochemistry.

[1]Feldmann, et al., Anal Bioanal Chem (2018) 410, 661-667

[2]Raab, et al., Environ Chem (2022) in press.

[3]Heuckeroth, et al., Anal Chem (2021) 93 (16), 6335-6341.

Speciation and intracellular distribution of Arsenic in Sargassum algae

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[1]CNRS /Université de Pau et des Pays de l'Adour/E2S UPPA, IPREM, UMR 5254, Pau, France, [2]UT2A, Pau, France, [3]Bordeaux Imaging Center, Imagerie Electronique, Université de Bordeaux, Bordeaux, France, [4]BRGM, Orléans, France

For the last decade, an unprecedented amount of Sargassum algae have washed ashore on the beaches of the Caribbean 1. Sargassum accumulates a high concentration of pollutants, with up to 115 mg As/kg of dry weight 2. They are dealt with by deposing them along the shoreline, where they degrade, producing leachates with high As concentrations that can reach freshwater systems, causing environmental issues. An in-depth characterization of As speciation and distribution in Sargassum is essential to understand the mechanisms of As uptake and leaching, and to assess the risk for the environment. The study of As speciation on Sargassum with HPLC-ICP-MS showed that inorganic As species are the main components, but that organic species, especially DMA, but also AsB and TMAO, are also present. It also revealed that the fraction of organic As increases with the degradation of the algae. The speciation was also studied with X-Ray Absorption Spectroscopy on frozen samples, removing the need for pre-treatment and extraction. This enabled the determination of species such as As bound to sulfur and arsenosugars, demonstrating that fresh algae contains mainly inorganic As(III) and As bound to sulfur, with some As bound to carbon. However, during the decomposition of algae, As speciation evolves to more organic forms and As (V), possibly due to microbiological and oxidative processes during fouling. The distribution of As in the leaves, stems and floats of Sargassum was determined using nano-X-Ray Fluorescence, Nano secondary ion mass spectrometry (NanoSIMS) and Transmission Electron Microscopy. Their high lateral resolution, of around 70 nm, allowed the mapping at the sub-cellular scale. A sample preparation adequate for the three techniques enabled the obtention of correlative imaging of the same cell. It was shown that arsenic was mainly accumulated in the cell walls, in agreement with previous studies 3, with a small amount of arsenic also visible in the cell organelles.

The obtained arsenic distribution and speciation knowledge contributes to understand better the toxicity and environmental impact of the Sargassum and their As-rich leachates. It can enable the development of adequate remediation technologies in order to handle the stranded Sargassum.

Arsenic, speciation, Sargassum, algae, distribution, cell, spectroscopy, imaging

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On-line Species-specific Isotopic Analysis of Sulfur by Hyphenation of Capillary Electrophoresis with Multicollector-ICP-MS

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A method was developed[1] for a species-specific isotopic analysis of sulfur via on-line hyphenation of capillary electrophoresis with multicollector ICP-MS (CE/MC-ICP-MS). Instrumental mass bias was corrected by external correction with multiple-injection sample-standard bracketing approach. The isotope ratio measurement results obtained with the newly developed on-line CE/MC-ICP-MS method were compared with the results obtained via traditional MC-ICP-MS measurement. The traditional off-line method involved an analyte/matrix separation by anion exchange chromatography to separate sulfate ions from other sulfur species. By comparing the on-line results with the off-line ones, the most suitable data evaluation method was identified for the processing of the transient signals. The repeatability for the sulfate-δ34S value was 0.57‰ (2SD) and thereby only twice higher than the obtained with off-line measurements (0.30‰). The application of the method on real samples was accomplished by the analysis of naturally present sulfate in river systems.

River water sulfate, Sulfur isotopes, Species-specific isotopic analysis, Multiple-injection sample-standard bracketing approach

Faßbender, et. al., Analytical and Bioanalytical Chemistry (2020) 412:5637–5646.

Gadolinium-based contrast agents as emerging pollutants: From humans to the aquatic environment and back

Michael Sperling[1], Marcel Macke[1], C. Derrick Quarles[2], Uwe Karst[1]

[1]University of Münster, Münster, Germany, [2]Elemental Scientific, Inc., Omaha, USA

Gadolinium-based contrast agents (GBCAs) are a cornerstone for enhancing the image quality in magnetic resonance imaging (MRI) for medical diagnostics. Since their introduction in 1988, their use has increased dramatically, reaching about 45% of all MRI applications, summing up to more than 300 million doses administered to date.

As a result, hundreds of metric tons of gadolinium has been released into the environment already, rendering GBCAs an important group of emerging contaminants. While these compounds are difficult to ionize by electrospray ionization mass spectrometry, liquid phase separations coupled to inductively coupled plasma-mass spectrometry (ICP-MS) have shown promise for their determination in the aqueous environment as well as in drinking waters.

To investigate the distribution and fate of GBCAs in the environment, highly selective and sensitive methods of speciation analysis are required. In this work, a fully automated single platform approach for total metal analysis and syringe-driven chromatography coupled with ICP-MS was developed to identify and quantify several contrast agents in water samples. A method based on anion-exchange chromatography (IC) was set up to achieve the separation of the polar to ionic contrast agents, whereas the hyphenation to quadrupole-based ICP-MS led to highly sensitive element specific detection. Furthermore, an integrated inline-dilution function allowed for fast-external calibration from single stock standards to determine total Gd and GBCA concentrations. The developed IC-ICP-MS method enables a fast separation of several commonly administered GBCAs in less than two minutes, which is a significant improvement of analysis time in comparison to previously published methods. Limits of detection for the individual GBCAs between 11 and 19 pmol/L turned out to be sufficient for their detection and quantification in environmental samples without preconcentration. The possibility to determine total Gd on the same platform allowed for an integrated validation via mass balance.

Results indicated that the vast majority of gadolinium is still present in form of the original GBCA not only in surface waters having received inflow from wastewater treatment plants, but also in local drinking water originating from different water purification plants. This was investigated for drinking water samples from 30 cities in a densely populated region in Germany, which are supplied with water from different sources. The results clearly demonstrate that drinking water originating from rivers, contains significant concentrations of total Gd and macrocyclic Gd species.

gadolinium-based contrast agents; emerging pollutants; speciation analysis;IC-ICP-MS; on-line dilution; on-line calibration; drinking water

Analytical challenges for ICP spectrometry in clinical cases of severe poisonings and environmental and occupational exposure to metals

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Clinical ICP spectrometry contains devils in the details and is analytically challenging in cases of severe poisonings and occupational or environmental exposure to metals.

In the clinical laboratory, emergency cases can happen. The selection of the appropriate material (blood or serum, urine, hair, tissue) must be carefully considered. Often only a very low volume of blood or urine is available, or just one single hair in a forensic application. The concentration of the toxicant in the low amount of sample could be either in the low environmental concentration range or significantly above the linear calibration range in the case of an acute intoxication. The concentrations of available QC samples can be in a completely different range than the real samples. The total amount of an element (such as for As, Cr, Hg) does not always give a clear toxicological information and additional time-consuming speciation is required. In other cases information about the distribution of the analyte between red blood cells and the extracellular compartment of the blood is relevant for diagnosis and therapy, e.g. for Cr(VI) or methyl-Hg.

We discuss these analytical challenges for ICP-OES and ICP-MS in different clinical cases. Examples are environmental exposure to Co or As, accidents with Cr(VI) and As(V), acute Hg intoxications or suicide attempts with Tl. For Tl we also describe analytical details in a repeated poisoning of the life partner, which was characterized as a case of a Munchhausen by adult proxy syndrome (1).

In contrast to these clinical examples with higher elemental concentrations in body fluids we also discuss results of a recently performed biomonitoring for 73 elements (2) being mostly present in the ng/L range.

clinical ICP spectrometry, speciation, exposure to metals, poisoning

Pragst, Hartwig, Int J Leg Med, 2022, 136, 695-704

Heitland, Köster, J Trace El Med Biol, 2021, 64,126706

Certification of iAs in biological matrices: Why is it taking us so long

Zuzana Gajdosehova[1], Calvin Palmer[1], Patricia Grinberg[1], Indumathi Gedara[1], Zoltan Mester[1], Ásta Pétursdóttir[2], Rebecca Sim[2], AndreaRaab[3], JoergFeldmann[3], Stanislav Musil[4], Tomas Matousek[4], Kevin Kubachka[5], Mesay Wolle[6], Ben Wozniak[7], Stephen Springer[7], Hakan Gurleyuk[7]

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The toxicity of As depends on its oxidation state but also, whether it is present in its organic or inorganic chemical form. In general, organic As species are considered non-toxic, whereas inorganic As (iAs) is a class II carcinogen. The current regulations of maximum levels of As in food have recognised these differences by targeting specific As species in the regulations. For instance, the maximum levels of As in rice, were changed from total As to iAs (sum of AsIII and AsV), which mass fraction in rice can vary significantly. However, accurate quantitation of iAs can be challenging. We examined the published data of iAs in our biological tissue CRMs and found that the range spans over several orders of magnitude. This clearly indicates that there are several metrological challenges that need to be addresses.

We brought together an international team of experts in As analysis with the aim to identify possible sources of discrepancies in measured mass fractions of iAs in plant, marine and terrestrial biological matrices. Our results showed a good agreement in majority of analysed samples; however, we identified several possible pitfalls which could result in large discrepancies and will be discussed in details in my talk.

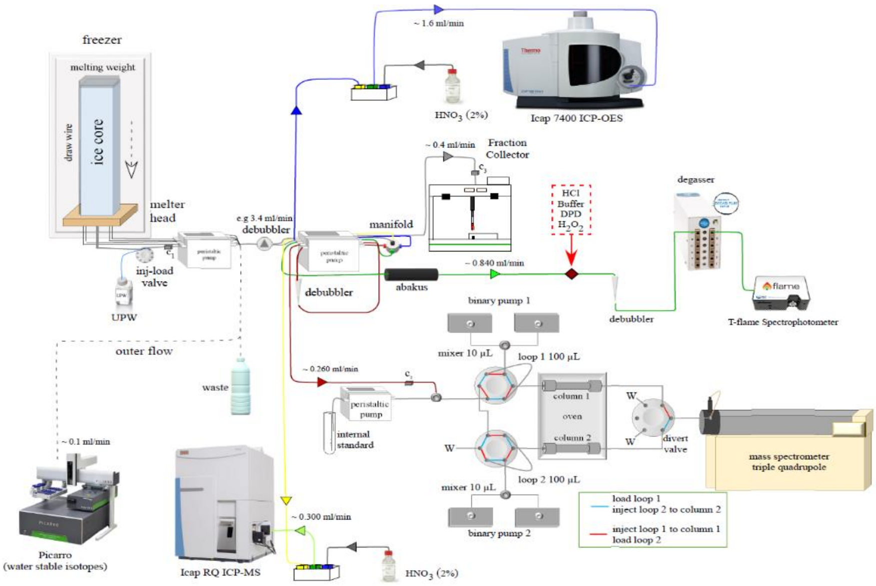
iAs, As speciation, round-robin study, metrology, CRM, reference materials

Pushing trace analysis to the limit, and beyond

Carlo Barbante[1,2], Pascal Bohleber[2], Marco Roman[2], Nicolas Stoll[3], Piers Larkman[2], Azzurra Spagnesi[2], Elena Barbaro[1], Matteo Feltracco[2], Federico Scoto[1,4], Andrea Spolaor[1], Warren Cairns[1], Remi Dallmayr[3], Frank Wilhelm[3], Ciprian Stremtan[5]

[1]Institute of Polar Sciences, CNR, Venice, Italy, [2]Ca‘ Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Venice, Italy, [3]Alfred Wegener Institute Helmholtz Center for Polar and Marine Research, Bremerhaven, Germany, [4]Institute of Atmospheric Sciences and Climate, CNR, Lecce, Italy, [5]Teledyne Photon Machines, Bozeman, Montana, USA

Modern chemical processes and the study and characterization of materials, the environment and food require the use of highly sophisticated chemical analytical techniques capable of determining and quantifying with high accuracy and precision the presence of substances at extremely low concentration levels. Microscopic investigation methods that allow the visualization and identification of specific atoms and molecules have considerably improved our understanding of natural phenomena and processes that occur at the microscopic scale. Snow and ice analyses is a clear example of this. By analysing the snow layers continuously deposited during the centuries and over millennia, it is possible to reconstruct the chemical composition of the atmosphere of our planet. Many chemical species are entrapped in the gaseous or particulate phase in the snow and ice. Thanks to sophisticated analytical techniques we are able to quantify their fluxes onto the Earth’s surface. This talk highlights the great potential for inorganic and organic compounds to be used as proxies for anthropogenic activities and natural processes, and will discuss future trends in research and opportunities in ultra-trace analysis.



ultra-trace analysis, laser ablation, single particle analysis

Development of sc-AF4/ICP-ToF-MS based method for the automated cleaning and multielemental analysis of individual cells

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Determining the metal content of single cells is a vital aspect of cellular analysis. It allows for the determination of different characteristics in cell populations, without falsely assuming homogeneity since variability among individual cells is considered. One of the greatest challenges in the analysis of single cells, quite often is the severe ionic background their samples exhibit.[1] With that in mind, Asymmetrical Flow Field-Flow Fractionation (AF4), as a cleaning technique, was combined on-line with the multielemental analytical capabilities of an Inductively Coupled Plasma-Time of Flight-mass spectrometer (ICP-ToF-MS). In that manner, the heavy ionic matrix of untreated cells' samples can be tackled, and their metal content can be determined for nearly the entirety of the periodic table.

As a proof of concept, commercial baker's yeast cells were analysed. The sc-AF4/ICP-ToF-MS combination yielded very promising results, with the system exhibiting the ability to effectively tackle matrices as severe as 3x105 mg/L sodium chloride (NaCl) or 50 mg/L ionic phosphorus (P). In the meantime, no hampering in the analysis of the cells was observed, due to clogging or otherwise equipment related issues. Furthermore, cells grown in heavy metal medium (Pb, 0.1-10 mg/L) were also analysed without prior cleaning, highlighting the ability for fast analysis without previous manual and/or laborious cleaning procedures. That fact, coupled with the ability of the ToF to detect the single cells' content for both the event related element (P) and the spiked element (Pb), on the same event, highlighted the immense potential of the further development and optimization of this fast, robust, and effective coupling.

In addition, new and versatile, python-based data treatment tools were developed, both for the detection of the cells, and for the reliable identification of pulses containing multiple elements' events. Their performance was tested against established methods [2], with the goal of streamlining the whole procedure for high throughput analysis. In that manner, it will be applicable to numerous life-science and environmentally related applications.

multi-elemental single cell analysis, ICP-ToF-MS, AF4, automated cell cleaning

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Surface Cleaning with Atmospheric Pressure Plasma Jets investigated by Optical Emission Spectroscopy and LIBS

Nikolaos Giannakaris[1], GustavGürtler[1], Thomas Stehrer[2], Michael Niebauer[1], Robert Kleštinec[3], Manuel Adlberger[1], Johannes David Pedarnig[1]

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Atmospheric pressure plasma jets (APPJs) are increasingly employed for industrial applications such as surface cleaning, modification of surfaces, deposition of coatings and for bio-medical applications such as skin treatment and bacterial inactivation. In this research, the plasma of an industrial APPJ device (Acerios, company Fronius International GmbH) is investigated and its capability in surface cleaning is examined. The device operates a spark discharge in Argon gas flow in the few kW power range resulting in a continuous and powerful plasma jet expanding into ambient air. We report on the measurement of APPJ plasma parameters by Optical emission spectroscopy (OES) and on the monitoring of plasma cleaning of surface-coated samples by OES and Laser-induced breakdown spectroscopy (LIBS). For the APPJ characterization OES spectra are measured using optical filters in the collection system. This enables to accurately determine the plasma electron temperature Te and electron number density Ne by applying the Saha-Boltzmann plot method for Ar emission lines [1]. For comparison, Te values calculated by the Boltzmann plot method for neutral Ar lines are inaccurate and inconsistent. For the APPJ cleaning experiments samples are coated with organic oil layers of thicknesses from 0.5 to 10 μm. The cleaning efficiency is calculated from OES and LIBS measured emission lines and bands of species that can be attributed to the contamination layer. LIBS is applied for chemical imaging of samples before and after plasma spot and line cleaning [2]. Spatial profiles of the cleaning efficiency are measured. We find a strong influence of various parameters (plasma jet, sample contamination, cleaning process) on the efficiency of APPJ plasma cleaning. For instance, the cleaning as determined from the CN violet band emission measured in situ by OES becomes more efficient at higher plasma generator current.

Atmospheric pressure plasma jet, Argon plasma, LIBS, Surface cleaning, Plasma temperature, Saha-Boltzmann equation.

Giannakaris, et.al., “Atmospheric Pressure Plasma Jet: Accurate Determination of Plasma Temperature and Electron Number Density by Optical Emission Spectroscopy”, Plasma Sources Sci. & Technology, submitted, 2022.

Giannakaris et.al., Applied Spectroscopy, vol. 76, issue 8, p. 926-936, Sep. 2022

Metal fingerprint of individual pollen cells: trace metal determination by SC-ICP-MS

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Pollen is a key component of the plant's life cycle since it carries the male gametes for fecundation. Ensuring an optimal pollen production is crucial for both the fitness of the plant (i.e. the transmission of its gene pool to the next generation) and the agronomical yield (seed and/or fruit production). The acquisition and storage of essential metals (Fe, Cu, Zn, Mn…) is considered to be crucial for the quality of pollen grains. Therefore, it is strategic to develop analytical approaches to analyze metal homeostasis in pollen grains that are constituted of a single cell. The quantification of metals in pollen is extremely challenging since the amount of pollen produced by plants is generally very small. Nevertheless, pollen grains can be easily collected from flowers, with a high degree of purity. Therefore, this biological material is particularly well suited to implement single-cell approaches to study metal homeostasis.

In this work, pollen grains were collected from Arabidopsis thaliana plants by centrifugation and analyzed by SC-ICP-MS. The use of the ICP-MS in Single Cell mode allows to obtain the intrinsic metal content of a cell population in a cell-by-cell basis, more representative than the regular bulk analysis. In addition, the new NexION 5000 multi-quad ICP-MS offered a unique opportunity to quantify with accuracy some elements, which determination is otherwise compromised when using single quadrupole instruments. Metals like Zn, Fe or Cu were determined and quantified in individual cells of pollen. Among all these metals analyzed, the highest content was found for Zn.

The application of SC-ICP-MS with a dedicated system for the introduction of individual cells of pollen, together with the highly sensitive detection through a multi quadrupole ICP-MS has allowed the determination of a range of essential elements (Fe, Mn, Zn, Cu) at the level of attograms, including those highly interfered. This presentation will show the results of this study with a focus on the content of the most essential metals, the environmental and health implications and the capabilities of this technique to provide critical information.

pollen, ICP-MS, Single Cell, trace metals

New Applications of ICP-MS/MS and MC ICP-MS to study the chemical anthropocene

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Legacy heavy metal and species contamination still represents a major adverse threat for many aquatic and marine ecosystems within highly populated catchment areas because of their inherent toxicity, vast sources and persistence. Despite the ongoing reduction of emissions of such contaminants into the environment, the coastal zones of the North Sea still belong to the most impacted ecosystems worldwide. In particular, the ongoing evolution of coastal zones into industrialized areas, e.g. due to extensive shipping or the construction of offshore wind parks, offshore PTXor CDR activities within the framework of the ongoing energy transition and CO2 reduction in Europe even boosted the release of either known, but also of various new contaminants into the marine environment. Nowadays, due to changing industrial processes and product portfolios also other elements such as the REE beside PGEs and TCEs and also new element species indicate an increasing release into the environment beside other threats such as nano materials, micro plastic or organic contaminants. The accurate analysis of such contaminants is in particular of significance for public health concerns beside the overall future sustainable development and management of the coastal zones as required by EU wide legislation.

This contribution will highlight some recent examples of ICP-MS based elemental analysis and their application within the context of large scale environmental studies on the interactions of entire river catchments and coastal zones or new approaches for e.g. CO2 removal. The focus of this lecture will be in particular on the recent possibilities arising from the application of ICP-MS/MS for interference handling as well as on the role of new approaches for routine ultra trace analysis of emerging contaminants at ng/L levels, or its role as complementary technique for emerging research areas such as particle analysis.

marine environment, environmental analysis, trace metals, speciation

Logemann, et. al., Environmental Pollution, Volume 302, 2022, 119040.

Using ICP-MS/MS in complex environments - spatial distribution and possible sources of technology-critical elements

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Important knowledge gaps remain about the environmental behavior of the so-called technology-critical elements (TCEs). TCEs are key elements in modern life, as they are inescapable in various devices and applications. As high economic demands, short product lifespans, and low recycling rates may cause vast environmental impacts, TCEs are considered as potential emerging contaminants. Low concentrations of TCEs in the environment often result in complex and time-consuming sample preparation. Consequently, improvements in routine measurements of the TCEs are mandatory.

This work deals with the application of a recently developed ICP-MS/MS-based N_2O reaction cell method for TCEs analysis in complex environmental matrices. Here, 57 sediment samples from the German part of one of the most anthropogenic-influenced European rivers, the Rhine, were investigated. Elemental mass fractions including TCEs (Ga, Ge, Nb, In, Te, rare earth elements, and Ta) were determined, in conjunction with classical legacy pollutants such as Ni, Cu, Zn, Cd, and Pb. Finally, hierarchical cluster analysis, as well as principal component analysis were used to gain insights into the spatial distribution and possible sources of TCEs along the Rhine.

Mass fractions and corresponding geo-accumulation indices provide first indications of possible enrichment along the Rhine for all investigated elements. Statistical analysis revealed TCE behavior similar to that of classical heavy metals. In general, mass fractions of Zn, Ge, In, La, Sm, and Gd indicate significant anthropogenic inputs. Here, elemental fingerprints of stations elevated in Ge and In mass fractions imply possible atmospheric depositions generated, e.g., by combustion processes. Determined La and Sm anomalies are assignable to discharges at the City Worms. Gd shows more diverse input sources along the river, possibly stemming from the accumulation of Gd-based contrast agents in sediments.

In conclusion, this study indicates the potential of ICP-MS/MS to analyze less studied elements and provides evidence of significant anthropogenic loading of TCEs into the Rhine. The data presented here allows for a better understanding of the behavior of TCEs in a complex river system such as the Rhine as an important source of TCEs to the North Sea.

Multi-element analysis, ICP-MS/MS, multivariate statistic, emerging contaminants

Detecting nanoparticles in suspensions with ICPMS using microdoplet injection

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Engineered inorganic nanoparticles (eiNPs) are emerging technological compounds that need to be characterized for composition, size and number concentration in a variety of sample types. Single particle inductively coupled plasma mass spectrometry (sp-ICPMS) is widely used in this context because established sample introduction systems can be used without any hardware modifications. Assessing the transport efficiency and the absolute sensitivity, however, challenge this approach, when dealing with complex matrices in particular.

Mircodroplet (MD)-based sample introduction mitigate uncertainties in sample transport efficiency and sensitivity by continuously monitoring droplet size and injection frequency. It further achieves a comparably low sample load in the ICP and reduces the abundance of molecular ions and may increase sensitivity at the same time. This approach, in combination with a high-sensitivity sector field instrument equipped with a “Jet”-interface was employed for eiNP determination in various matrices, including synthetic aqueous suspensions or extracts of consumer goods and also for their direct analysis in organic suspensions. By optimization of the instrumental parameters, the absolute sensitivity of the MD-based sampling was improved with the “Jet” interface and the mass discrimination of the MS was reduced. Thereby the sensitivity for high m/z isotopes like 197Au was increased about 3-fold while low m/z isotopes like 27Al were detected with about 400 times higher sensitivity in aqueous suspensions. The accuracy and reproducibility of the approach was demonstrated in several interlaboratory comparison studies, where Z-scores of between -0.5 and 0.5 were achieved.

The low sampling rate of the MDG is also beneficial when analyzing suspensions in organic media, because the addition of oxygen to the ICP can be avoided. Comparing conventional and the “Jet” interface again led to an increase in sensitivity and reduced mass discrimination. The analysis of Ag, and TiO2 NPs in toluene, mesitylene was feasible after addition of 1 mM dodecanethiol to stabilize the suspensions. The MDG-based sampling approach thus provides a flexible, robust and accurate means to detect and size eiNPs in a wide variety of media.

Online coupling of AF4 to ICP-MS/MS and MALS for a comprehensive characterization of oligonucleotide-functionalised gold nanoparticles involved in a miRNA-based assay

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The growth in the knowledge of nanomaterials has brought about an improvement in the development of different technological and scientific fields. However, after their synthesis and before their use, nanomaterials must undergo various modifications to improve their properties or to turn them into recognition elements by combining them with different biomolecules. These functionalisation reactions can lead to unwanted changes in the structures, so it is necessary to obtain a complete characterisation and quantification of functional nanomaterials from their synthesis to their final form to ensure the success of subsequent applications. Particularly, in the case of nanostructure-based assays it is necessary to know both the actual bioconjugate-nanoparticle stoichiometry and variations in size or stability.

Currently, there is no single technique that provides all this information on its own. Here we propose the use of the integrated AF4-UV-Vis-MALS-ICP-MS platform as a powerful tool to achieve an adequate characterisation of functionalized inorganic nanomaterials. Firstly, the Asymmetrical Flow Field-Flow Fractionation (AF4) allows the differentiated fractionation of the species, without the need to remove the possible excess of reagents or the contribution of dissolved inorganic ions. Like most hydrodynamic techniques, it can be easily coupled on-line to any flow detector, such as UV-Vis, MALS and ICP-MS. UV/Vis absorption provides information on the aggregation state of the structures, while light scattering techniques, such as Multi-Angle Light Scattering (MALS) give information on the morphology and hydrodynamic size of the different nanostructures. Finally, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) provides composition information and elemental ratios along the nanostructure’s peaks, which can be used to disclosing the mixture of different species.[1]

An example of the use of the AF4-UV-Vis-MALS-ICP-MS platform for comprehensive characterization of engineered AuNPs surface-modified with oligonucleotides designed for miRNA biomarkers detection is here presented.

Nanoparticle characterization, AF4, MALS, AuNPs, miRNA

Bouzas Ramos et al. Analytical Chemistry (2018), vol. 91 (5), 3567–3574

Exploring the boundaries in the analysis of large particles by SP-ICP-MS: from microplastics to nanoclays

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The analysis of particles by single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) requires sample introduction systems that guarantee transport efficiencies similar to those obtained with dissolved and nanoparticle standards across the size range covered. Nebulisation systems based on linear pass spray chambers and micronebulisers are commercially available for the introduction of intact cells in ICP-MS and their individual analysis in single cell mode. The use of these sample introduction systems in SP-ICP-MS has opened the way to analyze particles out of the nanoscale.

In this work, a linear pass spray chambers equipped with different micronebulisers has been evaluated for the introduction of particles of different nature and morphologies, such as microplastics, with spherical and irregular shapes up to several micrometers, and nanoclays, with thickness in the range of a few nanometers and lateral dimensions up to several micrometers. Whereas the transport efficiency for microplastics was kept constant up to diameters of 2-3 micrometers, in the case of clays it was limited to ca. 1 micrometer.

When detecting microplastics, no differences on the volatilization of the particles up to 5 micrometers was observed, whereas the detector counting limit was not reach for the 13C isotope with the largest particles measured. In the case of nanoclays, the application of different strategies to modify the range of sizes attainable has been also studied. For instance, the modification of the ion transmission or the use of different isotopes to modify the sensitive conditions have been tested. These strategies have allowed covering the whole size range of the suspensions monitoring the 27Al isotope and achieve a quantitative mass recovery with respect to ICP-MS analysis.

The performance and limitations of the methodology developed will be discussed through its application to different analytical problems, such as the detection of microplastics in environmental samples or the release of microplastics and from food containers.

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single particle; ICP-MS; microparticles, nanoclays, microplastics

Separation of ionic interference from nanoparticles in aerosol via AG-DMA-RDD-spICP-MS

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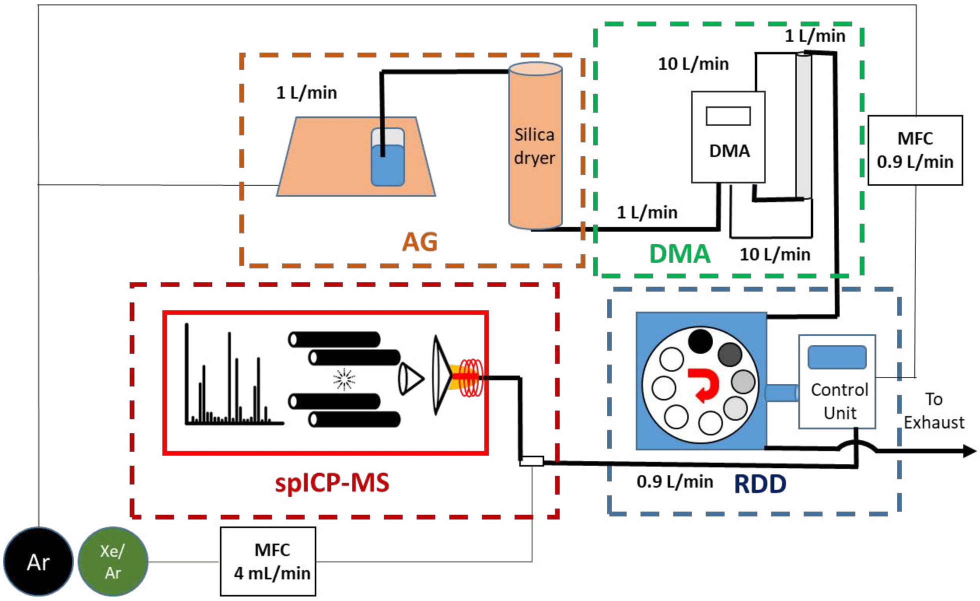
Recently, single-particle ICP-MS (spICP-MS) has been widely used for nanoparticles (NPs) characterization because of its ability to determine particle size distribution and elemental composition simultaneously (1). However, there are still some limitations. First, the particle number concentration is critical, since too less particles would be not statistically representative while too many cause double events. Second, the presence of ionic species may generate relevant background signals that affect the NP detection, especially when a dwell time in the range of millisecond is used (2). Third, the direct online method for NP detection from aerosol via spICP-MS has not been developed yet due to the need of argon as the carry gas for the plasma and an accurate and stable gas flow rate.

To solve these problems, we designed a setup for online NPs dilution and detection. A differential mobility analyzer (DMA) classifies by size the aerosol generated from an aerosol generator (AG), and the ionic interferences are minimized. Then, the online rotating disk diluter (RDD) dilutes and stabilizes the gas flow for single particle detection via ICP-MS.



Single particle ICP-MS, Aerosol, Online measurement, Rotating disk diluter, Differential mobility analyzer

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Novel processing algorithms to improve the quality of single-cell inductively coupled plasma-mass spectrometry data

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Inductively coupled plasma-mass spectrometry (ICP-MS)-based approaches to analyze nanomaterials and biological cells have experienced a decade of fast development and performance improvement. Through the combination of specialized sample introduction systems and data processing algorithms, the investigation of trace elements in single cells directly from a dilute suspension is becoming increasingly accessible.

In this work, an automated sample introduction system was used to map the endogenous elemental composition in Chlamydomonas reinhardtii green algae that were cultivated under physiological and iron depleted medium conditions. The setup included an on-axis total consumption spray chamber equipped with a microliter low-flow nebulizer. Particular focus was directed to the nebulizer argon gas flow to ensure a mild aerosol generation with minimum cell damage. Further plasma parameters were adjusted for highest signal intensities.

Data analysis was carried out with an in-house software tool written in Java that employs an iterative baseline search and a two step event detection including a split cell event correction. Special attention was given to the recognition and elimination of method-intrinsic measurement artifacts beyond pure statistical models. These cases include background fluctuations, event overlap and deviating signal peak shapes. Based on these observations, useful guidelines to improve overall data quality are presented.

Single cell-based distributions for six naturally occurring elements were separated from the background for both medium conditions. Importantly, cell count rates and thus concentrations were independent from the respective element. Furthermore, the observed cellular iron content showed significant differences depending on the culture media.

To investigate the effect of a potentially growth-limiting iron deficiency on the metabolic status of the algae, magnesium and manganese among others were quantified. These key trace elements play an important role in the light absorbing pigment chlorophyll and the water-splitting complex of the photosynthetic reaction center. A great advantage of this methodology is that no error-prone cell counting was needed in advance.

ICP-MS single-cell statistics algorithms algae iron-deficiency

Sample preparation strategies for nanoparticles analysis using laser ablation sampling single particle−ICP-MS

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Nanoparticles are used in a wide variety of fields, including material manufacturing, energy production, food processing, consumer goods as well as life sciences. Using materials in the nanometre size range changes their physicochemical properties drastically from those of the associated bulk materials creating novel characteristics useful for products such as catalysts, medical products, food technology, cosmetics and other household items, among many others. [1], [2] This widespread use in consumer goods raises questions about the impact of nanoparticles on the environment and human health. With single particles inductively coupled plasma mass spectrometry (SP-ICP-MS), a powerful tool for investigating nanoparticles was developed. [1]

However, conventional SP-ICP-MS allowing the simultaneous determination of particle size and number concentration, is limited to nanoparticles in suspensions meaning solid samples containing nanoparticles have to be dissolved, keeping the nanoparticles intact. Required sample pretreatment steps might induce changes in the occurrence of the prevailing nanoparticles (e.g., size distribution and number concentration). To overcome the problems associated with the preparation of stable sample suspensions, the measurement of the solid samples is recommended. The combination of laser ablation as the sampling technique and SP-ICP-MS for the analysis was introduced to include the benefits of solid sampling. [2] [3]This approach allows the sizing and counting of nanoparticles directly in a solid matrix with the advantage that embedded nanoparticles can be stored without changes in particle size. Moreover, spatially resolved information is accessible. [2], [3]

Similar to conventional SP-ICP-MS, LA-SP-ICP-MS also requires nanoparticle standards for signal evaluation. For this purpose, gelatine standards were prepared and investigated with laser ablation SP-ICP-MS. [3] In this work, dispersions of metallic and ceramic nanoparticles in polymer matrixes were produced using different sample preparation techniques. The goal was a random distribution of the nanoparticles within the standard, creating isolated nanoparticles with no agglomeration. The influence of the sample preparation procedures, as well as the impact of the laser wavelength and energy in the ablation process, were investigated and compared to aid in the further development of LA-SP-ICP-MS within various kinds of sample matrixes.

Laser ablation, Single particle analysis, Nanoparticles, Sample preparation

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Heritage lecture

Staying Connected with Analytical Spectroscopy...Lifelong Collaborations

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Advances in capabilities for ultratrace elemental analysis by atomic spectrometry appear to continue unabated. The introduction of ICP MS in the early 1980’s accelerated the initial pace, with sample preparation and analyte introduction technologies following in parallel. My scientific career began in the late 1970’s; in retrospect, I was in the right place at the right time ! This presentation encompasses some curated brief examples of my contributions over the past 50 years, engendering some “words of wisdom” that served me throughout my career to yield a lifetime of enjoyment and adventure in analytical atomic spectroscopy. I will provide evidence that meaningful collaborations help ensure that a life of science can continue after retirement!

Microsampling in atomic spectrometry: much more than analysing small volumes

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The term microsampling in atomic spectrometry has been evolving during the last decade, from the simple original meaning of targeting analysis of microsamples[1] to a more complex concept, which also includes the analysis of micro/nanostructures. In this regard, single event ICP-MS has enabled the development of a great number of applications for analysis of nanoparticles (NPs), cells or even micro plastics.[2] However, matrix effects often affect the quality of the results, and the application of traditional solutions in this context is not straightforward. Novel approaches for overcoming matrix effects in real samples when using single particle-ICP-MS are presented in this work. One of such approaches is based on the standard addition method and the calibration of the particle size is performed by two different methods: (i) by spiking a suspension of NPs standards of known size containing the analyte, or (ii) by spiking the sample with ionic standards. Another possibility for elements with more than one nuclide is applying isotope dilution approaches. The importance of different factors to achieve the best possible precision and accuracy when using ICP-TOF-MS will be discussed in the context of AgNPs characterization.Besides these applications, novel methodologies for the minimally invasive analysis of blood, via formation of dried blood spots, will also be discussed, and the potential of approaches based on LA-ICP-MS and/or LIBS, presented.

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single event ICP-MS; nanoparticles; dried blood spots; LA-ICP-MS; LIBS.

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SELM-1 as tool for the harmonization of quantitative Single Cell ICP-MS Experiments

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Single cell analysis using elemental detectors, namely ICP-MS, can be conceptually derived from the single particle ICP-MS experiments. Basically, once the cells are individually introduced into the ICP, the plume of ions generated can be directly measured using fast scanning mass analyzers in a sequential (quadrupole instruments) or quasi-simultaneous (time of flight instruments) way. However, cells are heterogeneous and fragile entities in comparison to nanoparticles. These characteristics increase the complexity of sample handling required to obtain reliable results from these experiments. Nowadays, a lot of work is done in the area of single cell ICP-MS using different quantification strategies. In order to obtain a normalized procedure for single cell inductively coupled plasma measurements (SC-ICP-MS), the quantitative characterization of the intra- and extracellular Se fractions of a Se-enriched yeast certified reference material SELM-1 has been carried out. The use of a standardized material (CRM) in this study will enable others to replicate, benchmark, and improve their procedures by using the same material.

In order to obtain a normalized procedure that can be applied to a wide analytical community, different sample preparation procedures have been studied. Best results were observed with a sequential washing procedure to isolate the cells from the extracellular Se content through which two fractions were obtained and analyzed by ICP-MS. After proving the cell integrity throughout the washing process by confocal microscopy, the Se intracellular fraction was determined by single cell-ICP-MS (SC-ICP-MS) as well as by acid digestion using microwave digestion. The extracellular Se concentration, has been directly determined in the washing solutions. The obtained results will demonstrate that with the appropriate sample preparation, SC-ICP-MS is a unique tool, which is capable providing quantitative information about intracellular and extracellular Se content in yeast at the individual cell level providing further granularity to speciation, toxicological and metallomics studies.

High-precision isotopic analysis – is the sky the limit?

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While originally rather considered a niche application within the ICP-MS community, studying natural variation in the isotopic composition of elements is now done in many labs for addressing a variety of scientific questions. While “standard” ICP-MS instrumentation suffices for the most straightforward applications only, a wider use requires the substantially higher isotope ratio precision offered by multi-collector ICP-MS (MC-ICP-MS). Geo- and cosmochemistry and the nuclear industry may have been driving forces for the development of MC-ICP-MS, meanwhile it has been demonstrated that high-precision isotopic analysis also has an important role to play in many other research areas, such as archaeometry, the environmental sciences and biomedicine, as also there, isotopic analysis may provide a more detailed insight and/or information that is complementary to that embedded in element concentrations. As a side effect of the broader availability of MC-ICP-MS instrumentation and its use in a continuously wider application range, increasingly more challenging situations are encountered. These challenges can entail the availability of minute amounts of sample only, isotopic analysis of target elements at ultra-low concentration, the request to limit the invasiveness of the analysis to the largest possible extent, extension of the application range to elements traditionally subject to severe spectral overlap, and the extension from bulk isotopic analysis to isotopic analysis of selected fractions or species of the target element. New developments in the instrumentation and the development of novel analytical approaches allow these challenges to be addressed successfully. Fruitful execution of such demanding applications rely on, among other, the use of alternative sample introduction techniques, such as a micro-flow injection system for stable injection of liquid microsamples, cold vapor generation for enhanced analyte introduction efficiency, or the use of laser ablation for direct isotopic analysis of solid samples. The use of higher Ohmic resistors in the Faraday cup detection systems allows working at lower target element concentrations, while increased mass resolution enables isotopic analysis of elements previously out of reach. Steps towards fraction/species-specific isotopic analysis reveal yet another level of useful information.Real-world applications carried out at the A&MS-UGent lab will be used to illustrate these novel approaches. Envisaged future applications will be discussed, as well as the further developments in the instrumentation required to be able to carry these out successfully.

MC-ICP-MS, laser ablation, cold vapor generation, fractionation, microvolumes

Benchmarking LA-ICP-MS ice core analysis: towards a high-resolution, quantitative signal interpretation

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A pressing frontier of ice core research concerns investigating the deepest and oldest ice at great detail, especially for a soon-to-arrive 1.5 million-year "Oldest Ice Core" or "COLDEX" records from Antarctica. Mastering this frontier demands high-resolution analysis due to layer thinning and accounting for post-depositional changes to the stratigraphy. Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) is especially suited to analyze chemical impurities in deep ice, offering both micron-scale resolution and micro-destructiveness. LA-ICP-MS for imaging on ice cores has afforded significant new insight regarding the physical signal origin at a resolution of 35 microns and finer: mostly soluble impurities such as Na have a close association with ice crystal boundaries, while insoluble impurities such as Al form clusters of particles in the ice. At the same time, this localized nature of impurities raises the question of how to identify stratigraphic layers with LA-ICP-MS, quantitatively and at highest possible resolution. Although it is clear that LA-ICP-MS is a potential breakthrough technology for investigating the chemical stratigraphy of deep polar ice, a number of technical and conceptual challenges still await to be mastered.

Here we illustrate recent progress in tackling this frontier by benchmarking LA-ICP-MS against other methods as well as conceptual simulations of the impurity distribution in the ice matrix and in a first-ever direct interlaboratory comparison between two LA-ICP-MS setups. Based on two instruments, differences and similarities in signals can be elucidated across scales, from hundreds to tens of microns in spatial resolution. We further show how assessing spatial variability with a conceptual model can help bridging the gap from mm-scale maps to the cm-scale of continuous flow melter signals. Our next goal is to analyze 55 cm long sections of ice cores in a large cryocell, combining for the first time imaging to study the interplay between impurities and the ice matrix, with line profiles to investigate the extremely thin climate proxy signals in deep ice. In this way, we may soon be able to access the full "dual use" potential of the technique in future ice core projects and the "Oldest Ice" quest.

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Trace element analysis of pharmaceutical products by inductively coupled plasma optical emission spectrometry using a multinebulizer

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The presence of elemental impurities in pharmaceuticals can potentially have adverse health effects and therefore must be carefully monitored. For this purpose, a simple, sensitive and matrix effect free analytical method for simultaneous determination of As, Cd, Hg and Pb from pharmaceuticals (i.e., commercial dosage tablets) by inductively coupled plasma optical emission spectrometry (ICP OES) has been developed. In order to increase the sensitivity of the analysis, a chemical vapor generation (CVG) method based on the synergistic association of a new multinebulizer and a dispersive liquid-liquid microextraction (DLLME) with a natural deep eutectic solvent (NADES) as extractant phase has been developed. The main experimental factors affecting the DLLME and the CVG procedures have been optimized using a multivariate analysis and under optimized conditions, the limits of detection (LOD) obtained with the proposed method are 2, 1.5, 2 and 1.8 µg/L for As, Cd, Hg and Pb, respectively. In addition, the trueness has been evaluated by recovery experiments in two commercial pharmaceuticals and the recovery values are within the range of 90-110%.

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Natural Deep Eutectic Solvent (NADES), Dispersive Liquid-Liquid Microextraction (DLLME), Multinebulizer, Chemical Vapor Generation (CVG), Pharmaceuticals

Elemental content is more than just a number: investigating the retention and binding mechanisms of U(VI) via ICP-MS

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In the context of a repository for high-level radioactive waste (HLW), uranium will be the main part of the radioactive inventory. Because of its chemo toxicity and alpha emitter half-lifes of 4.5*10^-9 (U-238) and 7*10^-8 years (U-235), it has to be stored safely without contact to the environment for several hundreds of thousands of years. Different natural and geotechnical barriers are expected to be applied in a HLW disposal to protect the leakage of hazardous substances e.g. the host rock, bentonite as buffer material and cementitious materials as construction or sealing material.

Since the usage of cementitious materials in a HLW disposal is very likely, the pH value of intruding water increases above 10 due to the leaching of cement or concrete. Although the behaviour of U(VI) in solution concerning speciation and retention is widely studied in the acidic and neutral pH range, studies in the hyperalkaline milieu are scarce. A moderate up to quantitative immobilisation of U(VI) could be observed in this pH range but the retention mechanisms are still not clarified.

In this study, the retention behaviour of U(VI) at pH 10-13 on different materials relevant for a HWL disposal and in different saline solutions (0.1-5 M) is studied by mass spectrometry with inductively coupled plasma (ICP-MS). The measurements at high ionic strengths (>0.1 M) with only small sample dilutions (1:10 or 1:3) are realised by a transient measurement method and a slightly varied sample introduction. Different experimental approaches allow to gain insights in the retention and binding mechanisms in the hyperalkaline pH milieu solely by determining the amount of uranium and other critical elements in solution. Especially the presence of Ca(II) plays a major role in U(VI) precipitation and adsorption.

high-level radioactive waste, ICP-MS, uranium, Ca-bridges

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Micro-Discharge Optical Emission Spectroscopy – Main component and trace analysis of saline solutions by generating micro plasmas directly in solution

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The fast and precise on site analysis of trace elements in highly saline solutions, e.g. brines or process solutions of the salt processing industry, is still a challenge. For typically used techniques, like ICP OES or ICP MS, samples have to be diluted multifold to avoid clogging of nebulizers, deposits on optical systems and memory effects. Additionally, application of special sample introduction systems capable to handle higher salt contents are recommended. Unfortunately, dilution of the samples often leads to concentrations which collide with limits of detection of the methods applied. Furthermore, ICP OES or ICP MS are usually limited to laboratory use only due to a high plasma gas flow rate and power consumption, making them time consuming and not suitable for real-time analysis and monitoring of industrial processes. Therefore, a fast and precise on site method which allows trace element analysis without unwanted interfering effects and despite of high salt concentrations would be preferable.

We investigated the potential of the Micro-Discharge Optical Emission Spectroscopy (µDOES®) for the main component and trace elemental analysis of Lithium salts and Na/K/Mg dominated salt solutions of industrial processes for the battery or fertilizer production. Optical emission spectroscopy was performed by generating micro plasmas directly in solution by pulsed high voltage discharges without the necessity of plasma gases such as argon. After adapting the conductivity of the solution and several plasma parameters like current, pulse duration, pulse number or electrode position, spectra have been acquired directly in solution. Limits of detection in the low ppb region, comparable to established ICP OES techniques, and a good linearity in the considered concentration range have been obtained after data processing.

The technique proved to be useful for a fast and precise main component and trace analysis of saline solutions. With the µDOES® system very good quantification parameters have been obtained for trace elements like Na, K, Al, Fe and Zn in lithium-containing salt solutions as well as for the analysis of Na/K/Mg dominated salt solutions.

trace analysis, samples with high salt content, sample preparation, µDOES, TXRF

Multi-element patterns in samples from urban green facades focusing on technology-critical elements using ICP-MS/MS

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Technology-critical elements (TCEs, e.g. Nb, Ge, Ta and the rare-earth elements, REEs) are a non-uniformly defined group of elements with limited availability in relation to global demand. Their chemical properties make them indispensable in high-tech applications across various fields, such as information and telecommunication technology, alloys or catalysts (1). Even though it can be assumed that the increased use of TCEs in recent decades has led to increased levels in the environment, little is known about the quantities and how these levels affect ecosystems (2, 3). In the course of the FWF-funded project TecEUS (P 33099-N; www.teceus.at), green facades and urban gardens in Vienna are investigated to monitor TCEs in the urban environment. The low abundance levels in combination with spectral interferences remain an analytical challenge for ICP-MS.

In this work, an optimized measurement procedure for the determination of 48 elements with ICP-MS/MS, validated with 7 plant certified reference materials (SRM1515, SRM1547, BCR-129, BCR-670, GBW07603, GBW10015, ZC73036a), is presented and multi-element patterns in plant, substrate and water samples from Vienna are discussed. Plant samples were taken from 2 green façade systems in 4 seasons from 8 different species. The samples were either washed or treated as unwashed replicates in order to distinguish surface dust from leave material. After drying, they were brought into solution with microwave-assisted digestion using HNO_3, H_2O_2 and HBF_4. ICP-MS/MS measurements were performed with nitrous oxide as reaction gas for isotopes with spectral interferences (Ge and REEs). Limits of detection range from 94 fg/g (Tb) to 180 ng/g (Ca) in the measured solution. The multi-elemental results were evaluated for patterns linked to species, sampling height and season.

This work provides tools for future analytical studies of environmental TCE levels to form a knowledge basis for prospective larger-scale dynamic scenario modelling. The findings help to investigate a potential human health impact by TCEs and contribute to formulate preventive precautionary recommendations.

urban greening, microwave digestion, plant samples, nitrous oxide

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Direct trace analysis of high purity materials with electrothermal vaporization coupled to optical emission spectrometry

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Digestion processes contain risks of contamination, loss of analytes and prevent a fast process accompanying analysis due to the high time-consumption. With stable matrices like oxides or graphites, it is almost impossible to bring such materials into a representative solution which excludes liquid sampling methods for their characterization. Solid sampling methods are often not sensitive enough for trace elements (XRF) or not suitable for powders and granulates without preparation (LA-ICP-MS). Electrothermal vaporization (ETV) as a sample introduction system for inductively coupled plasma optical emission spectrometry (ICP OES) combines direct solid sampling with high sensitive detection. For powdered samples, there is almost no sample preparation needed, which results in a fast direct multielement method, suitable for process accompanying analysis or quality control in the production of pure metals like tungsten or ultra-pure graphites for battery purposes.

The mass of samples, which can be totally vaporized in the graphite furnace of the ETV is usually limited by the stability of the plasma. With the assistance of an appropriate reaction gas, a separation of the analytes from the matrix is possible within the graphite furnace. Ideally the elements were released completely from the sample and were transported with a stable rate to the plasma and the "empty" matrix remains in the graphite boats. This optimized vaporization results in low loading and high mass of elements in the plasma, which leads to detection limits in the low ppb-range with ICP-OES. In the case of tungsten compounds, a matrix separation is fundamental, otherwise emission spectrometry can’t be applied due to the enormous spectral line density of tungsten. By optimizing the various parameters, a simultaneous determination of all relevant elements from main constituents to trace elements in all intermediate products in the production of high purity tungsten and graphites can be achieved with one measurement with ETV-ICP-OES.

ETV ICP OES material analysis trace elements

Expanding the isotopic toolbox In support of the sustainable development goals

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In this talk, an overview of the potential of modern isotopic analysis based on MC-ICP-(CRC)-MS in environmental-, geo-, life- and materials sciences will be given under consideration of the sustainable development goals (SDGs) as there are many ways chemists are working to support global sustainable development.

The use of natural variations of the isotopic composition (e.g. of Sr, Ca, Ni, Fe, Pb) as proxies to study natural and technological processes or trace provenance and migration as well as the application of enriched stable isotope tracers (e.g. Sr, Pb, Mg, Ni) will be discussed. The latter approach highlights the importance of data processing based on isotope pattern deconvolution.

The metrological challenges in reliable isotope ratio determination, such as precision, contribution of background levels, interferences, and instrumental isotopic fractionation, will be discussed on specific examples.

isotope research, MC-ICP-MS, collision cell

Smaller is better – applications of high precision isotope ratios by LA-MC-ICP-MS using a plasma shield and aerosol rapid introduction system

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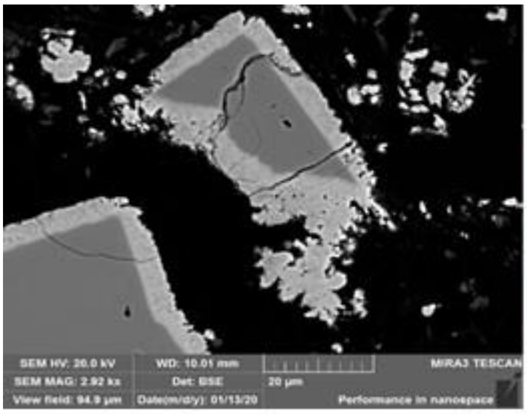
Recent plasma shield upgrade to the Nu Instruments NP3 multicollector inductively coupled plasma mass spectrometers (MC-ICP-MS) in combination with Teledyne CETAC Technologies aerosol rapid introduction system (Aris) has significantly enhanced signal intensity for isotope systems commonly measured by laser ablation (LA)-MC-ICP-MS, for example S, Sr and Pb.Consequently, this increase in signal intensity for isotope ratio measurements offers new opportunities in revealing complexities previously masked at lower resolution, the ability for simultaneous in situ sulfur (δ33S and δ34S) and trace element concentration measurements in sulfides and measuring samples with isotope systems previously below detection limit.Method validation using reference materials will be presented as well as practical applications for each isotope system using geological samples.



Laser ablation, MC-ICP-MS, plasma shield, isotope ratios

Robust potassium isotopic analysis of geological and biological reference materials using MC-ICP-MS with the ‘extra-high resolution mode’.

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[1]Ghent University, Ghent, Belgium

The development of new methods that allow for high-precision potassium isotopic analysis is reinvigorating the interest in potassium, not only in a geological context but also for biomedical applications. High-precision potassium isotopic analysis is hindered by the presence of argon hydride ions, the signals of which overlap with those of39K+ (38ArH+) and especially41K+ (40ArH+). These spectral interferences can be addressed with either a collision/reaction cell or the ‘extra-high resolution (XHR) mode’.(1,2) The introduction of the XHR mode in Neptune XT MC-ICP-MS instrumentation improves the mass resolving power from 9,000 (HR) to 15,000, which allows for high-precision potassium isotopic analysis on the interference-free peak shoulder of the 41K+ peak, which is 6-7 amu wide. Hot plasma conditions combined with high-transmission jet-type cones and the XHR mode provided a within-run, short-term external and long-term external precision for the delta 41K value of 0.02 ‰ (2se, N = 50), 0.03 ‰ (2SD, N = 7) and 0.06 ‰ (2SD, N = 163), respectively. The large spread in K isotopic composition observed for different biological RMs, up to 1.4 ‰, potentially indicates significant isotope fractionation effects accompanying biochemical processes.

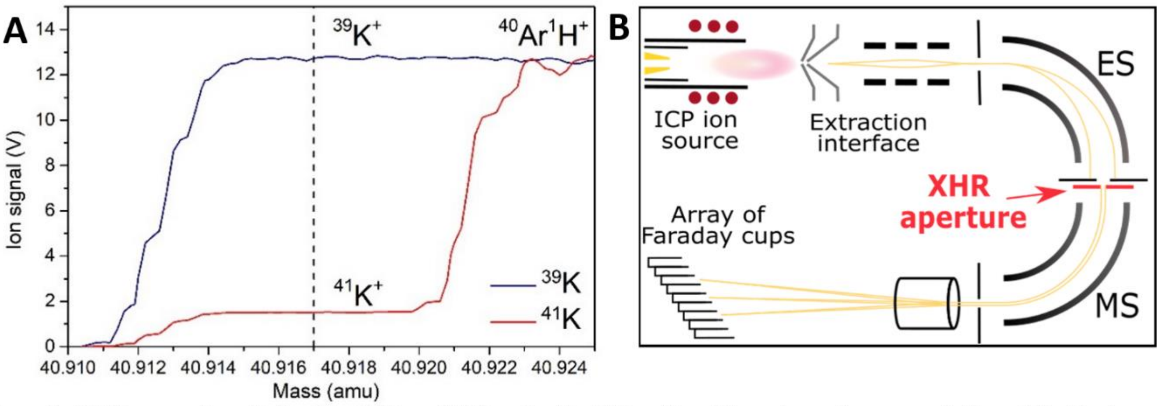

Figure 1: (A) Mass spectra obtained for 39K+ and 41K+ using the XHR option; (B) a schematic representation of The Neptune XT (ThermoScientific).

Potassium, isotopic analysis, MC-ICP-MS, extra-high mass resolution, biomedical applications

Hobin et. al., Analytical Chemistry 93 (2021): 8881-8888

Moynier et. al., Chemical Geology 571 (2021): 12014

Determination of inorganic mercury isotope ratios by Gas Chromatography coupled to MC-ICP-MS using a 199Hg/201Hg double spike

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It is well known that the measurement of the isotopic composition of mercury provides a wealth of information about the sources of mercury in the environment and the bio-environmental processes (both mass dependent and mass independent fractionation processes) leading to those values. However, it would be even more informative to be able to measure the isotopic composition of mercury species (both inorganic and methylmercury) in biological and environmental samples. For those purposes, the coupling of Gas Chromatography (GC) to Multicollector (MC) ICP-MS has been proposed (1,2). The classical arrangement includes de addition of a post-column flow of Tl as internal standard to compensate for changes in the mass bias factors during the long runs required for reliable isotope ratio measurements after GC-MC-ICP-MS coupling (1,2).

In this presentation we will describe the development an evaluation of an alternative procedure for mass bias correction in GC-MC-ICP-MS based on the addition to the samples of a double spike prepared by mixing highly enriched 199Hg and 201Hg inorganic mercury species. The principal advantage over the classical procedure is a ca. 10-fold improvement in sensitivity while avoiding the liquid nebulization of a Tl solution. The application of this alternative method for the measurement of mercury isotope composition in human hair will be also described in the presentation.

Gas Chromatography, Multicollector, ICP-MS, Mercury, Isotope ratio

Bouchet et al., Anal. Chem. 2018, 90, 7809–7816

Queipo-Abad et al., J. Anal. At. Spectrom., 2019, 34, 753-763

Isotope ratio measurements using ICP-MS/MS for source attribution of priority pollutants in air

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Heavy metals in airborne particulates are a serious health concern. Monitoring the levels of these metals in air and determining their sources allows for better control of toxic emissions and assessment of public exposure. NPL is using the latest generation ICP-MS instruments to expand its measurement capability for stable and radioactive pollutants. This presentation will outline the development and validation of a novel ICP-MS/MS method for isotope ratio measurements. It will identify a route to traceability for these measurements and their use for source apportionment studies of pollutants in ambient air. The application of tandem ICP-MS allows for robust interference removal, meaning minimal offline separation is required prior to analysis. Different approaches for isotope ratio measurements are considered including internal and external drift correction and mass bias correction methods.

Priority pollutants from samples around the UK have been identified. Nickel is a pollutant of key concern in some areas of the UK as it is the only metal where measured levels in one region regularly exceed legislated limit values. Improved source apportionment methods are vital to understand the origin of nickel in the air. Additionally, although levels of lead in ambient air have fallen significantly in recent years, they are still significantly higher than background levels, and knowledge of the source of this metal will help define improved removal or mitigation strategies.

ICP-MS/MS, ambient air, pollutant, lead, nickel

Cloud-Point Extraction: A Promising Sample Preparation Technique For Uranium-Thorium Dating Of Archaeological Samples

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Uranium-thorium dating is a widely used analytical technique in archaeology, especially for calcite-containing samples such as limestone, corals and speleothems (stalactites, stalagmites, flowstones).

The technique relies on the extremely different geochemical behaviour of uranium and thorium, the former being highly soluble in water while the latter being more prone to adsorption on solids. Typically, uranium will thus be transported in calcium-rich leaching waters, infiltrates soils and reach cave compartments where it becomes trapped inside secondary carbonates as the leaching water evaporates. The geochronometer then starts ticking and as time passes, part of the initial amount of 238U trapped in the carbonate disintegrates in its daughter isotopes, which produces 234U and 230Th, the ratio of which being a direct indication of the time of precipitation.

Nevertheless, this behaviour disparity makes the sample preparation step for isotopic ratio measurements complex: samples must be digested and purified with separation resins which implies the use of isotopic spikes to correct for U and Th losses, usually 236U and 229Th,that are not accessible to every laboratory owing to their radioactive nature.

Cloud-Point Extraction (CPE) on the other hand appears as an interesting alternative. The principle is to create a functionalised micelle system with a strong affinity for both uranium and thorium. This enables to quantitively capture these analytes directly from digestion solutions as a fast and simple purification step that allows us to get rid of any isotopic tracer. Following the entrapment of uranium and thorium in the micelle system, a centrifugation and resolubilisation step allows to reduce sample's volumes from a few mL to a few hundred of µL, thus limiting the dilution of the analytes and consequently increasing the signal obtained in ICP-MS. In turn, this enables the dating of small solid samples (~1mg) for which a higher volume of dilution would decrease the signal too much to be suitable for dating.

This combination of factors could open the technique to precious archaeological materials that are often constrained by strict preservation imperatives.

Here, we present the results of dating of speleothems and corals micro-samples. Samples were collected using a new micro-sampling system consisting of a portable-LIBS (field laser ablation device) combined with a laser-induced particle collection device. The collected particles were then prepared by CPE after carbonate solubilisation, and analysed by MC-ICP-MS.

Uranium-Thorium dating, Sample preparation, Cloud Point Extraction (CPE), MC-ICP-MS

Nanoparticles as a Younger Member of the Trace Element Species Family – A Food Perspective

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Engineered nanomaterials are nowadays widely integrated into consumer and industrial products. Nanoparticles (NPs) – discrete pieces of material with at least one dimension in the size range of 1 to 100 nm - have been intensely studied throughout the last two decades with regards to their synthesis, applications, and toxic effects. Alongside, suitable analytical techniques have been developed or adapted. Among these techniques are single particle ICP-MS and ICP-MS coupled to separation techniques like asymmetric flow field fractionation and hydrodynamic chromatography.

Food is one major source of exposure of consumers to NPs via the oral route. Recent years research has shown that inorganic nanoparticles can be found in food for various reasons. These include intentional addition of engineered NPs, release of engineered NPs from food contact materials, formation of incidental NPs during preparation or production of food, naturally occurring NPs, and food additives containing a fraction of particles at the nanoscale.

All these NPs might undergo changes in the food matrix or ultimately in the human gastrointestinal (GIT) system. Especially dissolution is of interest for human risk assessment, as complete dissolution in either the food matrix or the GIT system would imply that no nanos-specific considerations will be required. Dissolution testing can be performed in systems of various degrees of complexity. A currently suggested in vitro approach for assessing dissolution kinetics by the European Food Safety Authority is testing in a buffered solution at pH 7 and / or pH 3. Dissolved species are than separated from eventually remaining NPs by ultrafiltration with a 3 – 10 kDa filter. In more complex systems including enzymes and food components such a separation might not be possible. Additional techniques are required to quantify the amount of free ionic and molecular-bound species and to assess the degree of NP dissolution.

Another interesting research area, where NP analysis and “classical” speciation analysis meet, is the in vivo formation of NPs, i.e., particles that are formed inside organisms like fungi, yeast, plants, and mammals. Understanding the mechanisms requires both a characterization of the species involved in the formation of the NPs and the NPs themselves. Naturally formed NPs might be present in our food as well. The talk will present selected examples of nanoparticle analysis in food and share thoughts on how nanoparticles fit into the trace element species family.

Selenium speciation in biological samples – the advantage of a matrix-matched spike for isotope dilution and the analysis of novel high-protein foods

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Increasing evidence supporting the beneficial role of selenium in various areas of human health has resulted in widespread interest in the quantity and quality of the element in our diet. In more technical terms, we can define “quality” with reference to chemical speciation, where organic forms of selenium are widely accepted to provide more health benefits than inorganic species, and bioaccessibility, because only that which can be absorbed by our bodies has the potential to provide these health benefits. Foods and nutritional supplements containing selenium species produced metabolically, often predominately in the form of proteinaceous selenomethionine, are considered optimal. However, in this state selenomethionine is notoriously difficult to analyze due to the rigorous sample preparation required to break peptide bonds in a manner that is fully quantitative while still gentle enough to ensure no additional undesired speciation changes occur. At the National Research Council Canada we have recently developed a new Certified Reference Material, “SEEY-1”, which is selenized yeast enriched with selenium-82, which can be used as a matrix-matched spike for isotope dilution analysis of (proteinaceous) selenomethionine in selenized yeast and similar matrices. By using a matrix-matched spiking material, we are able to meet the isotope dilution requirement of sample-spike homogenization, which is impossible with the commonly-employed chemical selenomethionine spike which is unable to account for incomplete recoveries of selenomethionine from the proteinaceous form.

In addition to nutritional content, there has recently been an increased focus on the environmental impact of food production – particularly the detrimental effects of the meat-production industry – and for this reason there has been interest in movement towards a heavier reliance on alternative sources of proteins in our diets. In attempt to fill some of the knowledge gaps relating to the safety and nutritional content of these foods, we have examined the trace metal profiles of a number of novel protein-source foods, in terms of both total and bioaccessible content. Additionally, we have examined the selenium speciation of these foods for both leachable selenate and selenite, as well as total and bioaccessible selenomethionine.

selenium, selenomethionine, speciation, yeast, novel foods, Certified Reference Material

Determination of chlorine-containing compounds by GC-ICP-MS/MS in plastic-based pyrolysis oil samples

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Pyrolysis has emerged as an interesting option for recycling plastic waste. The plastic-based pyrolysis oil obtained is used as monomers source in the new plastic manufacture industry and as fuel source for engines. The high level of heterogeneity of the mixture of plastics often used as feedstock, including polyethylene, polypropylene, polystyrene, polyethylene terephthalate or halogenated polymers like poly vinyl chloride (PVC), supposes a drawback in their direct application in the industrial process due to its complexity.In this regard, PVC and other chlorinated plastics, can originate chlorine compounds after the pyrolysis reaction, what leads to the formation of HCl, a toxic and corrosive substance and other chlorinated organic compounds that could interfere in the downstream industrial process in which plastic pyrolysis oil are involved. Therefore, plastic-based pyrolysis oils must be upgraded through different process in order to low the chlorine content. Of course, information about the initial total chlorine content as well as the diverse chlorine-containing compounds present is of great importance for this purpose.

In this communication, we present a GC-ICP-MS/MS based method for the analysis of chlorine in real pyrolysis plastics oil samples. [1] The speciation and total quantification analysis of real samples was accomplished using generic Cl-containing standards after development and optimization of a compound-independent quantification methodology. Quantitative speciation analysis was carried out using a regular chromatographic column and an internal standard spiked (Fenchlorphos) in the samples. In the case of total chloride content, the analysis was performed after changing the column by an inert transfer line and resorting to external calibration with a chlorine-containing generic standard (5-Chloro-2 pentanone). Sensitivity and detection limit was also evaluated with the introduction of different gases (Ar:N2, Ar:He, Ar:Ne and Ar:CO2) to the plasma.

Detection limit as low as 1 µg/g was obtained under optimal conditions. For validation of both total and speciation methodologies a certified reference material was used. Several real pyrolysis oils obtained from diverse plastic sources were analysed with the methodology proposed.

Plastic-based pyrolysis oil, Chlorine compounds, ICP-MS/MS, GC

Freije- Carrelo, et. al., Anal. Chem. DOI: 10.1021/acs.analchem.9b01199

Speciation in non-conventional lipid feedstocks using liquid chromatography coupled to ICP/MS-MS

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To reduce the greenhouse gas emission in transport, the recent European Directive RED II will impose a minimum of 14% of transportation fuels coming from renewable feedstocks in 2030. To reach this objective, non-conventional oils (animal fat, waste cooking oil, Tall Oil …) must be processed to produce clean renewable fuels. However, the chemical composition of these complex matrices is mainly unknown and some contaminants even if present at trace levels can affect biofuel's production. Phosphorous is well known to cause severe problems of plugging and catalyst deactivation. More recently iron has been identified as a major contaminant in hydrodeoxygenation catalysts. Chlorine is also a critical element often present in biomass since it causes catalyst deactivation as well as serious corrosion problems in the reactor and downstream equipment's.

Some methods existed in the literature for the molecular characterization of conventional seed's oil (Palm, Rapeseed, etc.) but they cannot be directly applied to all the non-conventional oils without analytical developments. A proof of concept was recently demonstrated for the elemental characterization using supercritical fluid chromatography (SFC) coupled to ICP/MS in some bio-oil samples (1).

On the one hand, this communication will address the total elemental content of difficult elements such as Cl and P in non-conventional biofuel feedstock by means of inductively coupled plasma-tandem mass spectrometry (ICP-MS/MS) using a total sample introduction system, known as h-TISIS, and a conventional introduction system. A comparison with microwave-assisted digestion (MWAD) and organic dilution procedures will also be discussed.

On the other hand, it will be developed a multi-analytical methodology based on the hyphenation of a high-performance liquid chromatography (HPLC) to the ICP-MS/MS for elemental fingerprint, checking if the different chemical form of the previous elements present in the samples can generate non spectroscopic interferences effects in the analyte signal, such as matrix effects, during the analytical process. This elemental characterization will be then applied to establish the speciation during the transformation of non-conventional oils and animal fats to clean fuels.

non-conventional oils, contaminants, ICP-MS/MS, HPLC, speciation

Garcia-Montoto et al., J. Anal. At. Spectrom, 2020, 12, 2852 – 2858

Determination of Se and Hg species and HgSe particles in fish and fish–based products by HPLC-ICP-MS and spICP-MS

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Fish is an important source of high-quality proteins in the human diet and also provides many other important nutrients. Fishes can accumulate in their muscle tissues a vast number of elements, such as selenium (Se) and mercury (Hg), which are mainly bound to proteins. Se can be essential or toxic depending on its chemical form, its bioavailability, as well as the ingested dose (1). However, the biological significance of Hg is limited to its toxicity, which also depends on its chemical form. It has long been described that Se protects against Hg toxicity. Although a Hg-Se antagonism effect is generally observed, additive or even synergistic effects of Hg and Se have also been reported in the literature (2). In fact, HgSe nanoparticles (HgSeNPs) are thought to be an end product of the Hg detoxification process (3). Several works can be found in literature about Se and Hg speciation, as well as about HgSeNPs identification in edible fish. Nevertheless, to our knowledge, little information is available yet regarding fish-based products, such as lump, salmon and trout eggs or surimi and surimi-derived elvers. However, the consumption of this products in our society is continuously increasing, being more and more often introduced in our diet. In this work, Se species were determined in the water soluble protein fraction of highly consumed fishes (tuna, swordfish, farmed and wild salmon) and derived fish products by enzymatic hydrolysis followed by HPLC-ICP-MS and confirmed by HPLC-ESI-MS/MS, using both a reversed-phase C18 column and an anion exchange PRP-X100 column. In addition, Hg speciation studies were carried out by HPLC-ICP-MS using a reversed-phase C18 column. Concerning Se, the main species found in the fillet of the analysed fishes and in the derived fish products were selenomethylselenocysteine (SeMeSeCys) and selenomethionine (SeMet), whereas in case of Hg, MeHg was the major specie found. Finally, in order to study the Hg-Se interaction, the possible presence of HgSeNPs is investigated. For this purpose, different extraction methods were tested for HgSeNPs isolation from food matrices. spICP-MS was employed for screening analysis of the selected samples in order to identify HgSeNPs and to determine their concentration and diameter size.

speciation, selenium, mercury, HgSe nanoparticles, HPLC-ICP-MS, fish-based products

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How to Overcome Analytical Challenges Commonly Encountered in the Analysis of Cr and Cr(VI) in Environmental and Biological Matrices Using (µLC-)ICP-MS

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Chromium (Cr) mainly exists in the environment as trivalent Cr(III) and hexavalent chromium Cr(VI). Cr(III) is an important micronutrient, while Cr(VI) is an occupational lung carcinogen. The chemistry of Cr plays a major role in its cellular entry and toxic effects. Only Cr(VI) can easily pass the cell membrane. Once inside the cell, Cr(VI) is rapidly reduced to Cr(III). This reduction process can cause damage to cellular components. A sensitive and robust method for the simultaneous determination of Cr(III) and Cr(VI) has been developed. The method uses a hyphenated micro liquid chromatography system coupled to inductively coupled plasma mass spectrometry (µLC-ICP-MS). This presentation will highlight the analytical challenges (including pH dependency, contamination and soot deposit in ICP-MS) encountered during method development. The method has been applied to environmental and biological samples collected within a European human biomonitoring study. The study aimed to harmonize procedures for human biomonitoring. Human biomonitoring indicates exposure to chemicals by measuring either chemicals or markers of subsequent health effects in body fluids or tissues. This presentation will highlight the harmonization challenges (including interlaboratory comparison and availability of certified reference materials [CRM]). The human biomonitoring study evaluated the occupational exposure to Cr(VI). Samples were collected from 299 workers and 103 controls. The principal biomarker used for biomonitoring of Cr(VI) exposure at the workplace is total amount of Cr in urine. The main limitation of this biomarker is that it is not specific for Cr(VI) since it reflects exposure to both Cr(III) and Cr(VI). We studied the use of potential more specific biomarkers, such as Cr in red blood cells (RBC) and Cr(VI) in exhaled breath condensate (EBC). Cr in RBC reflects the exposure specifically to Cr(VI) since only Cr(VI) is able to pass though the red cell membrane. Cr(VI) in EBC can give specific information on the Cr(VI) levels in the lungs (main target tissue). This presentation will highlight the main findings of this study related to the analytical challenges (including low levels and stability). As indicated in this study, the analysis of Cr or Cr(VI) in environmental and biological samples is subject to challenges. Precautionary procedures needs to be taken during method development, analysis, sampling and storage. For the future success of chromium speciation in EBC, CRMs in water or EBC needs to be made available.Chromium, ICP-MS, human biomonitoring, toxicity, analytical chemistry, challenges, harmonization, coupling technique

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Extending the application range of ICP-mass spectrometry in microplastics characterization

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Concerns about the impact of microplastics (MPs) on the environment and human health were raised by scientists as early as the 1970s, but the global scientific community has only recently realized the magnitude of the problem. So far, however, little is known with respect to the occurrence and potential toxicity of low µm-range MPs, thus requiring the urgent development of novel, reliable, time-efficient, and robust analytical methodologies for their detection, quantification, size determination and identification. ICP-mass spectrometry (ICP-MS) was a priori not considered suitable for monitoring the carbon signals occurring upon the introduction of carbon-based particles into the ion source. In a recent proof-of-concept study carried out by the authors of this abstract (2020), ICP-MS based on C-monitoring was used for the first time ever for the characterization of MPs (1 and 2.5 µm polystyrene microspheres).(1) The approach used relied on the ultra-fast monitoring (with a dwell time of 100 µs) of transient signals using a quadrupole-based ICP-MS unit operated in single-event mode and registering the signal spikes produced by individual microparticles at a mass-to-charge ratio (m/z) of 13 ($^{13}C^+$). Meanwhile, the suitability of this approach has been confirmed by other research groups.(2,3) However, this only revealed the potential of single-event ICP-MS for the characterization of MPs and further development was/is still required to optimize this methodology and make it amenable to analyzing real samples.

This presentation will address the next steps in this context. First, the status of MPs characterization via ICP-MS operated in single-event mode will be reviewed. Attention will be paid to a broader size range (1 – 20 µm) and different polymer types (e.g., PS, PMMA and PVC). Furthermore, also the use of laser ablation (LA) as a means of sample introduction will be discussed. Figures-of-merit will be reported, and pros and cons of the methods developed will be highlighted. Finally, preliminary data for a wide variety of hetero-elements (e.g., additives, catalysts and/or constituents), will be presented, and the potential of this approach for identifying the type of particle will be evaluated through multi-element fingerprinting via single-event ICP-(ToF)-MS.

ICP-MS, single-event, laser ablation, microplastics

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Speciation Analysis of Gd-Based Contrast Reagents in River Water Using HPLC-ICP-MS

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Magnetic resonance imaging (MRI) is now one of the requisite imaging methods for medical diagnostics. Gadolinium (Gd) is used as the contrast agent for MRI to enhance the contrast of an image because of its strong paramagnetic property. Gadolinium-based contrast agents are administrated to patients in chelated form, because Gd3+ is well known for its toxicity. In recent decades, several studies reported that the apparent positive anomalies of Gd in the REE pattern are shown in rivers running through metropolitan areas [1,2]. It shows that a part of the Gd-based contrast agents is emitted to river water without being processed during the sewage treatments, even though the long-term risks of Gd-based contrast agents for living organisms are not well elucidated so far.

Recently, our group has developed a new HPLC-ICP-MS technique using the hydrophilic interaction chromatography (HILIC) column with the water-based eluent for the separation of Gd-based contrast agents [3]. In this study, the presented technique was applied to the speciation analysis to identify Gd-based contrast agents in river water in Japan.

River water samples were collected from the Muko River (Hyogo, Japan) in June 2018 and November 2020 near Sanda City, which is a suburban city with a population of 200,000. The concentrations of Gd in the samples collected in 2018 and 2020 (2018-O and 2020-O) were 97 ng L-1 and 51 ng L-1, and the magnitudes of the anomalies were calculated 39 and 17, respectively. The anomalies are much smaller than those reported in metropolitan areas, however it is very important to show that the anthropogenic Gd emission to the river is not only a matter in metropolitans but also a matter in small cities. Gd-species in the river water samples were also investigated using the HILIC-ICP-MS technique with the water-based eluent. As a result, 3 kinds of the cyclic type of Gd-based contrast agents, which are approve in Japan, were found in 2018-O and 2020-O. The concentration of these Gd-species makes up 70% of the anthropogenic Gd. The results clearly indicate that a part of Gd-based contrast agents pass through the WWTP without being treated.

Gd-Based Contrast Reagents, HPLC-ICP-MS

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The challenges and importance of accurate precious metal determination in electronic waste to support the Circular Economy Agenda

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Technology Critical Elements (TCEs) which includes precious metals such as gold, silver and platinum group elements are essential for mobile phones, laptops, energy efficient lighting and new green technologies including electric vehicles (EV) and wind turbines. They have unique properties, making them difficult to replace with alternatives. Due to their low natural abundance, limitations/interruptions to supplies and high demand, the UK and Europe primarily relies upon imports of TCEs. Furthermore, gold, silver and platinum group elements are also of high economic value. One mechanism to achieve sustainability and support the Circular Economy Agenda is through recovery of metals from recycling waste electronic goods.

However, there is a lack of validated analytical methods and suitable reference materials to support the recycling industry. Furthermore, the waste consists of a huge variety of materials, e.g. metal, glass, plastics, ceramics etc and is heterogeneous across tonnes, leading to challenges for sample preparation. For example, gold and silver are routinely present in electronic waste at the mg/kg level but their simultaneous analysis suffers from measurement challenges due to their differing chemical behaviour as gold only dissolves in aqua regia whereas silver is sensitive to hydrochloric acid. Precipitation of silver or incomplete extraction of gold during the preparation process could lead to underestimation of their concentration, impacting the value of waste and potentially the type of recycling stream used. Furthermore, analysis by ICP-MS may be hampered by the carryover of gold and potential precipitation of silver.

In this work, the development of ICP-MS based methodology for the determination ofgold and silver in a copper alloy CRM containing gold and silver at the mg/kg level will be discussed.It’s application to a real world sample of crude electronic scrap metal and to printed circuit boards will be presented. Finally, the remaining analytical challenges and future outlook will also be discussed.

Technology Critical Elements (TCEs), Circular Economy Agenda, electronic waste, WEEE, gold, silver, sample preparation, ICP-MS

Using ICP-MS coupling methods to analyse the geochemical influence on the radionuclide mobility in geological formations

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The development of a repository for high level nuclear waste (HLW) in deep geological formations is a very important task for the future. The long-term safety assessment for more than hundred thousand years needs a full knowledge of all processes of interaction between the radioactive waste and the surrounding host rock formations as natural barrier but also the interaction with the engineered barriers (1). A wide set of geochemical parameters can influence the retention of radionuclides originated from a leakage in a waste disposal for example competing ions released from the clay or cement concrete by infiltration of percolating water, natural organic matter (NOM) as complex forming ligands, changes in temperature or pH-milieu of the aquifer. To study the mobility of the analytes for example at high saline and hyperalkaline conditions (caused by the dissolution of clay and cement concrete in the presence of water), new analytical tools must be developed to get more insight into the possible interactions between metals and geochemical matrix (2). As speciation method, capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry (CE ICP-MS) was used to study the complexation behaviour of Eu(III) and U(VI) with NOM from different sources. The influence of metal concentration, the presence of competing cations from clay or concrete dissolution as well as cations from clay porewater on the complexation behaviour was analysed. For the sorption/desorption studies common batch experiments with the analytes and clay mineral suspensions are performed. Additionally, miniaturised column experiments (MCE) with online ICP-MS coupling allow for the visualization of sorption and desorption processes of europium and uranium on clay dynamically (3). LC hyphenation with ICP-MS leads to quantitative information on the elemental composition of the eluent from the mini column directly after determination of the UV/Vis-active compounds in the diode array detector of the LC.

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CE-ICP-MS, LC-ICP-MS, hyphenation, radionuclides, uranium, NOM, HLW disposal

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Metallic nanoparticles-assisted simultaneous and highly sensitive detection of multiple bacteria strains by laser ablation ICP-MS

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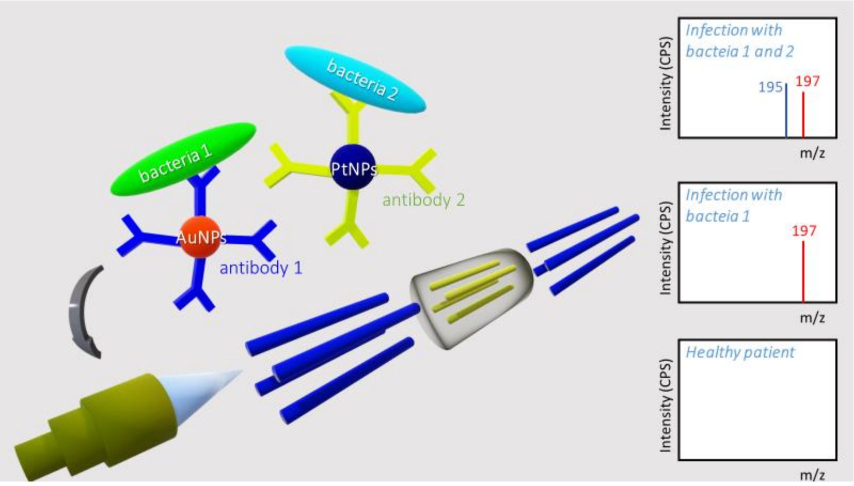
ICP-MS and metallic nanoparticles (MNps) used in synergy have provided extremely highly sensitive detection of biomolecules from a wide range of food, environmental and biological samples. Especially in the biomedical field, where exceptionally low limits of detection from matrix-rich clinical samples are necessary for early stage diagnosis, this approach provides a promising alternative to the standard used methods. Additionally, numerous diseases are associated with different strains of pathogenic viruses/bacteria, rendering vital their multiple, simultaneous detection. Elemental tagged ICP-MS detection is a powerful tool making the last objective feasible, challenged by the high specificity required for tagging each bioanalyte of interest with a specific MNp. Antibodies have been widely used the last years for anchoring MNps for immunoassays detection by ICP-MS. In this work, we present the simultaneous detection of 2 different bacterial strains by laser ablation ICP-MS (LA-ICP-MS). For this, gold and platinum Nps were bio-conjugated to different antibodies, specific to each chosen strain. The bioconjugation effectiveness was evaluated by X-Ray Photoelectron Spectroscopy (XPS) analysis. The results demonstrate a potential highly sensitive and simultaneous bacteria detection and are encouraging for the following application in real biological samples.



metallic nanoparticles, antibodies, bacteria detection, LA-ICP-MS

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LIBS-based multi-elemental analysis of agricultural soil

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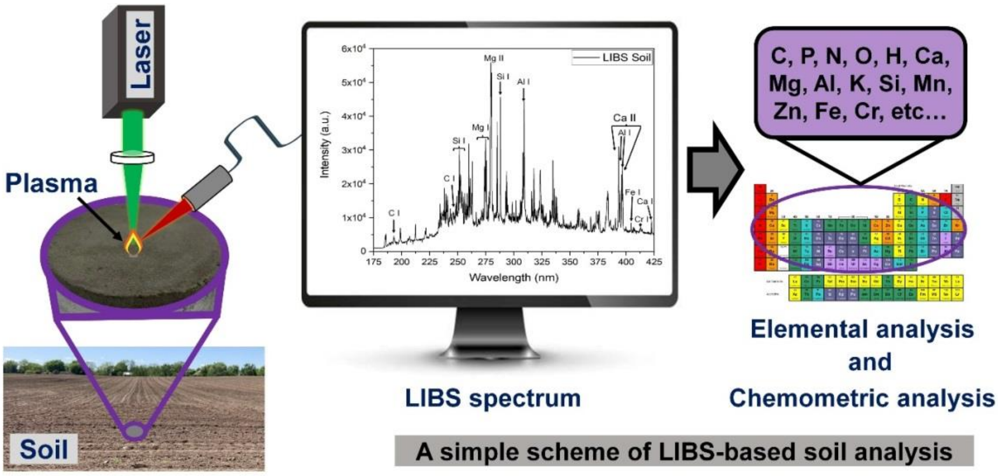
[1]Photonics Laboratory, Physics Unit, Tampere University, Tampere, Finland

Soil is a vital component of the climate system and environment. Global diversity and matrix complexity of the soil present major challenges to investigators. In this study, agricultural soil samples were examined using laser-induced breakdown spectroscopy (LIBS), an extremely versatile technique. LIBS enables rapid and simultaneous multi-elemental analysis of samples regardless of their physical state, with little/no sample preparation involved.

In our work, soil samples collected from 47 geographical locations in Finland have been investigated. The samples were sieved, dried, ground, and pressed into circular pellets. The LIBS measurements have been performed in an air atmosphere using a Q-switched Nd:YAG pulsed laser (30 mJ/pulse, 1064 nm, pulse duration 8 ns) under optimum conditions. LIBS spectra of the samples revealed characteristic emission of a wide range of elements, including C, N, P, etc., in different proportions. Figure illustrates a scheme of LIBS-based soil analysis. Plasma temperature and density have been evaluated for further analysis and quantification. Additionally, chemometric methods have been used to extract substantial information. The preliminary results from the analysis are promising. This work sets the stage for the development of a custom LIBS system for soil elemental monitoring.



A simple scheme of LIBS-based soil analysis

LIBS, soil analysis, carbon characterization, elemental analysis, chemometrics

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New Horizons lecture

Measuring microplastics and nanoplastics: from analytical method development to environmental impacts

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Understanding how human activities influence physical, chemical and biological cycles is a central component of modern geosciences. The natural environment is experiencing ever-increasing pressures from anthropogenic stressors, including the release of anthropogenic particles. The term anthropogenic particles covers a wide range of materials, including those which are manufactured at the nano-scale (e.g., engineered nanomaterials), generated incidentally (e.g., soot), or originate from the degradation of larger materials such as plastics, which form microplastics and nanoplastics (MnPs). Understanding the fate, transport, biological interactions and environmental impacts of MnPs requires the development of new analytical techniques for characterization and quantification as well as fit-for-purpose experimental approaches to elucidate their behavior and impacts across all environmental compartments. While some methodologies and approaches can be adapted from years of studying inorganic materials in a similar size range, there are particular challenges with measuring carbon-based materials. Increasing the complexity of the problem, MnPs is a catch-all name for a very heterogeneous suite of materials which include different polymer chemistries, sizes, and morphologies – all of which need to be characterized and could influence environmental impacts – but currently no standardized materials or analytical methods exist. To highlight some of the approaches we have developed related to atomic spectroscopy, in this seminar I will discuss 1) nanometrology developments, such as single particle ICP-MS, 2) how I turned the challenge of assessing environmental impacts of MnPs on its head by developing a platform to measure these materials by synthesizing metal-doped plastics to still take advantage of the capabilities of atomic spectroscopy, 3) moving beyond doped plastics to measure microplastics directly by carbon analysis and 4) perspectives on the most challenging hurdles to overcome in the field of plastics pollution to assess environmental impacts. Beyond the laboratory, I am keen to develop links between academic scientists, industry, policy makers and the public to understand how to use plastics in a sustainable way to reduce their negative impacts on the environment. In particular, I am to place MnPs in the context of global plastic pollution while also assessing (and improving) plastics regulation.

Laser Ablation Inductively Coupled Plasma Mass Spectrometry – One Method, Many Applications

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Laser Ablation Inductively Coupled Plasma Spectrometry (LA-ICP-MS) has contributed to more and more fields of sciences and is routinely applied in geology, environmental and materials sciences and has entered the biomedical research. Some recent applications will be highlighted.

Since the incorporation of time-of-flight mass spectrometers (TOFMS) some modifications and new developments of aerosol transport systems have been reported allowing to study aerosol formation phenomena and its implications in more detail. The benefits of low-disperson ablation cell over common cells will be emphasized. These fundamental processes are of major importance for fast transient signal recording, e.g. for 2-D and 3-D imaging. Therefore, some work was focused on direct ablation of bulk tissues to investigate the precision of direct removal layer by layer for 3-D image reconstruction. Examples on an organoid sample will be presented. Furthermore, the impact on diagnostics and treatment decisions will be discussed.

Latest developments have focused on substituting the well-known argon plasma source by a nitrogen plasma, which substantially reduces Argon interferences and opens new opportunities of operation. Some experiments and their outcomes on such plasma sources in combination with laser ablation and portable laser ablation will be presented and compared to the conventional argon plasma.

Spectroscopy magazine award

Opportunities for LIMS for the detection of signatures of life in future space exploration missions

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Various current (e.g., NASAs Mars2020 mission) and future space exploration missions (e.g., NASAs Enceladus Orbilander mission) are aimed at detecting signatures of life on Solar System bodies using a variety of complementary instrumentation. One of the major limitations is that lab-size instruments cannot be deployed in situ (i.e., on a landed spacecraft or rover). Despite their excellent performance in laboratory research, several instrumental parameters (e.g., required power, weight, and volume) are way above what is available on a landed platform. Therefore, the measurement capabilities of instrumentation designed for space exploration missions are limited and novel measurement methodologies and techniques are required for such challenging missions.

In this award lecture, the current measurement capabilities of Laser Ablation Ionisation Mass Spectrometry (LIMS) for the detection of signatures of life will be discussed in detail, presenting recent and ongoing laboratory research with prototype instruments for space research (1-3). Laser ablation (1) conducted on Mars analogue materials artificially inoculated with microbes and laser desorption studies (2-3) conducted on organic molecules important to life as we know it from Earth, will serve as basis for this discussion. LIMS as a measurement technique has not yet been applied in space exploration missions devoted to life detection. However, the recent developments and corresponding measurement results demonstrate that the technique, despite the current limitations, is truly a competitor to already applied technologies, e.g., pyr-GC-MS, which has been applied repeatedly since the first Viking mission on Mars in the 1970s.

LIMS, signatures of life, life detection, space exploration

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LIBS imaging: recent advances and perspectives

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The imaging capability of laser-induced breakdown spectroscopy (LIBS) has a high potential in various domains including biology, industry, geology and medicine (c.f. figure 1) [1,2]. This approach can be distinguished by its ease in use, multi-elemental capability, detection of light elements, as well as operation at ambient conditions. This is furthermore the only all-optical technique providing space-resolved elemental information with ppm-scale sensitivity and µm-range resolution. These advantages, make LIBS imaging very attractive to be used in research laboratories for routine investigations. However, advanced technological solutions must be found for this application since elemental imaging requires high sensitivity, sharp spatial resolution, high speed of acquisition as well as the ability to process a huge quantity of data. In this presentation, we will summarize the recent progresses made in the Light and Matter Institute concerning the implementation of the LIBS imaging. In particular, different examples of breakthrough applications, such as biomedical (figure 1.a and b) or industrial (figure 1.c and d) will be shown with the aim of illustrating the specificities and the great potential of LIBS imaging. Different perspectives will be finally discussed with a particular focus on the methods of tomorrow on the processing of data.

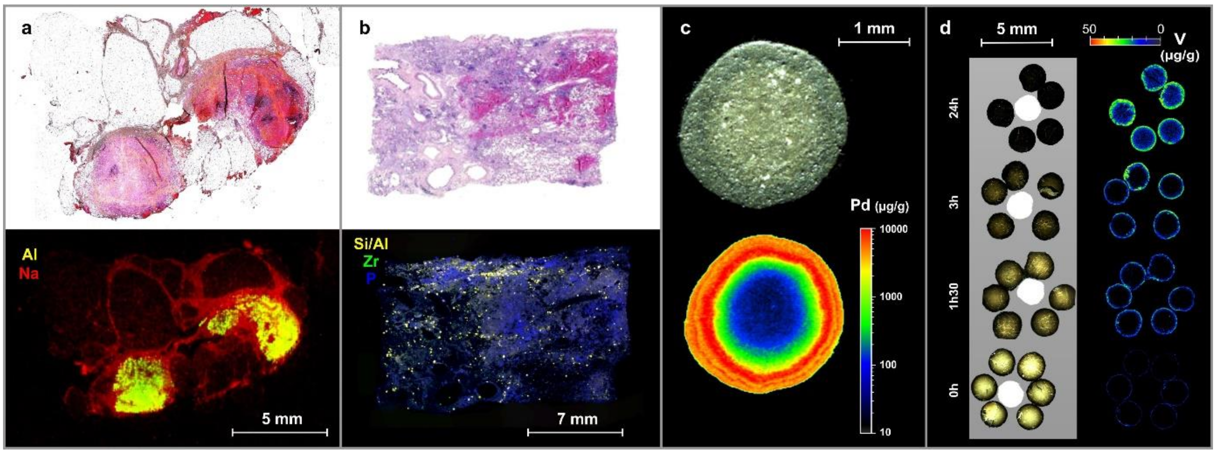

Figure 1. (a), Histologic analysis combined with elemental imaging that identified the metal responsible for a foreign body granuloma in a young patient at CHUGA. (b), Histological and multi-elemental images of a lung biopsy from a patient who worked in the World Trade Center rubble removal. (c) Demonstration of the distribution of the active element Pd of a catalyst supported on alumina, image representing a dynamic of 3 orders of magnitude in concentration. (d) Kinetics of impregnation of a heavy metal, Vanadium, during petrochemical treatments.

LIBS Imaging, elemental imaging, Micro-LIBS, data processing.

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Laser ablation and single cell ICP-MS as complementary techniques to determine target proteins in individual cells

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Over the last few years, single cell (sc) ICP-MS has been applied for the analysis of endogenous elements in individual cells to better understand their biological functions, to study the cellular internalization of metallic nanoparticles, and to assess the uptake of metallodrugs (1). Moreover, the use of metal-labelled antibodies allows the determination of specific biomolecules within the cells. The availability of high amplification labels is crucial for the determination of low concentrated cellular biomolecules. In this vein, metal nanoclusters (MNCs) are a great alternative to the commonly used polymeric lanthanide complexes as the hundreds of atoms forming the tiny metallic core provide high amplification of the target protein with lower risk of blocking antibody recognition sites (2). sc-ICP-MS can be used for a high throughput cell-by-cell quantitative determination of target biomolecules within cell cultures, but the biomolecules' distribution inside each cell cannot be afforded. This can be overcome by directly sampling the cells using laser ablation (LA) coupled to ICP-MS. Additionally, using a proper matrix-matched calibration strategy, which fully mimics the matrix of cultured cells, it is possible to obtain not only the qualitative distribution of the target biomolecules but also to determine their concentration. However, one of the main drawbacks for imaging at subcellular level is the loss in sensitivity when reducing the spot size and, thus, the use of high amplification labels is critical. In this work, we present sc-ICP-MS and LA-ICP-MS as complementary techniques to get a comprehensive study (determination and localization) of target proteins in individual cells. In order to achieve a significant amplification to detect proteins at low concentration levels in the cell, AuNCs and IrNCs labelled immunoprobes are employed. As a proof of concept, the sequential determination of proteins (apolipoprotein E, claudin-1 and methalotionein 2A) in individual human retinal pigment epithelial cells of different in vitro models (hRPEsv40, ARPE-19 and primary RPE) was pursued, both in cultured cells subjected to a pro-oxidative stress or pro-inflammatory treatment and control cells.

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Single cell, Laser ablation, Imaging, Metal nanoclusters, Immunoprobe, Proteins

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LA-ICP-MS analysis of Deuterium in polymers for assessment of the water content

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Polymers cover a wide range of favorable physical and chemical properties that are of utmost relevance for highly demanding applications. In electronic devices, polymers are often used as coating or encapsulation material which requires both high chemical and physical resistance but also insulating properties. However, in the course of the component's use, the polymers physical and mechanical properties can change massively, causing the protective/insulating effect of the coating/encapsulation to be lost over time, which in extreme cases can lead to device failure. A parameter known to significantly influence the degradation of polymers is the water content, which is usually determined using indirect procedures such as thermo-gravimetric analysis, differential thermal analysis, or dynamic vapor sorption [1]. Although well established, these techniques are connected with severe drawbacks, such as the limitation to bulk investigations and the bias caused by the release or uptake of other volatile species.

In this contribution, a new approach for the assessment of the water content in polymer samples is presented. The developed procedure is based on the preliminary treatment of a dried polymer sample with Deuterium enriched water (D_2O), and the subsequent LA-ICP-MS analysis of the Deuterium content in the polymer, enabling a reliable determination of the water uptake. Measurement of Deuterium is performed by monitoring the signal from the polyatomic ArD ion formed in the plasma, an approach which has been presented recently by Galbacs et. al for the ICP-MS analysis of Deuterium in liquid water [2]. For the conducted LA-ICP-MS investigations, a special ablation chamber has been constructed, which allowed to reduce the influence of remaining humidity. Moreover, a thorough optimization of the ablation parameters was necessary. Pressed pellets made from polymer powders containing defined supplements of deuterated organic compounds have been used as calibration standards, demonstrating a linear correlation between the measured ArD signal and the Deuterium content of the sample, enabling spatially resolved measurements of Deuterium in polymers down to the permille range.

LA-ICP-MS, Deuterium, polyatomic ions, polymers, water content

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Quantitative compositional depth profiling of non-conductive technical coatings with radio frequency GD-OES

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Since more than four decades, glow discharge optical emission spectroscopy (GD-OES) has evolved as a highly successful technique for compositional depth profiling (CDP) of surface layers and coatings on metals [1]. Improvements in hardware and data treatment methods have steadily expanded the range of applications and analytical accuracy. The introduction of radio frequency (RF) powered sources extended the range of applications to non-conducting technical layers, e.g. polymer coatings [2]. However, quantitative analysis of polymers and other types of non-conductive coatings presented several new challenges:

- Lack of control of the discharge parameters in the GD plasma
- Strong influence on the spectral intensities (emission yields) from hydrogen
- Determination of the density and thereby sputtered depth
- Lack of suitable reference materials for calibration of certain elements, e.g Sr and Ba

Techniques to deal with these difficulties have been developed and successfully refined to achieve improved accuracy also in complex coating types [3]. In this work, the development of an improved user-friendly correction method for the influence of hydrogen will be presented. The method is based on the use of bulk reference materials to determine correction constants to offset the influence of hydrogen on the emission yields. The outgassing of small hydrogen in the very early stage of the discharge results in intensity gradients reaching a steady – state after stabilisation. The ratios of the early signals to the steady state are used to calculate the correction constants. Examples of quantitative depth profiling of polyester coatings, primer coatings and anodized aluminium layers using RF GD-OES will be presented and discussed.

Glow Discharge, Radio Frequency, Optical Emission, Depth Profiling, Quantitation

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Gaseous and particulate species formation in LA-ICP-MS

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It is known that some elements, such as Hg, exhibit a significantly longer single pulse response (SPR) duration than other in sample analysis via laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS). One of the major hypotheses explaining this difference in transfer behavior is that most elements are transferred as an aerosol while Hg is transferred predominantly in the gaseous phase, which will result in a significantly larger expansion of the Hg plume inside the ablation chamber, different flow characteristics through the connective tubing and a much wider SPR profile and corresponding longer SPR duration. [1, 2]

Recent work focusing on fast biomapping of Hg and Se distributions included an in-depth evaluation of the SPR profiles of these elements in comparison to that for Cu, which was selected to represent elements being transported in the particulate phase. It was found that Cu and Hg indeed have very distinct SPR profiles, which correspond to the hypothesis of the formation of particulate and gaseous species for Cu and Hg, respectively. However, when measuring the SPR profile of Se at a sufficiently short dwell time, it was discovered that two peaks were present, one short, fast peak and one longer peak and that these two peaks could be separated by changing the length of the connecting PEEK tubing. It was hypothesized that, upon ablation, Se was transported in both the particulate and gaseous phase, that these two phases behave independently and that the total SPR profile consists of the combination of both. [3]

Follow-up experiments will focus on investigating the effect of laser parameters, such as the laser energy density, on the formation of gaseous or particulate species and on an evaluation whether other elements with similar physicochemical properties, e.g., boiling point and enthalpy of sublimation, exhibit the same behavior as Se. In addition, it will be evalated whether or not the matrix has an effect on the formation of one species over the other, which could play an important role in calibration approaches.

LA-ICP-MS, single pulse response (SPR), bio-mapping

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Optical emission spectroscopy by LIBS combined with electric spark discharge: element analysis of steels and polymers

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Spark-OES is a widely used and advanced element analysis method in the metal-producing industry. LIBS is another analytical technique that can be used for nearly all kinds of materials [1]. However, this technique is suffering from relatively high limits of detection for several elements and from plasma emission properties that can depend on the matrices. In our research, a combination of spark discharge and laser ablation is used for plasma formation and optical emission spectroscopy (Laser Ablation-Spark Discharge-OES, LA-SD-OES). For the spark discharge two different electric circuits are used. The first circuit consists of a 25 nF capacitor that is charged with a high voltage of up to 3 kV. It is triggered by a laser-induced plasma generated by focusing a low energy laser pulse (µJ to several mJ) on the sample. The second circuit consists of a modified commercial spark discharge generator used in Spark-OES. For conductive samples only one electrode is used. For non-conducting samples like polymers two electrodes are used and the laser beam is focused in between the electrode tips. The LA-SD-OES spectra reveal high intensity enhancement and ionic spectral lines in comparison to LIBS. Moreover, this method offers high spatial resolution and well-defined measurement spots in comparison to spark-OES [2]. A strong influence of the steel sample composition on the line intensities of Fe and other elements (matrix effect) has been observed with LIBS whereas LA-SD-OES does not show this undesired behavior [3]. The hardness, grain size, and phase of steel samples are analyzed to correlate the matrix effect to a physical property of the specimen. From our measurements we conclude that LA-SD-OES enables the element analysis of industrial steel largely independent of the composition and structure of samples while in LIBS the matrix effect has to be taken into account. With LA-SD-OES, element emission lines with high excited state energies are observed which can be used to investigate also non-conductive samples such as polymers.

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Laser ablation; Spark discharge; LIBS; Steel; Matrix effect; Polymers

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Solution-Cathode Glow Discharge Optical Emission Spectrometry for high salinity samples: Are organic additives beneficial?

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The Solution-Cathode Glow Discharge (SCGD) atomization excitation source coupled to Optical Emission Spectrometry (OES) has become a viable alternative to traditional elemental analysis techniques, like Atomic Absorption Spectrometry (AAS) or Inductively Coupled Plasma (ICP) thanks to its simplicity and low limits of detection, which are comparable to those obtained by ICP-OES. The SCGD simplicity relies in its atomization/excitation capabilities using low power (<100W) and gas consumptions (no pressurized gas required), allowing its implementation in mobile set-ups for continuous in-situ measurements. Another important feature is its elemental coverage, which includes metals, semi-metals and even halogens, with minor matrix effects due to the presence of concomitant ions.

Part of its simplicity comes from the lack of nebulization step for the atomization, as the actual plasma can scrutinize and transfer dissolved atoms into the plasma phase in a complex process. The described analyte transfer mechanisms include ion sputtering, droplet ejection and volatile compound formation, being possible that the three mechanisms coexist altogether. In this sense, the addition of organic substances to improve the analytical signal, like carboxylic acids and alcohols, which improve the analytical response of the SCGD-OES approach is a widely used strategy. Nevertheless, recent results show that the benefits in the use of additives disappear with high concomitant ion concentration.

The present communication will discuss the impact of additives with specific salts, trying to envisage how they affect the analytical response, and extending it to a complex matrix, seawater. More specifically, the analytical response will be related with different discharge characteristics important in the analyte solution-to-plasma transfer process and the excitation conditions.

Elemental Analysis, Glow Discharge, Solution-Cathode Glow Discharge, plasma-liquid interaction, Seawater

Plasmas, Droplets, and Acoustic Fields: Century-Old Tools to Understand Abiotic Chemistry on the Early Earth

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Theorizing on the chemical origins of life on Earth has been a long-standing scientific endeavor. Most efforts over the past several decades have focused on laboratory chemistry that could have yielded complex molecules seen in modern life (e.g., amino acids, nucleotides, and carbohydrates). The Hadean Earth (4 – 4.5 Gya), the time when life likely began on Earth, had numerous energy sources that could have been essential to yield these biologically relevant monomers from simple inorganic precursors (e.g., CO2, CO, H2O, N2). These sources include UV radiation from the Sun, pH and potential gradients in hydrothermal vents, aerosols from crashing waves, impactor-induced shockwaves, and wet-dry cycling in shallow ponds/lakes.

Plasmas have been used for abiotic synthesis since the classic Miller-Urey experiments in the 1950s. Unfortunately, most of those experiments were carried out in conditions not representative of the early Hadean Earth. This presentation will focus on a different approach to explore pre-biotic synthesis using plasma. Specifically, we apply realistic early Earth conditions to plasma reactors for chemical synthesis. Additionally, plasmas are used not as a mimic for lightning, but as a diverse energy source to enable unique chemistry. Once desired species are made, the high-energy reactants responsible for this chemistry and mechanism(s) of product formation are determined.

In one example, the potential role of plasma-droplet interactions in prebiotic chemistry will be discussed. Gaseous ions and highly charged droplets can drastically enhance reaction rates of carbon-nitrogen and carbon-oxygen bond formation. Early Earth likely had numerous sources of ions and charged droplets that could result in such unique chemistry. These systems are being tested with a solution-cathode glow discharge (SCGD), which consists of an atmospheric-pressure glow discharge on a solution surface that also produces highly charged droplets. Polymerized products formed from plasma-droplet interactions are recorded in real-time with mass spectrometry (MS). Most recently, we are exploring the use of an acoustic resonator to trap changed droplets and extend reaction times. Conditions that most impact abiotic peptide and oligonucleotide formation will be discussed.

Plasma ionization, droplets, ion-molecule chemistry, acoustic fields

Physical characterization of a microwave plasma jet and TOF-MS coupling optimization

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In this work, an atmospheric pressure plasma source with a frequency of 2.45 GHz (Sairem, Décines-Charpieu, France) is used as an ionization source for a time-of-flight mass spectrometer (TofWerk, Thun, Switzerland). The final aim is to develop an analytical procedure (including preliminary sample preparation) for the detection of substances that could contaminate food products and plants. The introduction of the sample is made as an aerosol mixed to the argon discharge gas using a peristaltic pump, a nebulizer and a cyclonic chamber. Initially the interface between the plasma source and the mass spectrometer is at ambient air. Under these conditions, the plasma can be subject to external perturbations and the plasma source/TOF-MS coupling could be improved.

Before any analytical experiments, a physical study of the argon plasma jet was done without liquid introduction, in a free jet configuration at atmospheric pressure (100 W injected power, 5 L/min Argon flow). Optical emission spectrometry and ICCD camera measurements with or without band-pass filters (335 nm and 810 nm, FWHM = 10 nm) were used to characterize the plasma jet emissions. Mass spectrometry was used to determine ionized species due to the interactions of the argon plasma jet with the ambient air species. These results will be presented as well as the plasma characteristics (gas temperature and electron density) calculated from the optical spectra.

The installation of a 30 cm long tube between the source and the TOF will be used to isolate the plasma from the ambient air and to ensure a plasma source/TOF-MS coupling in a controlled atmosphere. This length is necessary to prevent the spectrometer entrance from too high temperature. Experimental characterizations of the plasma will be carried out in these new conditions. Optical spectra and excited species spatial distributions will be measured. And the plasma results and properties obtained from the two setups will be compared.

Plasma, mass spectrometry, optical emission, microwave, temperature, electronic density

Investigation of low temperature plasmas induced in gaseous mixtures by EUV or laser pulses

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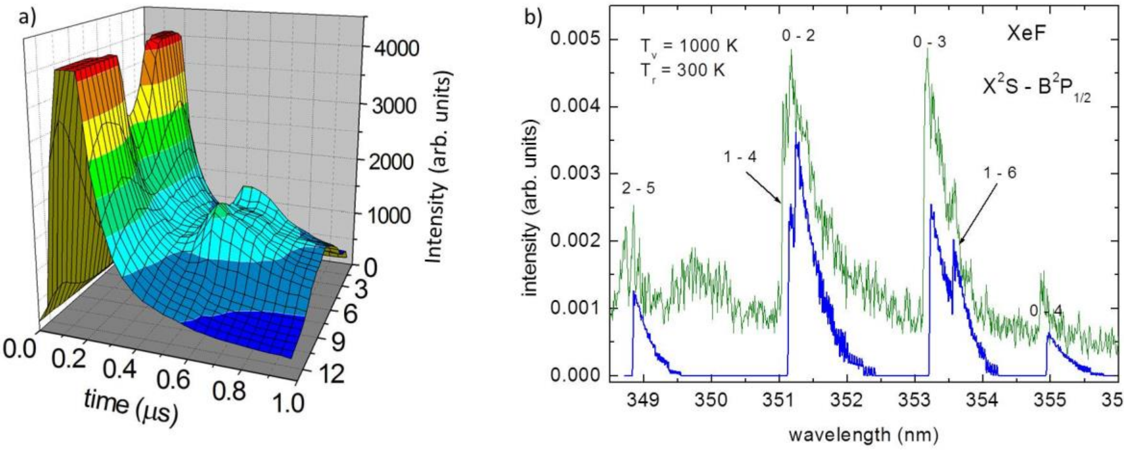
In this work, low-temperature plasmas, formed in gaseous mixtures were investigated. Plasmas were created by intense extreme ultraviolet (EUV) pulses [1,2] or various factors accompanying laser plasmas produced in an ambient gas under low pressure. A purpose of the work was to determine the ionic/molecular composition of plasmas and the resulting, potentially reactive species. Cold plasmas induced using both systems, emitted radiation in a wide wavelength range, from vacuum ultraviolet (VUV) to visible light (VIS). A dynamics and molecular composition of such plasmas was measured using spectrometers and a streak camera operating in VUV - VIS spectral ranges. Multiple emission lines corresponding to ionic and atomic species together with the molecular bands originating from various species were recorded. Numerical simulations of molecular spectra allowed to estimate rotational and vibrational temperatures of the induced plasmas. As could be expected, plasmas created in both experimental systems were characterized by different temperatures and dynamics. Spatio-temporal measurements performed using the streak camera indicated a few times longer lifetime of the induced low temperature plasmas, compared to the driving, EUV or laser pulses.

Figure 1. Plasma optical emission: a) spatio-temporal intensity distribution, b) XeF spectrum



laser produced plasma, EUV induced plasma, molecular spectra, plasma dynamics

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Surface-assisted flowing atmospheric-pressure afterglow mass spectrometry (SA-FAPA-MS)

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Ambient desorption/ionization high-resolution mass spectrometry (ADI-HR-MS) is a rapid and effective technique for the direct analysis of a, preferably, untreated sample. One of the remaining challenges is the accurate quantification of analytes in complex and matrix-heavy samples [1]. Therefore, preceding separation steps are often used to remove the matrix.

In this talk, we will report on the advantages of using chemically modified surfaces, precisely thin layer chromatography (TLC) plates, as sample substrates for direct analysis of liquids and dried residues by plasma-based ADI-MS. Cyano- and dimethyl-modified silica demonstrated promising properties, as both yielded analyte signals about 100 times higher compared to other surfaces when probed with the flowing atmospheric pressure afterglow (FAPA, cf. Hieftje et al. [2,3]) source. In terms of sensitivity, analyte amounts were detectable down to the low fmol range. In general, it has been shown that the chemical compound class of the analyte plays an important role in the whole desorption and ionization process.

The capabilities and advantages of the approach were not only demonstrated for basic standards and standard mixtures of selected compound classes but were also observable in the accurate quantitation of analytes in matrix-heavy samples. Results on real samples were validated by HPLC experiments. The comparison showed a better time efficiency of our presented method, which we refer to as surface-assisted (SA-)FAPA-MS. This approach represents a promising sampling strategy for ADI-HR-MS analyses of simple samples and samples with analytes in complex matrices.

Flowing Atmospheric-Pressure Afterglow, Ambient Desorption/Ionization, Surface-Assisted, Mass Spectrometry

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Multi-element analysis in different matrices using nitrogen microwave inductively coupled atmospheric pressure mass spectrometry (MICAP-MS)

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Inductively coupled plasma mass spectrometry (ICP-MS) emerged as a powerful technique for trace analysis of soil due to its multi-element capability, high sensitivity and low sample consumption. However, despite its success and widespread use, ICP-MS has several persistent drawbacks, such as high argon gas consumption, argon-based polyatomic interferences and the need for complicated RF-power generators. Unlike argon-based ICP, the nitrogen microwave inductively coupled atmospheric pressure mass spectrometry (MICAP-MS) uses nitrogen as plasma gas, which eliminates high operating costs associated with argon-gas consumption as well as the argon-based interferences1,2. In this work, the applicability of MICAP-MS for elemental analysis in different matrices is investigated. For this purpose, a broad spectrum of samples was analyzed, including soil samples, steel, and components of lithium-ion batteries. Concentrations of selected elements are determined using MICAP-MS and validated with ICP-MS und certified values. Sensitivities, limits of detection and gas consumption for both methods are compared and discussed in detail. Performance of MICAP-MS under different nitrogen plasma gas concentrations is investigated and compared. Moreover, the performance of MICAP-MS in different matrices is investigated and discussed.

Microwave inductively coupled atmospheric pressure mass spectrometry (MICAP-MS); nitrogen plasma; multi-element analysis; soil; steel

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Tackling matrix effects in microwave induced plasma - optical emission spectrometry

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Easily ionisable elements (EIE) such as the alkaline or alkaline earth elements are well known to cause matrix effects to analytically used plasma sources in general and to microwave induced plasmas (MIP) in particular [1]. Using an axially viewed microwave-sustained, inductively coupled, atmospheric-pressure plasma (MICAP [2]) attached to a simultaneous spectrometer initially used for inductively coupled plasma – optical emission spectrometry (ICP-OES), we investigated matrix effects of Al, B, Co, Cr, Cu, Fe, Mn, Ni, Ti, V, Zn as well as the EIE Li, Na, K, Cs, Mg, Ca, and Ba on the emission signal suppression/enhancement for 105 emission lines of 42 elements. The attained data clearly show, that matrix effects are encountered not only for g/L concentrations of matrix elements, but as low as 50 mg/L with signal suppression of up to 25% on particularly affected emission lines. The magnitude of the matrix effect was not similar for all investigated matrix elements, but particularly pronounced for the alkaline elements. For the same concentration (mg/L), the matrix effect of the alkaline elements was found to decrease in the order Li > Na > K > Cs. However, if equimolar amounts (mmol/L) of alkaline elements were introduced into the MIP, the matrix effect on concomitant elements was similar in magnitude. It could also be shown, that neither optimizing microwave power (range 1.1 to 1.5 kW) nor nebulizer flow rate was effective in appreciably reducing these matrix effects. Based on these findings, the use of Li as "ionization buffer" is proposed. This concept is well known in flame atomic absorption spectrometry. By using a sewage sludge reference material, the effectiveness of 100 mg/L Li for supressing matrix effects in MIP-OES could be shown.

microwave induced plasma; MICAP; MIP matrix effects

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The value of the cellular metallome for immuno-mass spectrometry imaging by LA-ICP-TOFMS

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In this work, we show the successful integration of the concept of bioimaging the cellular metallome by LA-ICP-TOFMS into the toolbox of state-of-the-art imaging mass cytometry. Latest technological advancements in LA-ICPMS have enabled multi-element mapping at cellular resolution with pixel acquisition rates beyond 200 Hz (1,2). This provides the basis for the analysis of metal-conjugated antibodies together with endogenous metals with biological key functions at the single-cell level. The combination allows the characterization of heterogeneous cell populations with regard to cell types, functionality and cell state together with their intrinsic metal content. The effect of multi-step sample preparation protocols (including immunostaining) on elements intrinsically present in biological samples was systematically evaluated in this study. Validation exercises using a consecutive histologically stained tissue section and/or the correlation of the endogenous elemental pattern with cell types and histological features/structural markers as visualized by metal-conjugated antibodies proved to be essential to obtain reliable information. Quantification was achieved by multi-level matrix-matching calibrations established by gelatine micro-droplets (3).

In selected examples using different biological samples, the added value of imaging the endogenous metallome dimension next to metal-conjugated antibodies by LA-ICP-TOFMS is showcased. This biological validation proved the validity of the integrated metallomics/cytometry approach.

LA-ICP-TOFMS imaging, cellular metallome, immunostaining, single-cell analysis

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An interactive workflow for single-cell multiplexed image analysis

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Advances in resolution and throughput of highly multiplexed imaging modalities have enabled the routine study of single-cell features within tissue and suspension. Analogous to this development, the need for flexible yet sophisticated image analysis workflows for extraction of relevant single-cell information, has grown. Though there are a plethora of tools and workflows available, using standalone software tools for each step comes at the cost of automation convenience while automated workflows often limit interaction and adjustability. Here, we demonstrate the development of a customisable, yet stream-lined, human-in-the-loop workflow for the extraction of single-cell information from laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOFMS) images. The workflow focuses on strong single-cell segmentation performance for accurate cell-based information extraction, as well as various selectable analysis tools such as clustering algorithms & cluster analysis, lower dimension embeddings, correlation matrices and image similarity scoring. As this workflow is currently work-in-progress we aim to extend its functionality in future by integrating multiple data visualisation methods and channel-based signal amplification and or noise reduction. Overall, the described workflow aides in the efficient acquisition-independent analysis of highly multiplexed image data at the single-cell level.

image analysis, multiplexed imaging, LA-ICP-TOFMS, workflow, segmentation, single cell

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Ultra-trace isotope imaging by fsLA SF-ICP-MS: a new approach for U-series dating of archaeological biominerals

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U-series datings are method of choice for tens of years in various domains, especially in archaeology, thanks to a large applicability (from few thousand years to 600 ka), theoretically on a wide range of carbonate materials (from speleothems to biominerals). This radiometric dating method is therefore considered as an important tool for investigating the Middle and Upper Pleistocene, beyond the period of applicability of radiocarbon. Today, the geochronological potential of this method is still largely unexploited in this field due to the limitations of the common protocol, which involves sample dissolution with spike addition and ion exchange chromatography. This approach is not suitable for small, valuable samples with very low uranium content (ultra-traces, <10ppb) and showing particularly complex diagenesis (open systems). Yet, these characteristics are specific to many samples, which are very abundant on most archaeological sites (eggshells, teeth, snail shells, etc.), and not yet fully exploited.

We present here the development of an alternative approach for U-series dating of these specific samples, taking advantage of the coupling of a femtosecond laser ablation system with a high sensitivity sectorial field ICP-MS. The isotopic images produced, with an appropriate processing, allows spotting 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, and the possibility to study the incorporation and diagenetic processes within complex materials. This method also allows direct mesures of ultra-trace of 238U and its descendants, with detection limits in the range of ag/mg. Moreover, since the masses collected are of the order of a mg or less, this technique requires few preparation of the samples, and preserves their integrity. We will discuss here the new possibilities offered by this approach, particularly through its application to various biominerals from major prehistoric sites for the study of human evolution. These different examples will then lead us to consider new possibilities for U-series dating.

Laser ablation, SF-ICP-MS, Isotope Imaging, Ultra-trace, U-series dating, Archaeological biominerals

Nanoparticle tag counting for tissue imaging using single-particle ICP MS

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We report a new laser ablation technique employing a pulsed 2 940 nm laser and a simple ablation cell for digital mapping biomarkers in tissues using metal nanoparticle tags. Unlike the conventional laser ablation systems, where nanoparticles are ablated, we are able to desorb intact nanoparticles and count them in the single-particle mode using inductively coupled plasma mass spectrometry. The method is demonstrated on monitoring proliferating cells in 3D aggregates of human colorectal carcinoma cells. Precise counting of the tags in each pixel generates sharp distribution maps of a proliferation biomarker in the tissue. A mass spectrometer detects up to 83% nanoparticles of a selected element with a single particle detection limit. Advantageously, the desorption of nanoparticles from regions outside the tissue is strongly suppressed.

Acknowledgment

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nanoparticles; imaging; single particle inductively coupled plasma mass spectrometry; SP ICP MS; laser ablation

Multimodal bioimaging for the elemental and molecular investigation of liver cancer samples

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The presented study investigates the uptake of the metal-based pharmaceuticals cisplatin and gadoxetic acid in liver cancer samples by means of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). The examined tissue sections originate from an animal study, where rats with liver tumors were treated with the gadolinium-based MRI contrast agent gadoxetic acid together with Cisplatin as antitumor agent. Ten minutes after injection the livers were resected. As instrumental setup, a 213 nm LA system was hyphenated to a single quadrupole-ICP-MS using He as collision gas in kinetic energy discrimination mode. In addition to the elements Gd and Pt, the endogenous elements Fe, Cu and Zn were quantified and their concentrations within the tumor were compared with surrounding liver tissue. Region of interest (ROI) analysis reveals higher concentrations for all elements in the liver tissue with hotspots for Fe and Cu in connective tissues. Higher Gd concentrations in the liver fit the expected selective uptake of gadoxetic acid into liver cells as compared to tumor cells.

To gain complementary molecular tissue information, infrared (IR) laser imaging via quantum cascade laser (QCL) based microscopy was used to identify various tissue types. Especially blood vessels, liver lesions, tumor tissue and healthy liver regions are distinguished based on the amide C=O and ester C=O band representing variations in the lipid composition. Deeper structural information about pathological tissues is visualized by the detection of phospholipids acquired by means of matrix-assisted laser desorption/ionization-mass spectrometry (MALDI-MS). Therefore, 2,5-dihydroxybenzoic acid (DHB) was applied as matrix for positive ionisation mode to detect phosphatidylcholines (PC). Being part of cell membranes, the investigated PCs reveal the distribution of different cell types and the heterogeneity of the tumor itself. The combination of LA-ICP-MS with QCL-based IR microscopy and MALDI-MS as multimodal bioimaging shows a distinct isolation of tissue characteristics in the investigated liver cancer sample.

Multimodal Imaging

Correlative bioimaging of trace metals at micrometer and submicrometer scale by combining NanoSIMS, LA-ICPMS and µCT

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Correlative bioimaging of trace metals in cells and tissue shows a high potential for the investigation of the biochemical functions, biosorption and bioaccumulation processes of metals at cellular and subcellular level. Scientific progress in this field is directly related to new instrumental and methodological analytical developments and the combination of analytical techniques. Highest lateral resolution down to 50 nm can be achieved by Nanoscale secondary ion mass spectrometry (NanoSIMS). This technique relies on the sputtering of ions under high vacuum from a solid surface by focused positive or negative primary ion beams and the subsequent analysis of the produced secondary ions by a mass spectrometer. A recently developed radio frequency plasma oxygen primary ion source on our NanoSIMS provides high sensitivity and high spatial resolution for trace metal detection at cellular and subcellular level. For example, this novel ion source allowed for the first time mercury detection by NanoSIMS. Furthermore, we developed the combination of NanoSIMS with Laser Ablation ICPMS for correlative bioimaging of trace elements where NanoSIMS enables a nanoscale zoom of the same areas previously imaged by LA-ICPMS at microscale. In addition, X-ray computed micro tomography (µCT) completes the correlative imaging approach with a 3D image of the regions of interest.

This presentation introduces the NanoSIMS technique including the potential and applications of the novel O- primary ion source and discusses the approach for correlative imaging with LA-ICPMS and µCT. This will be illustrated by examples of our recent research: (i) method development for the first mercury analysis by NanoSIMS allowing the localization of HgSe particles in whale liver, and (ii) correlative bioimaging of Zn, Cu, and Mn in eggshells and laying hen tibia bones in the context of trace metal supplementation in animal nutrition research. Finally, challenges and limitations of this correlative bioimaging approach including sample preparation will be discussed.

Elemental bioimaging, NanoSIMS, LA-ICPMS, µCT, HgSe particles, trace metals

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Targeting structures on the micro- and nanoscale with hyphenated and single event ICP-MS

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ICP-MS has become the go-to method for the investigation of trace elements in complex biological and environmental systems. Recent technological and methodological advances have expanded the scope of ICP-MS and caused a paradigm shift for the investigation of micro- and nano-scaled structures. Especially facets like single particle (SP) and laser ablation (LA)-ICP-MS provide detailed and unique insights regarding individual nanomaterials as well as on the location of elements in highly compartmentalised microscopic structures, respectively.

In this work, we demonstrate novel approaches to trace and characterise individual nanomaterials designed for specific biomedical applications as well as nanopollutants in the environment using SP ICP-MS strategies. We will demonstrate new open-source software solutions for NP detection and signal calibration and additionally introduce the concept of large mass bandpass filters, which advance the characterisation of small and heterogenous nanostructures. Large bandpass mass filters are further useful for novel screening strategies to pinpoint particulate elements as well as to advance hyphenated ICP-MS. This has a high utility to study micro-scaled structures in complex biological environments. Using an immunohistochemistry approach for LA-ICP-MS, we will demonstrate the possibility to determine both endogenous elements as well as proteins in these microstructures.

SP ICP-MS, LA-ICP-MS, IHC, medicine, environment

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Assessing the behaviour of E171 and E551 food additives in confectionary products by means of bioaccesibility and bioavailability studies using spICP-MS, TEM and in vitro models.

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TiO_2 (E171) and SiO_2 (E551) are additives widely used as whitening and anti-caking agent in food industry. However, the EFSA's experts have re-evaluated their safety (1), concluding in 2021 that E171 was no longer safe (2). In addition, EFSA has published a guideline defining the criteria for assessing the presence of a small particle fraction mainly during the gastrointestinal process (3).

The main goal of this study was to evaluate the bioaccesibility and bioavailability of E171 and E551 in chocolate candies, powdered cocoa, sugar glass, and custard powder by using spICP-MS, TEM and in vitro models. The total content of Si and Ti was first determined by ICP-MS after acid mineralization. Si and Ti content was similar in all products except in chocolate candies which present the highest content of Ti and Si was not detected. The effect of extraction conditions on the size and morphology of the particles contained in the confectionary products was evaluated. Ultrapure water, Tris-HCl, lipase and pancreatin were tested as extractant agents under different extraction conditions (ultrasonic bath, ultrasonic probe, and manual stirring). The results obtained by TEM and spICP-MS revealed that the best extraction conditions were achieved by using ultrapure water and manual stirring. Under these conditions, the percentage of TiO_2 nanoparticles in all the products was lower than 30% except for sugar glass ((47 ± 2) %). In the case of SiO_2, the presence of particles between 250-500 nm was detected and this size range should be studied in gastrointestinal models, as indicated by EFSA guidance [3]. The bioaccesibility of TiO_2 and SiO_2 in the selected products was achieved after an in vitro gastrointestinal human digestion assay. The results showed that the bioaccessible fraction was matrix and particle type dependent. Cytotoxicity assays were performed with the intestinal fractions using Caco-2 cells and significant differences in the cell viability after 4 and 24 h of incubation were observed. Finally, preliminary bioavailability studies using the same cell line were also carried out to investigate the uptake, metabolism, and trans-epithelial transport of TiO_2 and SiO_2 particles found in these products.

E171, E551, spICP-MS, confectionary products, bioaccesibility, bioavailability

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Exploring single cell ICP-ToFMS for multiplexing protein determination in ARPE-19 cells using metal nanoclusters

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The heterogeneous nature of cell populations implies that cells of the same line, under the same conditions and external stimuli, may differ in the level of their metals and biomolecules expression. Considering this issue, the correct interpretation for the expression of target analytes (e.g., metals or biomolecules) in cell populations can be difficult to assess unless samples are analysed on a quantitative cell-to-cell basis. Therefore, the development of analytical techniques that allow the determination of elements and biomolecules in individual cells is nowadays crucial for the comprehensive study of biological systems.Single cell (sc) ICP-MS has been proposed for analysis of elements in individual cells. Furthermore, metal-tagged antibodies have been successfully used for the specific determination of proteins in cell cultures employing sc-ICP-MS (1, 2). Up to date, instruments equipped with sequential quadrupole mass analysers are frequently employed for sc-ICP-MS analysis, however multiplexed analysis is not possible with this instrumentation. The use of an ICP-ToFMS allows the simultaneous determination of proteins within individual cells by tagging each protein of interest with a different metal-tagged antibody. In this work, metal nanoclusters (MNCs; AuNCs, PtNCs and IrNCs) are employed as elemental labels for the simultaneous determination of three cytosolic proteins in individual retinal pigment epithelial cells (ARPE-19) by sc-ICP-ToFMS (microFAST single cell system coupled to ICP-ToFMS). The expression of proteins related to neurodegenerative diseases are explored in ARPE-19 cells under control and pro-oxidative stress conditions. The proposed methodology involves an immunocytochemistry protocol to label the target proteins with AuNCs, PtNCs or IrNCs. The huge amplification of the MNCs tagged antibodies, which have hundreds of detectable metal atoms per label, allows to overcome the potential loss of sensitivity of the ToF analyser compared to the quadrupole.

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Single cell, Multiplexing, ICP-TOFMS, Metal-tagged antibodies, Nanoclusters

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Oral Nanomaterials 8

Analysis of PTFE microparticles by ICP-Qms operated insingle-particle mode

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During the last decades, environmental contamination with plastics has become a major cause of concern. One of the significant classes of microplastics is fluoropolymers, which are widely used in various consumer products, and draw increasing attention due to the potential contribution to the widespread of perfluoroalkyl substances, PFAS, an emerging class of refractory organic contaminants. Although several studies regarding the environmental and health impact of fluoropolymers have been reported,there is a need for high throughput analytical means for studying the size distribution and concentration of fluoro-microparticles. In the present study, we propose to apply fluorine SP-ICP-MS analysis for the detection of fluorinated microparticles. Our analytical method is based on the earlier proposed approach for fluorine detection by ICP-MS through the formation of BaF+ ions (m/z 157). NexION 2000 ICP-qMS has been used for the method development. To reduce the level of interfering ions at m/z 157, reaction cell mode with O2 was applied.Since the introduction of only barium solution into the plasma results in a relatively high background signal at m/z 157, originating from polyatomic ions (138Ba18O1H+, 138Ba16O1H3+, and 138Ba17O2H+), optimization of the instrumental parameters to achieve maximal sensitivity for F analysis was performed. To this end, the intensity of the signal at m/z 157 with and without introducing F has been examined under different operating parameters: torch position, nebulizer gas flow, RF power, axillary gas flow, and O2 flow and RPq in dynamic reaction cell were optimized for maximal signal-to-background ratio for 138Ba19F+. Using microseconds dwell time the single-particle BaF+ spikes with signal intensities significantly higher than the background were detected in the samples containing PTFE microparticles. Under the applied operating parameters, PTFE particles larger than 0.93 μm can be detected. The limit of detection of 8.5 x 105 particles L-1 was achieved for an acquisition time of 100 seconds. The most frequent particle diameter of 1.2 ± 0.1 μm determined by SP-ICP-MS analysis is consistent with the average diameter of 1.2 ± 0.2 μm, detected by DLS.

PTFE, microparticles, Single-Particle-ICP-MS, Fluorine analysis

Critical evaluation of key parameters for the platinum nanoparticles characterization in complex matrices by SP-ICP-MS

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The use of metallic nanoparticles such as those of platinum (PtNPs) has exponentially grown in recent years, especially in the biomedical or technological fields. Their widespread application can produce adverse and unknown effects on the human health and the environment. Therefore, a complete characterization of PtNPs in relevant environmental and biological matrices is crucial to understand their associated risks. In this sense, techniques capable of providing full information about their mass and number concentration, size distribution and composition are required.

Lately, single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has emerged as one of the most powerful options for a sound detection, identification, and quantification of NPs. Its great potential as a NP sizing and counting technique has already been proved but this approach is based on several assumptions that must be considered. Reliable data will be obtained if multiple or incomplete events are minimized within the analysis. Also, signal overlapping must be avoided to achieve an adequate discrimination between NP events and background. Thus, the conditions influencing the performance of SP-ICP-MS, mainly related to data acquisition and processing, should be carefully addressed (1).

This work is devoted to the development and critical evaluation of an analytical methodology based on SP-ICP-MS for the correct characterization and quantification of PtNPs in terms of size distribution, and mass- and number-based particle concentrations in relevant environmental (waters and road dust) and biological (cell culture media) samples. To that end, key acquisition parameters such as dwell time, data points, dilution effect, and the method for the transport efficiency calculation have been thoroughly optimized. Various data treatment approaches have also been evaluated to achieve an appropriate discrimination between dissolved and particulate Pt. Nevertheless, our results highlight the need for the rigorous optimization and harmonization of those critical parameters in SP-ICP-MS for a reliable study of PtNPs in complex matrices.

Platinum nanoparticles, ionic platinum, single particle ICP-MS, complex matrices

Resano et al. Chem. Sci. 2022 13(16) 4436 – 4473.

SP-ICP MS analysis of selenium nanoparticles in yeast - the effect of the extraction procedure on the particle size distribution

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Se nanoparticles (NP) are the potential Se supplement in human and livestock nutrition, a chemotherapeutic agent in cancer treatment, and have antibacterial properties [1]. In addition to the physical and chemical methods of Se-NPs synthesis, biosynthesis with the use of bacteria, fungi and yeast is considered “green” and is recently widely researched [1].In this context, reliable methods of Se-NPs analysis are of the utmost importance. Single particle inductively coupled plasma mass spectrometry (SP-ICPMS) is an established technique for the detection, characterization and quantification of nanoparticles. However, the analysis of solid samples by SP-ICPMS requires their solubilization. When working with NPs embedded in complex matrices, the extraction may influence some of the characteristics of NPs (e.g. size, aggregation), so this is a crucial step in the analytical procedure and should be evaluated for a specific sample and NP type. The aim of the presented study was to investigate the influence of the extraction on the size distribution and concentration of Se-NPs by performing several extraction methods to release Se-NPs from yeast. Baking yeast (Saccharomyces cerevisiae) was cultivated in selenite amended medium. As a result of the yeast detoxification mechanism, selenite ions were reduced to elemental Se forming solid particles which could be observed on macroscopic scale as a change in color to red hue. Several procedures from the literature [2,3], and also newly developed, to extract Se-NPs from the yeast matrix were tested. They included enzymatic (laminarinase, xylanase, cellulase, protease) and chemical (SDS, NaOH, TMAH) digestion and mechanical (shaking with various beads, sonication) cell disruption. The extracts were analyzed by SP-ICPMS, resulting in the quantitative information on the number and mass concentration, and size distribution of Se-NPs. The results showed that the selected extraction approach influences the observed Se-NP size distribution, median size, concentration of NPs and the ionic fraction of Se. In general, enzymatic extractions resulted in broader size distributions and larger medians compared to the other procedures. To check whether the Se-NPs are dissolved or altered during extraction, a Se-NPs reference material was subjected to the same extraction procedures. The outcome was similar as for the selenized yeast: broadening of the size distributions of Se-NPs after the enzymatic digestion, thus suggesting that the enzymatic methods may generate new Se-NPs or modify the ones already present in the sample.

selenium, nanomaterials, nanoparticles, SP-ICPMS, extraction, yeast, Saccharomyces cerevisiae

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New Horizons lecture

European Rising Star Award for Plasma Spectrochemistry

Pushing the limits of elemental mapping via laser ablation – ICP-mass spectrometry with a nanosecond 193 nm kHz laser

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Since the introduction of low-dispersion ablation cells and rapid aerosol transport systems, 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 during transport maximizes the temporal analyte concentration spike in the ICP, which creates an enhancement of the signal-to-noise (S/N) ratios and thus, an improvement in sensitivity and limits of detection (LODs). Recent efforts at the A&MS research group of Ghent University were aimed at boosting the analytical figures of merit of our LA-ICP-MS setup and resulted in the development of the Aerosol Rapid Introduction System (ARIS) and a low-dispersion tube-type ablation cell, which meanwhile has been integrated in the state-of-the-art Cobalt ablation chamber of the Iridia LA-unit (Teledyne Photon Machines).[1-3] Under optimal conditions, single pulse response profiles of approximately 1 ms duration (FW0.01M, full peak width at 1% of the maximum peak height) can be achieved with this LA-setup coupled to a fast-scanning ICP-mass spectrometer, which is approaching the peak profiles typically obtained in single-event ICP-MS for metallic nanoparticles, biological cells and microplastics.[1] This paves the way to kHz pixel acquisition rates for elemental mapping. In a recent work, the analytical performance of the setup was evaluated using a nanosecond 193 nm ArF* excimer-based laser capable of firing laser pulses at a laser repetition rate of up to 1 kHz. A highly linear response based on the integrated signal intensity was achieved across a wide range of laser repetition rates (10-1,000 Hz) upon ablation of a NIST SRM 610 glass and it was demonstrated that ionization efficiency losses did not occur at higher laser repetition rates.[1] The capabilities of the setup will be illustrated via the results of high-resolution elemental mapping applications in interdisciplinary contexts such as revealing the quantitative distribution of elements across polished thick sections of Antarctic H chondrite meteorites.

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Some recent advances in LA-ICP-MS at the beginning of the image century

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Over the years, laser-ICP-MS ablation has become an essential technique for the analysis of solids in laboratories. The reason for this success is relatively simple. It is based primarily on the direct micro-sampling capabilities of the lasers used, whose nanosecond or femtosecond pulse technologies are now very mature, and on the remarkable detection capabilities of ICPMS technologies (quad, triple quad sector field, Time of Flight, multicollector) that allow to meet many analytical needs in vast fields of application, ranging from geosciences to archaeometry, biomedical, etc.

If laser-ICPMS ablation was for a long time considered as a technique with "some potential" but limited in terms of accuracy restricting its use, great advances in the understanding of ablation processes and particle formation mechanisms together with the advent of new generation of ablation cells with short washout time, have literally propelled this technique to the forefront of analysis. If implemented under the right conditions, this technique should now be considered as accurate and precise for solid analysis. These advances have also given rise to a fascinating new approach that atomic spectrometry could not escape in this early 21st century where communication is increasingly visual: atomic and isotopic imaging. After the "wow effect", imaging is now a strong trend to provide concrete answer in many cases.

We will illustrate these remarks through several examples of applications developed in our laboratory. The use of isotopic imaging and in situ sampling methods for U/Th dating of biominerals to date archaeological sites previously occupied by hominids. We will also present applications in the context of rare diseases with new elements in the direct detection of bacteria, notably involved in Lyme disease.

Single cell metallomics

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Metals play a pivotal role in the molecular machinery of life. In fact, bio(re)active metal species exhibit a wide range of biological functions and toxicities, which are concentration depended and interconnected through delicate balances among different metals and metal species. Up to date, many biochemical functions and potential biomedical applications remain largely unexplored. Nearly 20 years ago the term metallomics was coined emphasizing the need for integrating different fields of (bio)metal science. The terminology implies the capacity for omics type metal analysis with the aim of revealing quantity, structure and function of metals in the context of biological systems. Thus, at its core metallomics is a challenging analytical exercise and nowadays, a significant share of research relating to this omics discipline is still technology driven.

In this lecture, recent key developments of the elemental method portfolio will be discussed, showing customized solutions for different tasks, engaging in high throughput multielemental- and speciation analysis. A major emphasis will be on single cell metallomics. We will showcase the power and limitation of these methods for unraveling biological function of metals when applying to advanced in -vitro and in vivo models. We will cover toxicity studies on nanoparticles and preclinical studies on metal based anticancer drugs.

Multimodal imaging to study the uptake of nanoparticles and their biological effects in tissues

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While nanoparticles continue to expand their range of applications in the materials sciences, health sciences and in many other areas of research and industrial applications, there is increasing concern about their uptake, distribution and possible health effects in the body.

Inductively coupled plasma-mass spectrometry (ICP-MS) in combination with dedicated sample introduction systems is one of the most powerful methods to study nanoparticles in tissues. In our current work, we focus on using laser ablation(LA)-ICP-MS imaging to investigate the distribution of elemental constituents of the nanoparticles as well as endogenous elements in rat lung tissues and on their long-range transport to other organs after particle instillation. Quantification is performed by using gelatine-based matrix-matched internal standards. Total elemental imaging as well as single particle (sp)-based ICP-MS imaging provided valuable complementary information.

Due to the comparably large size of the organ slices, micro X-ray fluorescence (µXRF) is used to pre-screen the samples, giving rise to the observation of areas of higher concentration of the nanoparticles in the lung tissue. Additionally, for selected types of particles, including silica as well as cerium, aluminium and manganese oxides, µXRF revealed higher phosphorous concentrations in the areas of exposure with the nanoparticles, indicating a biological response. Infrared (IR) imaging based on a quantum cascade laser (QCL) indicated stronger ester absorbance bands, thus linking the effects observed in µXRF to elevated lipid concentrations.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) imaging analysis of lipids in the tissue samples confirmed that in tissues affected by the nanoparticles, various lipid classes are elevated, while others are depleted in comparison with healthy tissue, thus indicating fibrotic processes being initiated by the nanoparticles. Fibrosis in the lung tissues was subsequently confirmed by microscopic and immunohistochemical imaging.

In conclusion, it was shown that exposure to and biological effects of nanoparticles in rat lung tissues can be investigated successfully by LA-ICP-MS imaging and a series of complementary imaging techniques based on spectroscopy in different spectral regions as well as mass spectrometry.

LA-ICP-MS; multimodal imaging; nanoparticles; toxicology; lung tissues; µXRF; IR imaging; MALDI-MS imaging, immunohistochemistry

Time-dependent uptake of different arsenic species in Chlamydomonas reinhardtii

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Arsenic and its compounds are well-known pollutants, especially in surface waters. They are released into the environment from both natural and anthropogenic sources. Generally, arsenic species can be divided into two classes: organic and inorganic species. Inorganic species are assumed to be more toxic and have even been classified as carcinogens, yet adverse cell effects of both classes to mammalian as well as plant cells have been reported. It is therefore important to research the metabolism and bioavailability of arsenic species.

In recent years, single cell ICP-MS (sc-ICP-MS) was established as a tool to quantify elemental contents in cell populations on a per-cell level. Using this method, heterogeneous distributions of desired elemental contents in an entire cell population can be determined.

Prior to the experiments, employed gas flows were optimized for maximum transport efficiency of cells. Very low nebulizer flows of about 0.2 L/min proved to be most useful, leading to the assumption that shear forces are exerted on the suspension during nebulization. To combat cell losses in the process, fixation protocols were applied to different cell types. A flow cytometry method was developed to obtain accurate cell counts in each sample. Afterwards, the time-dependent uptake of both organic (arsenobetaine, dimethyl arsinic acid) and inorganic (arsenite, arsenate) species in the model organism Chlamydomonas reinhardtii (C. reinhardtii) was observed using sc-ICP-MS. The cells were incubated with the respective compounds. Arsenic distributions in each cell population were determined after varying incubation times and a statistical evaluation was performed. In comparison, the species showed different time dependencies in their uptake behaviour. Overall, arsenite was ingested most readily, while organic species proved to be least bioavailable.

Overall, sc-ICP-MS provides an easy-to-use, fast, and reliable tool to determine elemental distributions of ingested compounds in C. reinhardtii. Using this method, the bioavailability of metal-containing, toxicologically relevant compounds can be monitored.

single cell, single particle, ICP-MS, arsenic, toxicology, C. reinhardtii, environment

Determination of the endogenous metal contents in blood cells via single-cell tandem ICP-mass spectrometry (SC-ICP-MS/MS).

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Getting information on the extremely low contents of endogenous metals in individual cells is a novel and highly important area of research. Knowledge of the metal fingerprints of different cell types opens up the possibility of distinguishing between healthy and diseased cells, since the latter are expected to have abnormal metal metabolism.(1) ICP-mass spectrometry (ICP-MS) is one of the most powerful techniques for ultra-trace elemental analysis, but when operated in a traditional bulk approach, in which a digest of many cells is analyzed, only the average concentration is available.

Alternatively, single-cell inductively coupled plasma-mass spectrometry (SC-ICP-MS) provides information on the content(s) of the target element(s) in individual cells (e.g., average and median concentration, concentration distribution).(2) As such, SC-ICP-MS shows promising features for the early detection and treatment of various diseases as well as an evaluation of the efficacy of therapeutic treatment,(3) but this approach is still in a very early phase. A major issue hampering the application of the technique is the scarcity of reliable data on the metal contents in individual cells and the lack of appropriate validation.

In this work, the potential of SC-ICP-MS for evaluating changes in the homeostasis of blood cells will be presented. Special attention will be paid to QA/QC of the analytical protocol, including aspects such as calibration, internal standardization, matrix effects, repeatability/reproducibility, etc. The results of a biological consistency test and of serial dilution experiments were used to further assess the validity and relevance of the method developed. Finally, mass distribution results obtained for various endogenous elements (e.g., Ca, Cu, Fe, Mg, Mn, P, S, Sr and Zn) in red blood cells (RBCs) and peripheral blood mononuclear cells (PBMCs) will be used to demonstrate the potential of the method.

Single-cell inductively coupled plasma-mass spectrometry (SC-ICP-MS), Metallomics, Blood cells, QA/QC

Corte Rodríguez et. al., Anal. Chem., 2017, 89, 11491-11497

Galé et al., Int. J. Mol. Sci., 2021, 22, paper nr: 9468

Liu et al., Anal. Chim. Acta., 2021, 1177, paper nr: 338797

Characterization and fate of metal species at the soil-plant interface

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Metals are used in a large variety of different fields (medicine, agriculture, defense, new technologies), this massive use leads to a significant pollution of our environment (soil, rivers, oceans...).

Understanding the mechanisms of mobilisation, uptake and toxicity of these metals (Copper, Rare-Earth element...) considering the soil microorganisms, the soil/plant interface (rhizosphere) and the plants represents a major stake. The description of the involved metal species needs state-of-the-art analytical techniques based on hydrophilic interactions liquid chromatography (HILIC) coupled with mass spectrometry techniques (MS). These methods rely on the combination of elemental (inductively coupled plasma mass spectrometry – ICP-MS) and molecular (high-resolution electrospray mass spectrometry – HR-ESI-MS) mass spectrometric detection.

A large variety of metal complexes such as nicotianamine, organic acids for the plants and bacterial siderophores like pyoverdins and small peptide chains for the bacteria are involved in these mechanisms, complexing both toxic and essential metals.

The highlighting of these systems can allow the identification of the major ligands involved in metal management by plants and microorganisms in the soil-plant interface.

plant, soil, microorganisms, rare earth elements, copper, metallomics, metallophores

Single-cell and High-resolution Analysis Of Elements in Cell and Tissue Cultures Using LA-ICP-MS

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Nickel (Ni) and titanium (Ti) are most commonly used as joint replacements. In some cases, such as inflammation, bacterial infection or increased mechanical stress can cause these elements to be released and penetrate surrounding tissue or even accumulate in specific organs. Only a few methods can be used for the analysis of ultra concentrations of ions in animal fluids and tissue, but almost no one can also characterize the distribution of the ion. Even though laser ablation inductively coupled plasma spectrometry (LA-ICP-MS) is an analytical method for analyzing an inorganic sample, especially geological ones, today, it is being used more and more to determine the distribution of elements in different types of biological samples Bioimaging using LA-ICP-MS can be used to clarify questions of biomedical research such as bioaccumulation and bioavailability of elements in the tissues and provides insight into the basic chemical composition of living organisms. [1, 2,]

The main objective is to develop a method to determine the distribution of elements at the cellular level, which means a mapping with a resolution at the level of micrometers. From a chemical point of view, a high sensitivity method for the determination of selected elements (Ni, Ti) in tissues or even in individual cells will be developed and the behavior of these ions in the animal organism will be characterized.

Single-cell analysis, bioimaging, LA-ICP-MS, High-resolution analysis

Mikulewicz et al., Biological Trace Element Research, 142 (2011) 865-889

Doble et al., Chemical Reviews, 121 (2021) 11769-11822

Exploring the cycling of metals and metalloids in mushrooms with ICPMS-based methods

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Fungi are indispensable constituents of our environment and fulfill crucial roles as symbionts, decomposers, etc. Some macrofungal species are well known for their ability to accumulate certain elements in their fruit-bodies. For example, the violet crown cup Sarcosphaera coronaria can take up incredible amounts of arsenic, namely up to 9000 mg/kg dry mass, and we recently discovered that Thelephora penicillata can contain immense concentrations of cadmium, arsenic, copper and zinc in its fruit-bodies. The underlying reasons for this behavior are still obscure.

We employed various hyphenated ICPMS-based techniques, such as high performance liquid chromatography (HPLC) - ICPMS or laser ablation (LA) – ICPMS to gain a better insight into the biotransformation and translocation processes of selected elements in mushroom fruit-bodies. For example, biomapping with LA-ICPMS revealed that both mercury and selenium are concentrated in an often distinct and narrow layer on the peripheral tissues of porcini mushrooms (Boletus edulis and closely related species). Furthermore, a sensitive and robust HPLC-ICPMS method for vanadium speciation allowed us a detailed investigation of the unique vanadium-containing compound amavadin in the fly agaric mushroom (Amanita muscaria). Speciation analysis via HPLC-ICPMS is also the method of choice for determining the chemical forms of arsenic present in macrofungi. Especially in the case of edible mushrooms, this can be very helpful for consumers, since arsenic's toxicity mainly depends on its chemical form.

biogeochemical cycle, mushrooms, speciation analysis, biomapping, arsenic, vanadium, cadmium, mercury, selenium

Braeuer et. al., Anal. Bioanal. Chem. 2022; https://doi.org/10.1007/s00216-022-04240-y

Braeuer et. al.,. J. Anal. At. Spectrom. 2021; https://doi.org/10.1039/D0JA00518E

Braeuer et. al., Anal Chim Acta. 2019; https://doi.org/10.1016/j.aca.2019.04.004

Extreme isotope fractionation of cosmic dust during atmospheric passage

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Annually 40,000 tonnes of extraterrestrial material accumulate on the Earth, predominantly in the form of micrometeorites (e.g., [1]), particles 10 to 2000 μm in size. While a continuum likely exists between the precursor materials of micrometeorites and those of macroscopic meteorites, particular micrometeorites sample solar system reservoirs currently not represented in meteorite collections, demonstrating their importance. Upon entering the Earth's atmosphere, micrometeorites decelerate in a few seconds from velocities of km s-1 to cm s-1 [2]. Deceleration causes melting and evaporation by pulse heating, which effectively modify the original texture, chemical composition, and isotopic ratios of micrometeoroids [3]. Here, the potential of Fe isotope ratios to constrain the degree of modification during atmospheric passage is explored, in addition to routinely applied geochemical proxies, such as O isotope or Mg/Al ratios. While the ejection of Fe-Ni beads lowers the Fe content of a melted micrometeorite, this process does not significantly influence the Fe isotopic composition, as metal-silicate isotope fractionation at high temperature is limited. In contrast, evaporation during atmospheric passage lowers the Fe content of the precursor and shifts the Fe isotope ratios to heavier values following a mass-dependent relation [3]. Recent advances in multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) enable the analysis of micrometeorites at high precision, despite their small sizes. This can be achieved via pneumatic nebulization MC-ICP-MS, after sample digestion and chromatographic isolation, or alternatively via nano- or femtosecond laser ablation MC-ICP-MS, with a typical precision on the order of ~0.05 to 0.20‰ for δ56Fe (2SD). Various strategies have been developed to deal with instrument mass discrimination, relying on internal correction using Ni and/or sample standard bracketing (e.g., [4]). While the initial Fe isotopic ratios of chondrites, meteorites that did not experience melting or differentiation, display a relatively narrow range (0.005 ± 0.008‰ for δ56Fe, [3]), micrometeorites exhibit δ56Fe of up to ~40‰. As such, the measured Fe isotope ratios can be used to (1) trace the degree of mass-dependent isotope fractionation and volatilization to better constrain peak temperatures and duration, (2) correct the effects of evaporation on O isotope ratios, which are commonly used to link micrometeorites to their respective parent bodies, and (3) confirm the extraterrestrial nature of fossil micrometeorites, extracted from sedimentary rocks. Combined, these findings stress the value of isotopic tools to better constrain the source of extraterrestrial materials and their possible modification during transfer from parent body to planetary surface.

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Downhole fractionation of Rb from Sr during laser ablation ICP-MS/MS

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Recent advances in tandem mass spectrometry (ICP-MS/MS) have facilitated the inline separation of isobaric interferences using reaction cell chemistry. This enables the measurement of radiogenic isotopes in systems in which the parent and daughter products are isobaric (i.e., 87Rb decays to 87Sr, 176Lu to 176Hf), thereby drastically reducing sample preparation and analysis time. Here we separate 87Rb from 87Sr using SF6 as a reaction cell gas in the octopole reaction cell of an Agilent 8900. We measure 85Rb on-mass and calculate the corresponding 87Rb, and measure 86Sr and 87Sr mass-shifted as SrF (at masses 105 and 106, respectively) to determine the 87Sr/86Sr and 87Rb/86Sr ratios. This enables the determination of in situ isochron dates using the Rb/Sr system in geologic materials by laser ablation (LA) ICP-MS/MS. Use of the reaction cell also has the benefit of eliminating isobaric interferences on 87Sr from doubly charged rare earth elements (164Yb++, 164Er++), which is important for analysis of Sr isotope ratios in minerals that incorporate significant quantities of rare earth elements (i.e., apatite, feldspars).

High-Rb minerals such as micas and feldspars are some of the most common minerals in the Earth’s crust, and have traditionally been dated using Rb/Sr by conventional bulk analysis techniques. In situ measurement of these phases via laser ablation allows the textural context to be preserved during analysis, opening up a wealth of possibilities to examine the geochronologic history of a wider range of rock types and minerals than current accessible techniques (i.e., U/Pb in zircon and other phases). Here we investigate the effect of laser parameters (fluence, repetition rate, spot size) on the downhole fractionation of Rb from Sr in natural micas, nano powdered mica pressed powder pellets, and glass. We find that the downhole fractionation of mica glass is more similar to that of natural micas than the DHF of the mica nano powder pressed pellets.

downhole fractionation

Accurate measurements of the isotope ratios of Sr, Zr and Fe without isotope standards. Truth or fiction?

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Knowledge of the isotopic composition is important for the understanding of many physical and chemical processes occurring in nature. Subtle isotopic changes of stable isotopes are the result of the phenomenon of isotope fractionation, which is a division of different isotopes of a given element between coexisting phases.

The main problems in measuring isotope composition by multicollector mass spectrometry (MC-ICP-MS) is the necessity to correct for themass discrimination effect and effectively correct matrix effects, which may be eliminated byperfect sample cleaning.

Commonly used calibration methods that simultaneously correct the effect of mass discrimination and reduce the influence of the matrix components (Optimized Regression Model and Internal Standard) require a standard of known isotopic composition. These types of standards are expensive, have limited availability, and their use is limited by the MC-ICP-MS geometry. Moreover they are often not commercially available, or it is necessary to obtain a solution with a specific batch number, since only this solution has the characteristic isotopic composition.

We proposed the use of commercially available standards of monoisotope elements as calibrators in accurate isotope measurements by MC-ICP-MS. Our preliminary experiment were focused on well-defined isotopic systems for which standards with known absolute isotopic ratios (Sr, Zr, Rb) are available. We used a properly prepared mixture of yttrium and niobium as a calibrator in Optimized Regression Model (ORM) and in Internal Standard (IS) method . The trueness and precision of results obtained for Sr and Zr by ORM and IS were compared, thus proving the correctness of our approach. Then a mixture of cobalt and manganese was used as a standard to measure the iron isotope ratios in the model samples. Trueness and precision of the results obtained by IS-Standard-Sample Bracketing method and ORM-Standard-Sample Bracketing calibration were compared.Finally, we used the developed method to measure Fe isotope ratios of in historic gallium ink manuscripts.

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Multicollector ICP-MS, Accurate isotope ratio, iron, monoisotopic calibration.

The effect of roasting on boron isotope ratios in coffee beans: Implications for the determination of geographical origin of coffee

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High precision 11B/10B isotope ratio measurements have recently emerged as a promising tool for tracing geographical origin of plant-based food and beverages, including coffee. The lack of knowledge on how volatility of boric acid, a predominant chemical form of boron in plants, may affect the isotopic composition of boron in coffee beans during the process of roasting is a remaining challenge, complicating the analysis and interpretation of boron isotope data. In this work, the combination of δ11B values of green and roasted coffee beans provided by major coffee producers and experimental modelling enabled the study of the influence of roasting on the isotopic composition of boron in coffee beans. A small but consistent difference in δ11B values between green and roasted coffee from the same locations was observed, with the latter having lighter boron isotopic composition. Experimental data showed that the isotopic difference between green and roasted coffee can be attributed to boron isotope fractionation occurring during evaporation of capillary water from coffee beans at the early stage of roasting. The plausible mechanism accounting for this fractionation involves preferential partitioning of 11B isotopes into undissociated boric acid, B(OH)3, in aqueous media followed by volatilisation of B(OH)3. Importantly, however, bias towards lighter δ11B values induced by roasting was small relative to the wide range of δ11B values (≃53‰) observed for green coffee beans from different regions worldwide. This implies that 11B/10B isotope ratios in roasted coffee are a potential marker of regional differences in coffee origin.

isotope fingerprinting, MC-ICP-MS, provenance studies

Assessment of DGT sampling for tracing Sr and Pb isotope signatures in soil by MC-ICP-MS

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Radiogenic isotope signatures of Sr and Pb in soils are important tracers in the determination of e.g., food provenance, animal migration, and contamination sources and therefore widely applied in numerous fields of research spanning from environmental science to archaeology, ecology, and forensics. One common sampling strategy is to use equilibrium-based soil extraction methods to assess labile fractions of Sr and Pb available for biological uptake. Critically, these methods produce complex sample matrices which make subsequent sample preparation for isotope ratio analysis by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) resource- and time-consuming.

Diffusive gradients in thin films (DGT) provides an alternative sampling strategy for assessing labile Sr and Pb fractions in soil. DGT mimics diffusion-based element supply and uptake by biota such as plants and enables concomitant matrix separation and analyte preconcentration during sampling. Yet, simultaneous sampling of Sr and Pb by DGT in soil has proven especially challenging given the conditions of high ion competition with major matrix cations (Mg, K, Ca) and typically trace- to ultra-trace levels of Sr and Pb present in soil porewater. Here, a novel DGT method was evaluated under laboratory conditions for MC-ICP-MS-based assessments of Sr and Pb isotope ratios in soils and compared to equilibrium-based extraction methods when applied to natural soil samples. (1) Moreover, the transfer of Sr and Pb isotope signatures from different soil types (n = 5) to different plant species (n = 3) was studied in greenhouse experiments.

Results showed that DGT enables quantitative sampling of labile Sr and Pb under natural conditions (pH = 4.8-8.2; I(NaNO3) = 0.01-0.1 mol L-1; γ(Ca2+ = 50-160 mg L-1 in synthetic soil solution matrix), permitting the accurate assessment of isotopic variations without significant isotopic fractionation and with low uncertainty (uc,rel = 0.01-0.03 %). Isotope ratios determined by DGT showed excellent correlation with those measured in soil extracts ($R^2 \geq 0.99$) and plant tissues ($R^2 \geq 0.99$). Implications for environmental analysis and source tracing of Sr and Pb, along with future possibilities of DGT in isotope research will be discussed.

Diffusive gradients in thin films, Passive sampling, Isotope ratio analysis, Mass spectrometry

Wagner et al., Anal. Chem., 2022, 94 (16), 6338-6346

Investigation of the biogeochemical cycle of Pb, Hg and Cd from the 1990s up to the present at Terra Nova Bay (Antarctica) by isotopic analysis

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Antarctica plays an important role in the study of the Earth's climate system because of its great distance from the main sources of pollution. In fact, the atmosphere above it is the least affected by human activities and is therefore analysed to study natural atmospheric processes and to monitor the global impact of human activities on the environment. Heavy metals such as Pb, Hg and Cd, known to be toxic at low concentrations, can combine with fine particulate matter and be transported over long distances to Antarctica. Here, atmospheric precipitation contributes to the passage of airborne pollutants into the sea, disturbing natural biochemical processes. The main processes controlling the distribution of trace metals in the marine environment are related to inputs from natural and anthropogenic sources via the atmospheric and oceanic circulation, removal through deposition in sediments and accumulation in biota by biochemical pathways. In the context of the Italian National Program of Research in Antarctica, the levels of Pb, Hg and Cd in sediments and marine organisms sampled in the coastal waters of Terra Nova Bay (Ross Sea, Antarctica) and their bioaccumulation and biomagnification through the trophic network have been studied, but not completely elucidated1,2.

Therefore, recent work was aimed at measuring their isotopic signature in order to provide new insights into the origin of heavy metals and their transfer through the various environmental compartments and to highlight possible variations compared to the past. In particular, the investigation comprises representative marine organisms (the fish Trematomus bernacchii and the mollusc Adamussium colbecki), marine sediments and suspended marine particulate matter, surface snow and sea ice, collected at Terra Nova Bay in the 1990s and during the 2021-2022 campaigns. The isotopic analysis of Pb has been performed at the University of Genoa using a quadrupole-based ICP-MS, with the aim of also assessing the non-radiogenic isotope 204Pb. Subsequently, the isotopes of mercury and cadmium will be evaluated at the University of Ghent using a multi-collector ICP-MS for precise and reliable isotope ratio measurements at the ultra-trace level.

Lead, mercury, cadmium, isotopic analysis, ICP-MS, Antarctica.

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New Quantification strategies for short transient signals based on Microdroplet Generators

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Short transient signals with multi-elemental information are becoming more and more relevant in the field of ICP-MS analysis. In particular in the area of ICP-ToF-MS and quasi simultaneous detection of the entire periodic table as well as a plethora of different applications appropriate quantification strategies are highly needed. Especially in the field of imaging (LA/ICP-MS) as well as single particle/cell ICP-MS quantification is challenging. A promising tool in this regard is the application of a Microdroplet Generator (MDG) [1] on-line coupled with the respective sample introduction system.

In this oral presentation we will highlight our latest developments regarding an universal, reference material free quantification approach for (i) imaging as well as (ii) single particle ICP-ToF-MS. (i)A challenge in elemental imaging is the absence of appropriate and matrix-matched reference materials. Several strategies have been developed in the past already, but mostly reference materials are produced in-house and laborious to produce. Furthermore, comparability among different are hard to achieve. Our approach relies on the combination of a MDG on-line with LA/ICP-ToF-MS. By means of this approach micro-droplets (containing the aqueous standard) and sample aerosol upon ablation are introduced in parallel into the ICP-ToF-MS. This approach allows for matrix-independent multi-elemental and direct quantification of solid samples in the application area of elemental imaging. (ii)Single particle- as well as single cell-ICP-(ToF)-MS approaches are well established. However, quantification of elemental contents in single particles and cells is still challenging - in particular when high ionic matrix load is present as well.

We combined isotopic dilution (ID) with MDG-sp-ICP-ToF-MS for nanoparticle size-determination. By means of our approach, matrix independent size-determination of platinum nanoparticles was achieved and were in perfect agreement with TEM data. [2] In future studies, our on-line ID-MDG-sp-ICP-ToF-MS approach is also applicable for multi-elemental nanoparticles as well as single cell applications.[3]

ICP-ToF-MS, Microdroplet Generator, Laser Ablation, Calibration, single particle-ICP-MS

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Beta decay dating by LA-ICP-MS: from reaction chemistry to applications in geochronology

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Recent improvements in ICP-MS instrumentation where a reaction cell is sandwiched between two mass filters (called MS/MS) allowed opening the field of beta decay dating to laser ablation-based in-situ applications. Protocols have been developed and applied to most long-lived beta decay systems relevant on geologic timescales (^{40}K-^{40}Ca, ^{87}Rb-^{87}Sr, ^{176}Lu-^{176}Hf and ^{187}Re-^{187}Os). In this contribution I want to outline that it is a long way from discovering the principles of ion-molecule reactions essential for circumventing the corresponding isobaric interferences to setting up protocols that allow for obtaining accurate results on a long-term basis that are sufficiently precise to be relevant for better understanding geologic processes.

Arguably the currently best-studied beta-decay system utilized for in-situ dating studies is the ^{87}Rb-^{87}Sr system. From decades of research, e.g., Cheng et al. 2008 (1) it is well-known that several reaction gases (e.g., O_2, N_2O, SF_6, CH_3F) allow more or less complete separation of $^{87}Sr^+$ from $^{87}Rb^+$. Most laboratories have settled on N_2O because of its strong reactivity and ease of use. The biggest challenge for laser-based analysis is to find material that is well-characterized (ideally even homogeneous) in Rb/Sr ratios and Sr isotopes. Nano-nanoparticulate pressed powder tablets as from the CPRG standard Mica-Mg fulfill best such characteristics (2). However, accurate results can only be achieved if further materials exist where Rb-Sr ages for are known to better than 2% (3). Testing the scale of “matrix-effects” requires several examples of the growing list of datable minerals by Rb-Sr, for example biotite, muscovite, K-feldspar and beryl. This level of method development can be contrasted with the last long-lived beta-decay system potentially relevant for geochronology where no analytical protocols currently exist, the ^{138}La-^{138}Ba system. This system is potentially highly relevant as it could allow dating REE-mineral deposits. However, severe obstacles exist. Here I will show how some of them can be circumvented and how the way forward can be envisioned.

geochronology, LA-ICP-MS/MS, in-situ beta decay systems, ion-molecule reactions

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Rösel, Zack, GGR, 2022, 46, 143-168

Heritage lecture

Fifty years of pioneering human exposomics with a little help from plasma spectrochemistry

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Exposomics is the study of the exposome and relies on internal and external assessment methods. The exposome can be defined as the exposures of an individual in a lifetime and how those exposures relate to health. Internal exposures depend on different fields of study for instance; genomics, metabonomics, lipidomics, transcriptomics and proteomics. Use of biomarkers are commonalities in these fields for measurement of e.g. exposure, effect and susceptibility. Assessment of external exposures relies on measuring environmental stressors e.g. airborne contaminants present as gases, vapours or particulate matter. Although major advances in both chemical identification and quantitative analysis have been achieved today, exposure assessment and exposure characterisation remain the weakest part in environmental and occupational exposure risk assessments. Several determinants of toxicity are of importance for potential adverse health effects caused by air contaminants. Thus, the major life-long aims of our environmental exposome studies have been to characterize airborne particulate matter with respect to mass and number concentrations, particle mass size distributions, morphology, solubility, bio-accessibility, surface characteristics, hygroscopicity as well as frequency and intensity of exposure. In many situations biological measures of exposure that determine an internal dose are often preferred because they are more relevant to the health outcome studied. Traditional biological measurements of defined biomarkers, also named targeted analyses, measure a target element, metabolite or reaction product in body fluids have become a key part of exposure assessment. However, over the course of recent years of analytical developments, ICP-OES and ICP-MS has offered additional important untargeted information, especially in elemental exposome-wide association studies.

The aim of this presentation is to illustrate how analytical technology in combination can provide detailed information of the characteristics of the exposome in a variety of environmental settings. Special attention will be given to elemental metrology, aerosol sampling requirements, individual particle characterization, elemental speciation, targeted and untargeted measurements of biological samples relevant in exposomics studies in metal producing industries, welding operations, additive metal manufacturing and in Arctic indigenous populations. In this context, it is important to emphasize that understanding and characterization of the exposome depends also on assistance from other scientific disciplines and colleagues. This will be demonstrated by unique examples where e.g. electron microscopy, HPLC-ICP-MS, LA-ICP-MS and modelling have been applied.

European Award for Plasma Spectrochemistry

A Journey of Continued Contributions to Plasma Spectrochemistry: Focus on Metrology at the Nanoscale

Heidi Goenaga Infante [1]

[1]LGC National Measurement Laboratory, Queens Road, Teddington, Middlesex TW11 0LY, United Kingdom

To mark our success with the 2023 European Plasma Award, the first part of this lecture will highlight some key contributions of my research group to analytical advances in the plasma spectrochemistry area over the past few years. This will feature advances in novel fractionation analysis techniques in the areas of elemental speciation, metallomics and nanomaterials characterisation. In particular, reducing the uncertainty and improving the sensitivity of speciation measurements from small to large molecules like metalloproteins, pushing the boundaries of analytical technology to enable multi-element species quantification and their characterisation in very small samples and developing high accuracy measurements for nanomaterial quantification in complex samples using complementary hyphenated ICP-MS approaches.

Examples of contributions to emerging measurement opportunities and challenges associated with clinical applications in the plasma spectrochemistry field, where developments are fast moving will include (i) novel automated standard preparation and calibration strategies for quantitative multi-elemental imaging of tissue relevant to critical and rare diseases and (ii) traceable quantification of protein biomarkers of metal metabolism disorders enabling diagnosis and guiding therapeutics.

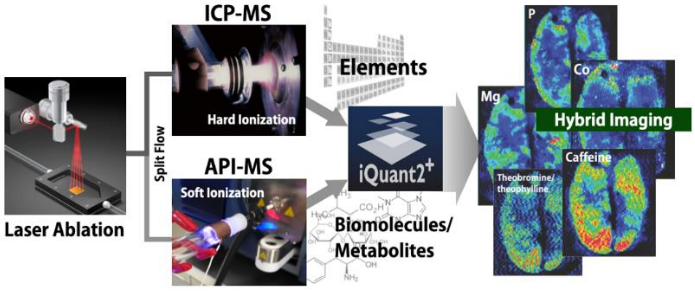
Finally, the last few minutes of the lecture will focus on the development of metrology workflows and multi-technique platforms for the accurate determination of number concentration of colloidal nanoparticles. The learning experience from collaborative international comparison studies for assessment of methods and materials will be discussed. Moreover, advances towards the characterisation of reference materials for number concentration of nanoparticles (including mixtures) in suspension will be highlighted.

Simultaneous Imaging of Elements and Biomolecules by ICP-MS and Atmospheric Pressure Ion Source-MS

Takafumi Hirata[1], Hui Hsin Khoo[1], Menghao Yang[1]

[1]Geochemical Research Center, The University of Tokyo, Tokyo, Japan

The understanding of metallomics on the level of single cells is an ultimate goal in the development of the field. The laser ablation sampling technique combined to ICP-MS is a sensitive and quantitative analytical tool for elemental mapping of biological tissue samples. The argon plasma used in the ICP is so powerful that that no species information on the introduced molecules remains, which is a major problem in environmental and biochemical research. To overcome this, we are trying to develop a new ion source to couple with LA for organic mass spectrometry, aiming for simultaneous imaging analysis of metals and biomolecules from a single sample (i.e., hybrid imaging analysis). The most significant advantage of the hybrid imaging analysis is that information concerning possible functional linkage between metal ions and biomolecules can be derived. Ultimately, we hope to apply the technique to derive clues in designing molecules in DDS (drug delivery system) studies.For elemental analysis, "hard ionisation" using ICP ion sources is required to improve quantification, whereas for biomolecular imaging analysis, "soft ionisation" is required to reduce fragmentation of the biomolecules. Our newly developed atmospheric pressure ion (API) source based on a dielectric barrier discharge utilising Ar gas, ionises biomolecules such as amino acids, sugars and peptides emitted from the sample aerosol produced by the LA method. The ion source based on the barrier discharge has several unique features such as (i) being an atmospheric pressure ion source, leading to the ion source to be acceptable of dry aerosols produced through the laser ablation, (ii) has high excitation temperature, and (iii) low kinetic temperature, obviating the risk of decomposition of organic compounds. Through our preliminary results, we found that the [M–H+] base peak (the strongest ion signal) was obtained from most of the amino acids and vitamins, indicating that the molecules could be ionised with minimum destruction (fragmentation).(1) The API source developed here is also powerful enough to ionise the biomolecules in sample aerosols generated by the laser ablation technique, and thus, the simultaneous imaging analysis of elements and biomolecules can be made from the identical ablation pits through a split-flow technique into the respective ICP and API sources. In this presentation, basic principles of the technique and several applications of the hybrid-imaging analysis will be demonstrated.



ICP-MS, API-MS, Laser Ablation, Hybrid Imaging, Dielectric Barrier Discharge

Khoo et al., Metallom. Res., 2022, 1, 44-54.

JAAS Emerging Investigator award

Defining the Limits of Nanoparticle and Microparticle Classification for spICP-TOFMS Analyses

Alexander Gundlach-Graham[1], Sarah Szakas[1], Hark Karkee[1], and Raven Buckman[1]

[1] Department of Chemistry, Iowa State University, Ames, IA, USA

Single-particle inductively plasma time-of-flight mass spectrometry (spICP-TOFMS) is used to analyze mixtures of nano- and micro-particles from a wide range of environmental sample types. With spICP-TOFMS, researchers aim to classify anthropogenic particle fractions based on multi-element signatures and to record the particle-mass (i.e. size) distributions and number concentrations of diverse particle types. However, the accuracy of these measurements requires an understanding of the fundamental structure of spICP-TOFMS data and the development of consistent approaches to detect, classify, and quantify particles in natural samples.

In this presentation, I will discuss the limitations of the spICP-TOFMS for the classification of diverse multi-element and single-element anthropogenic and natural particle types. I will discuss how the measurement process in spICP-TOFMS produces fractionated apparent particle compositions, even for pristine particle samples with conserved elemental ratios. I will explore how this fractionation can be modeled with Monte Carlo simulations and understood based on Poisson statistics. To accurately classify single-element and multi-element NPs, one must account for the variance introduced by the measurement process itself. Only after accounting for measurement variance, can distinguishing characteristics, such as element composition or element ratio, be used to label individual particles. In this presentation, I will discuss the use of particle-type detection limits for the classification of particles with the same major elements.(1) In addition, I will discuss the application of machine learning and hierarchical clustering analysis (2) approaches for the identification and classification of particles with heterogeneous elemental compositions. I will discuss the results from two case studies that involve the analysis of cerium-rich and titanium-rich anthropogenic and natural particles. Through the lens of these studies, I will examine the current state of the art of spICP-TOFMS as a tool to classify and quantify diverse nanoparticle types.

nanoparticles, single-particle ICP-TOFMS, Poisson noise, detection limits

Szakas, et al. Environ. Sci.: Nano, 2022, 9, 1627-1638

Mehrabi et.al., Environ. Sci.: Nano, 2019, 6, 3349-3358

The use of ICP-MS/MS to overcome interferences for the determination of technology critical elements relevant to the urban mine and recycling industry

John Entwisle[1], Christian Ward-Deitrich[1], Stanislav Strekopytov[1], Ahmad Abukashabeh[1], Sarah Hill[1], Heidi Goenaga-Infante[1]

[1]LGC National Measurement Laboratory, UK, Teddington, United Kingdom

Printed circuit board (PCB) and autocatalyst waste streams hold highly valuable elements which are critical for modern technology. It is important to accurately quantify these elements in end-of-life electronic and automotive products to determine the correct recycling process and financial viability of the bulk waste. This directly supports the EU Circular Economy Agenda and the United Nation Agenda for Sustainable Development Goals (SDG), Responsible Consumption and Production, SDG Indicator 12.5.1, Recycling rates. Accurate analytical methods with small uncertainties, together with appropriate matrix matched certified reference materials (CRM), are required for reliable quantitation of these elements in these challenging complex matrices.

The National Measurement Laboratory (NML) at LGC is producing an automobile catalyst CRM, certified for Pd, Pt and Rh. This presentation will show the first use of ICP-MS/MS reaction cell gas technology for the simultaneous accurate determination of these elements in a complex real-world sample. The autocatalyst contains elements such as Zr and Hf at the percent level, causing significant interferences on Pd and Pt due to oxide ions ZrO+ and HfO+. Isotope dilution (ID) calibration was applied for Pd and Pt whilst exact single matching approach was utilised for the monoisotopic element Rh, delivering SI traceable quantification with low uncertainty. Novel efforts made to improve the precision of measured isotopic ratios (the largest contributing factor to the combined measurement uncertainty) will be discussed. The same autocatalyst material was used as the sample in the international interlaboratory comparison study CCQM K160 with results from participating national metrology and designated institutes agreeing well with consensus value.

The developments have been extended to the European Metrology Programme for Innovation and Research (EMPIR) MetroCycleEU project where the NML is tasked with developing SI traceable methodology for these elements, together with Au, to evaluate a candidate CRM for PCB waste. Details of reaction gases used to overcome interferences for this challenging complex matrix, for example, ^{206}Pb++ interference on ^{103}Rh, will be discussed. Extraction and digestion challenges will also be discussed together with observations and insights for future improvements.

E-waste, CRM, PCB, autocatalyst, Platinum, Rhodium, Palladium ICP-MS

Validation of a method for determination of nanoparticles in mussels using single particle inductively coupled plasma mass spectrometry

Are Bruvold[1,2], Stig Valdersnes[1,2], Katrin Löschner[3], Andre Marcel Bienfait[3]

[1]Norwegian Institute Of Marine Research, Bergen, Norway, [2]University of Bergen, Bergen, Norway, [3]National Food Institute, Copenhagen, Denmark

Nanoparticles (NPs) have properties that may differ from their dissolved constituent elements or larger bulk counterparts and thus may have different functions, bioavailabilities and toxicities.Establishing NP concentration levels are of importance both for the risk assessment of NPs of anthropogenic origin and as a variable to study biogeochemical processes in the environment. Single particle inductively coupled plasma−mass spectrometry is capable of quantitative determination of mass and number concentration of inorganic nanoparticles at environmentally relevant concentrations. However, few standardized or validated methods exist making it difficult to ascertain the metrological quality of the available data. The current work aimed to establish and validate a generic method for the determination of NPs of different elements in mussels as a proxy for seafood. To this end, a new low-cost and robust protease mixture was utilized for sample digestion, and open source data processing was used for transparency, reproducibility and to establish a detection limits on a statistical basis using false positive and false negative probabilities. Performance characteristics were determined following EURACHEM guidelines. We anticipate the method to be a starting point for a routine method for the determination of NPs in seafood.

SP-ICP-MS, seafood, marine environment, validation, nanoparticles

Are you using a reference material that is fit for purpose for method validation of ICP-MS measurements?

Thomas C. Meisel[1], Peter C. Webb[2], Alessandra Rachetti[1], Valentina Dietrich[1]

[1]Montanuniversität Leoben, Leoben, Austria, [2]The Open University, Milton Keynes, UK

Reference materials are important cornerstones of method development and quality assurance. Certified reference materials provide anchor points for measurement traceability chains. For spectroscopic measurements of more complex solid materials sample digestion is an essential part of the sample preparation procedure in order to get the material into solution. However, transforming elements from a solid state into an ionic species in aqueous solution also breaks the traceability chain. Hence utmost care must be taken to ensure that recovery of the analyte is complete. Matrix-matched reference materials can help to validate the sample digestion step.

For the study of isotope ratios, major and trace element mass fractions in geological materials, the vast quantity of RMs used in the literature are basalts (e.g., USGS BCR-2 and BHVO-2). The reason for the extensive use of basaltic RMs in validation is their ease of digestion and, as a consequence, the high reproducibility of the reference values. For example, basalts are often used for validating measurement procedures for rock materials that are difficult to fully digest, such as ultramafic rocks which can contain chromite, a refractory mineral of the spinel group. Hence, chromite-bearing peridotites should be used for validation purposes when peridotites are being measured.

Meisel et al. demonstrated that the matrix and the accessory mineral compositioncan behave very differently during acid digestion even with nominally the same minerals (1). A systematic study of natural grafitesamples, using microwave-assisted acid digestion at elevated pressure showed highly variable results. Obviously, the degree of crystallinity of the grafite is an important factor influencing for the extent of digestion. Here again a certified grafite reference material digests easily whereas a natural flake grafite resists acid attack. Thus, not only is matrix matching of the RM to the sample target according to rock type of importance for validating sample digestion procedures, but a detailed knowledge of the mineralogy, particularly of minerals that are difficult to digest (e.g., chromite, grafite or zircon) for both the reference material and the sample are of utmost importance to ensure complete recovery and optimum data quality.

Sample preparation, reference materials, acid digestion, method validation

Meisel et.al., Geostand Geoanal Res, 2022, 2, 223-243

Ultratrace determination of β-conglutin food allergen by means an aptamer assay based on ICP-MS detection

Daniel Torregrosa[1], Miriam Jauset-Rubio[2], RaquelSerrano[1], Marketa Svobodova[2], Guillermo Grindlay[1], Ciara K. O'Sullivan[2], Juan Mora[1]

[1]University Of Alicante, San Vicente del Raspeig, Spain, [2]University Rovira i Virgili, Tarragona, Spain

Lupin is a leguminous plant employed in food industry as a protein source alternative to milk and soy in breads, cookies, pasta, etc. (1) However, the increasing use of this ingredient is related to a rise in reported mild to severe allergic reactions, mainly due to the presence of the globulin proteins, particularly β-conglutin (2,3). Therefore, this protein has been designated as the Lup an 1 allergen by the International Union of Immunological Societies (IUIS) and lupine has been added to the list of substances requiring mandatory advisory labelling on foodstuffs sold in the European Union.

The goal of this work was to develop different competitive aptamer assays based on inductively coupled plasma mass spectrometry (ICP-MS) detection for ultra-trace β-conglutin determination in flour samples. To this end, two competitive aptamer assay schemes were developed using either thiolated aptamers conjugated with Au nanoparticle (AuNPs) or biotinylated aptamers with Streptavidin-AuNPs. The influence of both AuNPs size (i.e., 20/40 nm) and ICP-MS detection mode (i.e., conventional vs single particle) on aptamer assay figures of merit were evaluated for both approaches.

Irrespective of the aptamer assay scheme and ICP-MS detection mode, analytical figures of merit improved with AuNPs size due to the higher number of atoms per NPs affords higher signals. For the thiolated aptamer assay, it was observed that β-conglutin detection limits (LoD) improved 2-fold for the single particle mode with regard the conventional one. However, when operating the biotinylated aptamer assay, the latter mode provided better results (5-fold improvement). Under optimal conditions, the best β-conglutin LoD (2 pM) was provided by the biotinylated aptamer assays operating conventional ICP-MS detection and 40 nm AuNPs. These results suggest that, for competitive aptamer assays, conventional detection can be more advantageous than single particle. When compared to previous works, the proposed method significantly improves β-conglutin LoD (i.e., one/two order of magnitude). Different flour samples containing lupin were successfully analyzed by means this approach with accuracy and precision according to European Conformity guidelines for analytical methods of food contaminants.

β-conglutin, aptamer, nanoparticles, single particle, inductively coupled plasma mass spectrometry

Ballester et al., J. Food Sci., 1984, 49, 14-16

Lovik et al., Norsk Epidemiol., 2004, 14, 155-160

Villa et al., Comp. Rev. Food Sci. Food Saf., 2020, 19, 3886-3915

Sensitive determination of halogens in liquid samples using nebulization-assisted LIBS

Cristina Méndez-López[1], Luis Javier Fernández-Menéndez[1], Cristina González-Gago[1], Jorge Pisonero[1], Nerea Bordel[1]

[1]University Of Oviedo, Department of Physics, Oviedo, Spain

The high excitation threshold of halogens makes their determination through Laser-Induced Breakdown Spectroscopy a complicated task. Utilizing vacuum chambers to detect resonant lines in the VUV or noble gas atmospheres to enhance less-intense lines in the IR are common strategies to detect them through their atomic emission. However, the use of molecular emission resulting from the recombination of the halogen and an alkali-earth metal (Ca, Sr, Ba) is often a more convenient approach. In the absence of a suitable alkali-earth element, nebulization-based addition of the element has been carried out with great results for fluorine determination in solid samples [1].

A complementary approach is presented in this work, but in this case halogens (F, Cl) are determined in an aqueous sample that is continuously nebulized on an auxiliary solid target containing calcium. This methodology allows for fast, easy determination of halogens in liquid samples with ppm detection limits. The optimization of the experimental methodology, the proposed data treatment procedure and the results are presented in this work.

LIBS, nebulization, halogens, molecular emission, liquid samples

Álvarez-Llamas et.al., J. Anal. At. Spectrom., vol. 32, pp. 162-166, 2017.

Potential of LA-ICP-ToF-MS imaging to underpin absolute SERS quantitation in a cancer model

Aristea Anna Leventi[1,2], Kharmen Billimoria[2], Dorota Bartczak[2], Karen Faulds[1], Duncan Graham[1], Heidi Goenaga-Infante[2]

[1]University Of Strathclyde, Glasgow, United Kingdom, [2]LGC National Measurement Laboratory, Teddington, United Kingdom

The use of nanomaterials in the healthcare industry has been at the forefront of scientific research, with nanoparticles commonly adopted as drug delivery systems with improved tumour targeting capabilities. [1] Surface enhanced Raman scattering (SERS) has been widely explored for the detection of nanomaterials at a single-cell level, as it offers unique sensitivity and selectivity in a non-destructive manner. However, the capability of absolute quantitation by SERS remains a challenge due to the lack of well characterised standards available for calibration, a fact that hinders the clinical use of this technique. [2] Several techniques have been used for the investigation of nanoparticle (NP) distribution within biological samples with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) being recognised for providing the sensitivity, selectivity, degree of spatial resolution and quantitative character required for most biomedical applications. Due to the lack of certified reference materials available for quantitative LA-ICP-MS imaging, in-house calibration standards are commonly prepared. Conventional approaches include the manual preparation of gelatin droplets, films and cryo-sections although more recently, the automated production of calibration standards as micro-droplets of ionic solutions has been reported for the quantification of multiple elements, addressing some of the challenges associated with manual standard preparation. [3] This work discusses the development of a multi-modal platform involving particle counting and fast LA-ICP-ToF-MS imaging strategies for the characterisation of suitable SERS nanoprobes consisting of gold nanoparticles (AuNPs) and the SERS reporter 1,2-bis(4-pyridyl)ethylene (BPE). Calibration standards were prepared by printing of gelatin droplets spiked with the Au:BPE nanoprobes. NP spikes were preferred over ionic spikes since differences in aerosol transport have been observed when NPs are present (instead of ions) suggesting the need for NP-based materials as calibrants to achieve accurate quantitation data for real samples. Analysis of the calibration standards by LA-ICP-ToF-MS at a spatial resolution of 5 µm, demonstrated the homogeneous distribution of Au:BPE nanoparticles in the droplets . The standards were then analysed by SERS mapping and different data processing approaches were investigated. The resulting calibration model was based on the BPE signal, correlating the SERS response to the total Au concentration (R^2: 0.9029), demonstrating the potential for further use for SERS calibration.

LA-ICP-ToF-MS, calibration standards, SERS, quantitative imaging

Lan, Mol. Imaging 2022, 2022, 3507383.
Goodacre, TrAC Trends Anal. Chem. 2018, 102, 359–368.
Schweikert, Anal. Bioanal. Chem. 414 (2022) 485-495.

LIBS imaging of secondary uranium mineralization and associated mineralization in uranium ore

Karel Novotný[1], Ivo Krempl[1], Markéta Holá[1], Jan Dobeš[1], Vojtěch Wertich[2], Jaromír Leichmann[2], Viktor Kanický[1]

[1]Department of Chemistry, Faculty of Science, Masaryk University,, Brno, Czech Republic,
[2]Department of GeologicaSciences, Faculty of Science, Masaryk University

High sensitive elemental techniques for imaging elements distribution in minerals with microscopic-scale resolution have become more and more important in geological studies. Along with the routine EMPA and recently developed LA-ICP-MS methods, Laser-induced Breakdown Spectroscopy (LIBS) is increasingly being utilized. Contrary to the EMPA and LA-ICP-MS technique, a vacuum or additional excitation source is not needed; therefore, the instrumentation can be much simpler and cheaper. Moreover, the response is generally very fast, which is particularly crucial for fast elemental imaging.

In the Czech Republic, several important locations are connected with the mining of uranium ores. Massive development of mining started after World War II - due to the military and civilian demand for uranium. Nevertheless, after 1989 mitigation program for uranium mining started and the last uranium mine was closed in 2017.

Although uranium mining has been stopped, research on uranium ores and minerals from mining sites is still important. It is an essential part of basic geological and mineral exploration research (eg. study of rock alteration or associated mineralization) or study of environmental impact and mine remediation. Moreover study of mobility and transport mechanisms of uranium in the environment is crucial in searching for a locality for the spent nuclear fuel final repository and simulation based on the similarity between uranium ore and spent nuclear fuel is convenient.

From the point of view of the mobility of uranium in the environment, its increased solubility in water is critical. It is mainly related to oxidation processes affecting uranium minerals in hydrothermal deposits. Laser-induced breakdown spectroscopy (LIBS) was applied to create images revealing elements' distribution and possible migration in uranium ore samples from different locations. Obtained elemental images help to distinguish different phases and reveal secondary mineralization containing oxidation products. Additionally, the signal correlation of some elements (correlation between different emission lines) helps identify other associated minerals. Fast LIBS scanning made it possible to analyze the big sample area containing different mineral phases of uranium ore, including associated minerals.

Imaging, LIBS, uranium ore, secondary uranium mineralization, associated mineralization

Holá, et al., Spectrochimica Acta Part B 186, (2021) 106312

Multimodal imaging determined the presence of mercury in regions of the brain affected by Parkinson's disease.

David Bishop[1], Roger Pamphlett[2,3]

[1]University Of Technology Sydney, Ultimo, Australia, [2]The University of Sydney, Sydney, Australia, [3]Royal Prince Alfred Hospital, Sydney, Australia

Environmental toxicants are suspected to play a part in the pathogenesis of idiopathic Parkinson's disease (PD) and may underlie its increasing incidence. Mercury exposure in humans is common and is increasing due to accelerating levels of atmospheric mercury, and mercury damages cells via oxidative stress, cell membrane damage, and autoimmunity, mechanisms suspected in the pathogenesis of PD. We therefore used autometallography (AMG), immunohistochemistry, and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to compare the cellular distribution of mercury in the tissues of people with and without PD. AMG and immunohistochemistry determined that mercury was present in neurons affected by the disease, such as those in the substantia nigra, motor cortex, striatum, thalamus, and cerebellum. Mercury was seen in oligodendrocytes in white and grey matter, and often colocalised with Lewy bodies and neurites. The presence of AMG-detected mercury in PD was confirmed with LA-ICP-MS, which demonstrated other potentially toxic metals in the locus ceruleus and high iron levels in white matter. Mercury was found in similar proportions of the locus ceruleus of people with and without PD, however those without PD had no mercury present in the substantia nigra, striatum, or thalamus. The similar frequency of mercury in the locus ceruleus of people with and without PD suggests these two groups have had comparable previous mercury exposures, but that PD brains have a greater predisposition to take up circulating mercury. While this post mortem study does not provide a direct link between mercury and idiopathic PD, it adds to the body of evidence that metal toxicants such as mercury play a role in the disease.

LA-ICP-MS, Mercury, Parkinson's disease

Laser spectroscopy and laser spectrometry for elemental imaging of cancer tissues

Pavel Porizka[1], Hana Koprivova[1], Katerina Kiss[2], Jakub Buday[1], Lukas Brunnbauer[3], Milan Kaska[2], Andreas Limbeck[3], Jozef Kaiser[1] ,

[1]Brno University Of Technology, Brno, Czech Republic, [2]Charles University, Faculty of Medicine in Hradec Kralove, Hradec Kralove, Czech Republic, [3]Technical University of Vienna, Vienna, Austria

It has been shown that cancerous tissues change the chemical composition of cells [1]. These changes in elemental composition can be observed using Laser-Induced Breakdown Spectroscopy (LIBS) or Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), where imaging of biotic (e.g., C, P, Ca, Mg) and trace (e.g., Zn, Cu) elements provide information about the distribution of soft tissue elements and, consequently, the location of cancerous tissue.

This paper deals with a correlative study using LIBS and LA-ICP-MS in a sample of healthy human skin, four samples of malignant tumours (squamous cell carcinoma, malignant melanoma, basal cell carcinoma, and epithelioid angiosarcoma), and one sample of a benign tumour (pigmented nevus). Analysis was performed using both techniques for all these samples, and spatial distributions of selected elements were constructed. This work aims to show the potential of correlation of data obtained from both analytical methods, which could be used for the possible diagnosis of cancer as a complementary technique to classical histological examination.

LIBS, LA-ICP-MS, cancer

Kiss et.al., Journal of Analytical Atomic Spectrometry, 36, pp. 909-916 (2021)

Molecularly imprinted polymers and labelled antiobodies - tools for determination of proteins by LA-ICP-MS

Tomáš Vaculovič[1], Lívia Rigasová[1], Marcela Vlčnovská[2], Kristýna Zemánková[2], Kristýna Pavelicová[2], Viktor Kanický[1], Markéta Vaculovičová[2]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic,
[2]Department of Chemistry and Biochemistry, Faculty of Agrisciences Mendel University, Brno, Czech Republic

Determination of specific proteins is the key to the understanding of processes in the organism or development of diseases. Unfortunately, determination of heteroatoms as are P, S, Fe, Cu, Zn is insufficient for this purpose. Hence, the biorecognition tools for their determination by LA-ICP-MS are being developed. Two approaches are available: labelling of antibodiesand molecularly imprinted polymers1. Their development and utilization for biological samples in combination with LA-ICP-MS analysis will be presented.

biorecognition tools; proteins; LA-ICP-MS; molecularly imprinted polymers

Vaneckova et.al., Talanta 2019, 198, 224-229

imageBIO266 & imageGEO193

High-speed, high-resolution imaging

- Includes TwoVol3 & DCI2
- High-frequency laser source
  - Up to 1000 Hz
- Redesigned beam delivery system
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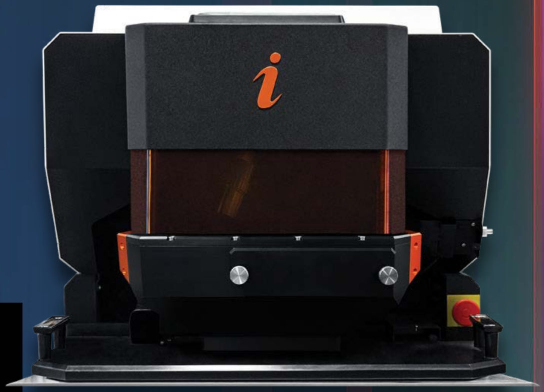
- Redesigned microscope system
  - Unmatched sample viewing



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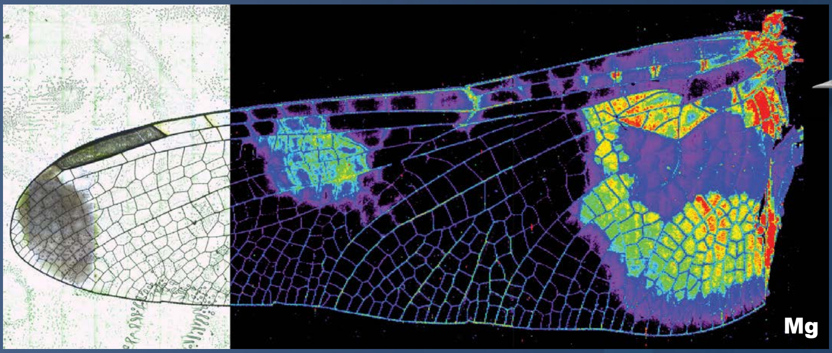


Dragonfly Wing

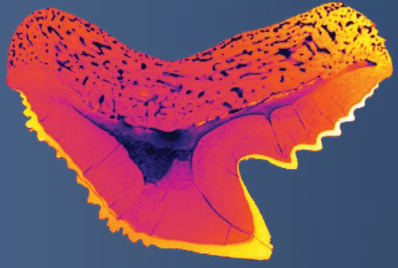
iolite
An Elemental Scientific Company

LIBS-ICPMS: Simultaneous LIBS & LA-ICP-MS

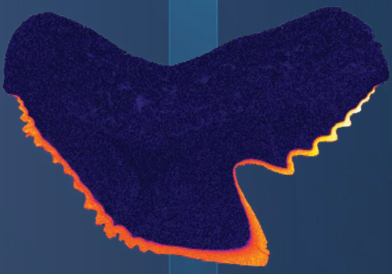
ESLumen

- Full elemental coverage for high-speed imaging
- Full spectra collection from 190-1100 nm
- Detection of difficult elements i.e., H, O and F
- Detection of every element on the periodic table

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



Ca422



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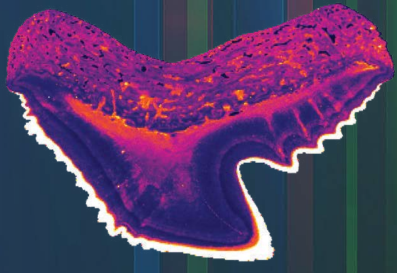


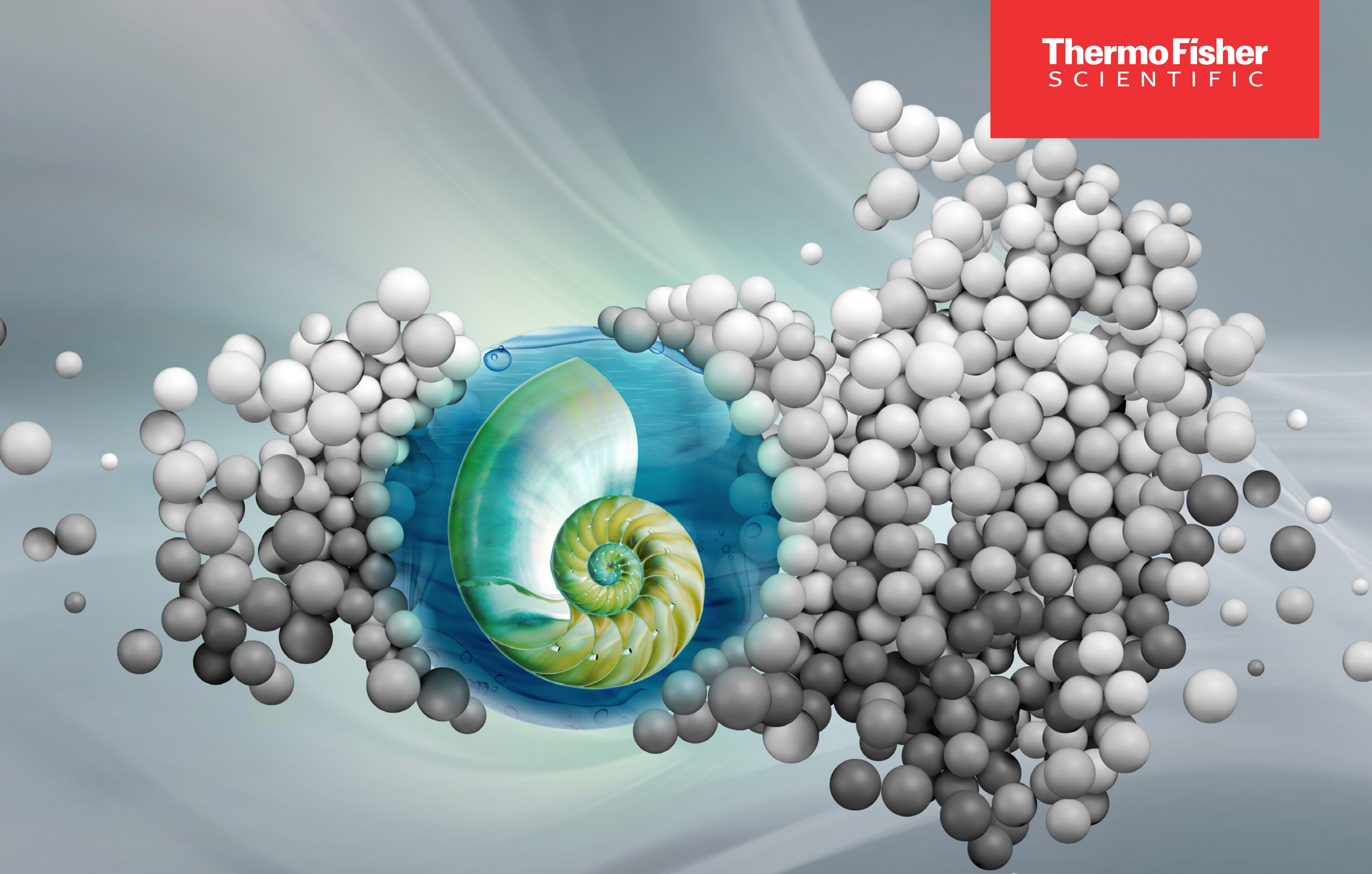
^{66}Zn

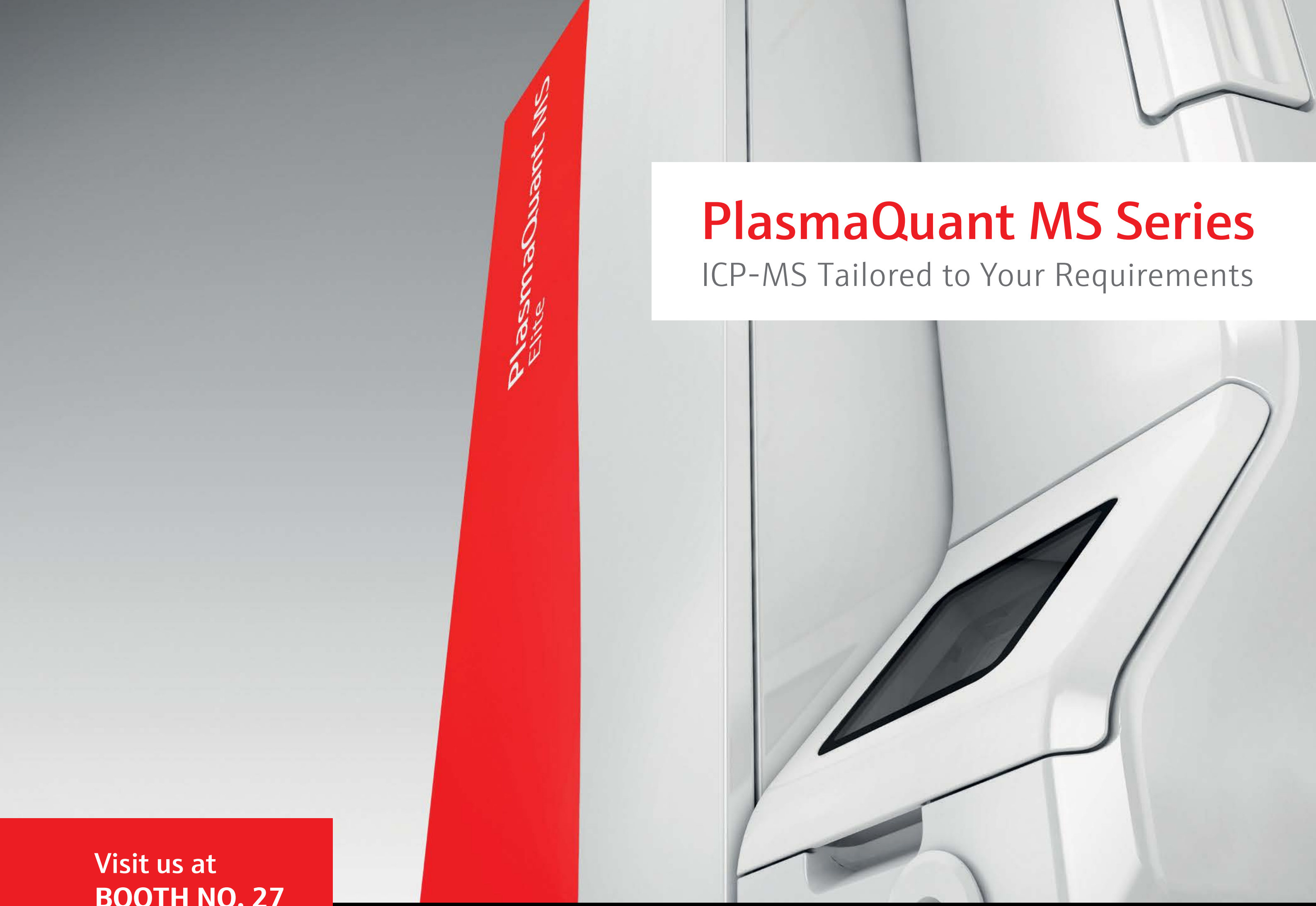
**Images courtesy of Ben Manard,*
Oak Ridge National Laboratory

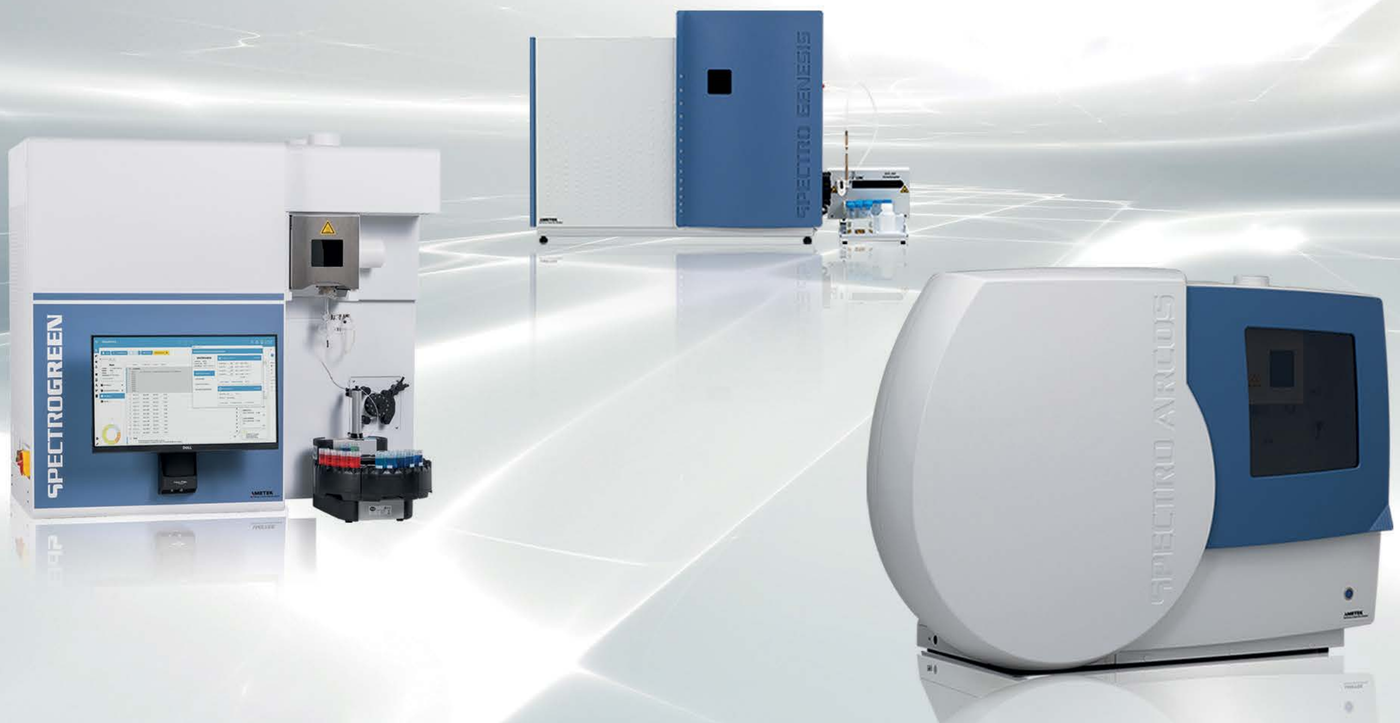
Elemental Scientific
LASERS

icpmslasers.com


WORKFLOW, MAXIMIZED
DOWNTIME, MINIMIZED
Avio® Max Series ICP-OES




PlasmaQuant MS
Elite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SPECTRO ARCOS

Poster abstracts

Deep eutectic solvents as green extractant phase for the elemental analysis of edible oils by microwave plasma atomic emission spectrometry

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Elemental analysis of edible oil samples is essential due to the possible presence of heavy metals harmful to human health. Therefore, and with the aim of developing analytical methodologies more respectful with the environment, the association of miniaturized liquid-phase extraction techniques (LPME) for the separation and concentration of the analytes of interest and the subsequent elemental detection by microwave plasma atomic emission spectrometry (MP-AES) is specially promising. Specifically, in the present study the dispersive liquid-liquid microextraction (DLLME) procedure is used with the consequent reduction of both sample and extractant phase consumption. Besides, a deep eutectic solvent (DES) is employed as environmentally friendly extractant phase for the extraction of iron, copper and lead in samples of soya bean oil, sunflower seed oil and extra virgin olive oil. The DES is prepared by mixing choline chloride and ethylene glycol at the molar ratio of 1:2 at 80 °C until a homogeneous and colorless liquid is formed.

The extraction step is optimized using multivariate analysis consisting in two steps: a Plackett-Burman design followed by a central composite design. After optimization of the extraction step, figures of merit of the method were evaluated, showing adequate linearity, repeatability as well as limits of detection and quantification. Finally, all analytes showed concentrations bellow the maximum concentration allowed by current legislation with recovery values close to 100% in all the samples analyzed, indicating absence of significant matrix effects.

Acknowledgement. The authors are grateful to the Spanish Ministry of Science and Innovation (PID2021-126155OB-I00) and the Regional Government of Valencia (Spain) (CIPROM/2021/062) for the financial support. The authors also extend their appreciation to Ministry of Science, Innovation and Universities for granting the Spanish Network of Excellence in Sample Preparation (RED2018-102522-T). This article is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Deep Eutectic Solvent (DES), Dispersive Liquid-Liquid Microextraction (DLLME), Edible oil, Microwave Plasma Atomic Emission Spectroscopy(MP-AES)

Stability of low temperature plasma radiation in high frequency electrodeless light sources

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One of the main applications for the high-frequency electrode-less light sources (HFEDLs) is a usage in atomic absorption spectrometers (AAS), as they fulfill several important criteria, such as intensive and narrow spectral lines, stability of radiation, as well as long lifetime [1]. Their electrode-less structure is also useful for spectroscopic studies of low-temperature plasma due to the decreased possibility of undesired impurities.

A light source, that is stable for a set amount of time is a requirement for a spectrometer to perform qualitative measurements. In this work we investigate several aspects of stability of radiation of HFEDLs containing arsenic. HFEDL is a spherical bulb with short sidearm, filled with a working element and a buffer gas, here, arsenic and argon, respectively. The lamp is inserted in the coil of excitation generator and is excited by changing magnetic field operating at 100 MHz frequency. When the lamp is operated at lower power values, mostly the spectrum of argon is observed, as it is easier to excite. The intensity of arsenic spectral lines rapidly increases when increasing the excitation power.

When the light source is switched on or after the change of supplied power, it requires a warm-up time of about 5-15 minutes to stabilize the radiation output. Our measurements show that when the lamp has reached its stable phase, value of fluctuations was about 0,33% over the period of 40 minutes. In the case of arsenic at some point excitation processes within the HFEDL may lead to overheating. This results in so-called self-modulation [2], when intensity of emitted radiation changes periodically, with a period of approximately 30s for the lamps analyzed. This phenomenon is not much investigated although is quite interesting from fundamental point of view.

Acknowledgements – This work was supported by the project “Strengthening of the capacity of doctoral studies at the University of Latvia within the framework of the new doctoral model”, identification No. 8.2.2.0/20/I/006 and the Latvian Council of Science project No. lzp-2020/1-0005

arsenic, high frequency electrode-less lamps, spectroscopy, stability, self-modulation

Ganeev et al., Spectrochimica Acta Part B 58 (2003) p. 879–889

Zinge et.al., Proceedings of SPIE (2014) Vol. 9421, 94210G-1

Determination of lanthanides in food samples by ICP-MS after their initial preconcentration on functionalized mesoporous silica materials

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Lanthanides (Ln) are increasingly used due to their unique catalytic, magnetic, optical and chemical properties in various branches of clean energy, high technology, as well as in agriculture and medicine. As a consequence, they enter the environment and are eventually taken up by living organisms from the atmosphere, water and soil. The growing number of "anthropogenic" Ln anomalies in various environmental compartments indicates that they have become newly emerging pollutants. Metals present in soil and surface waters are mostly taken up by plants, which can be hazardous both for the plant and plant consumers. Due to the fact that the mechanisms of environmental and human toxicity of lanthanides are still poorly understood and require further research, it becomes necessary to monitor Ln concentrations in various samples, including food [1].

Direct determination of Ln in food is difficult due to their low concentration and the complexity of the sample matrix. The spectrometric techniques, such as inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), often have an insufficient limit of detection or suffer from matrix interferences. Therefore, in many cases separation/preconcentration of Ln step becomes necessary to overcome these problem. Solid phase extraction (SPE) based on different solid sorbents has been widely used for the preconcentration and separation of Ln from various samples. However, nanomaterials based on ordered mesoporous silica (OMS), due to high specific surface areas, high porosity, regular porous organization, and high pore volume, thermal stability and the capability to attach a wide variety of organic moieties onto their surface should yield more interest [2].

The aim of the study was to investigate the suitability of MCM-41 materials modified with 3-mercaptopropyltrimethoxysilane for pre-concentration and separation of Eu, Gd and Dy from food samples before ICP-MS determination. Various parameters influencing the efficiency of separation of Eu, Gd and Dy on the tested sorbents, such as e.g. sample pH, type and concentration of eluent, eluent volume, were optimized. The developed SPE-ICP-MS method was used to determine Eu, Gd, Dy in various food samples.

lanthanides, elimination of interferences, modified mesoporous materials, separation

Arciszewska et al., submitted for publication

Florek et al., Dalton Trans. 2016, 45, 14832.

Comparison of Se nanoparticles and selenite effects on As, Pb and Se uptake and accumulation rice seedlings

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Selenium (Se) is an essential element for humans and a beneficial micronutrient for plants. The present study investigated the foliar application of Se nanoparticles (SeNPs) or sodium selenite during the cultivation of rice seedlings and its impact on Se, As and Pb concentrations.

Rice seedlings (Oryza Sativa L.) were cultivated in a greenhouse under controlled conditions. The experimental design was a randomized 3 x 2 factorial scheme with three Se concentrations (0, 0.5 and 5.0 mg/L) and two Se chemical forms (SeNPs-synthesized according to Boroumand et al. (2019)- and sodium selenite-Na_2SeO_3). Foliar applications of the different Se sources and doses were performed in the morning at the days 20, 23, 40, and 43. Plants of each group (n=6) were sprayed until the solution was uniformly distributed on the leaves surface. On day 45, the plants were harvested, roots and shoots were washed, and oven dried. Arsenic, Se and Pb was determined by ICP-MS.

The application of SeNPs at 5 mg/L, as well as the application of selenite at 0.5 and 5 mg/L increased the uptake of As and Pb by the roots. The groups treated with SeNPs at 5 mg/L and selenite at 0.5 and 5 mg/L presented higher [As] in roots (4.8; 5.6 and 4.5 mg/kg, respectively) compared to the control group (2.7 mg/kg). Similarly, the Pb content in the roots also increased in the groups treated with SeNPs at 5 mg/L and selenite at 0.5 mg/L (8.3 and 8.2 mg/kg, compared with 5.9 mg/kg in the control group). On the other hand, the application of SeNPs at 0.5 mg/L slightly increased Se concentration in the shoots (from 0.16 to 0.84 mg/kg), without influencing the concentration of As and Pb in roots and shoots. It was observed a trend for Se accumulation in the aerial part when applied as SeNPs, and possibly an increase of Se-translocation from shoots to roots when applied as selenite.

The present study indicated that foliar application of SeNPs at 0.5 mg/L can be an alternative for agronomic biofortification of rice with Se. However, future studies are necessary to evaluate whether at this concentration of SeNPs it is possible to observe an increase in grain Se content.

Selenium, nanoparticles, rice seedlings, agronomic biofortification, ICP-MS

Boroumand et al., Mater. Res. Express, 2019, 6, 0850d8

Characterization of the corrosion behavior of copper in sulfur-containing environments using LA-ICP-MS and LIBS

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Due to its excellent conductivity, copper is commonly used as a metallization in the semiconductor industry to provide electrical contact between electronic devices. To assure reliable application of electronic devices even in harsh environments, it is important to study the resistivity of the metallization material to prevent device failure. Here, especially environments containing elevated temperatures, humidity and gaseous sulphur species are of concern. Combined with an applied bias typically present in electronic devices, these conditions can significantly influence the lifetime of a device due to corrosion of the delicate connections.

In this work, we use a custom-built weathering chamber enabling the exposure of copper samples to a defined atmosphere containing H2S, SO2, and humidity. Additionally, a bias can be applied to each individual sample to emulate realistic conditions within an electronic device. Evolution of the corrosion process is assessed by analysing samples after different exposure times with different weathering conditions. For the characterization we use Laser-Induced Breakdown Spectroscopy (LIBS) for the direct detection of oxygen and hydrogen, which can indicate the formation of oxides and hydroxides during the weathering process. LA-ICP-MS is used to monitor the sulfur signal which is expected to be the main constituent of the formed corrosion products. Depth profiling of the weathered samples is used to investigate the composition of the corrosion layers in relation to the depth whereas imaging is used for assessing the homogeneity of the formed corrosion products.

LA-ICP-MS, LIBS, Imaging, Depth profiling, Copper corrosion

Determination of Aluminium in Food by ICP-MS: Influence of Microwave Digestion Parameters on the Recovery

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Aluminium (Al) is a metal that can be found in the crust of the earth and occurs naturally in drinking water and agricultural products. Humans are exposed to aluminium through the consumption of food and drinking water, and the use of consumer products and pharmaceuticals. Official food control requires validated methods for the analysis of aluminium in food and feed. The European Committee for Standardization has published a European Standard (EN) for the determination of Al by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (EN 17264:2019).

In a proficiency test (PT) organised by the European Union Reference Laboratory for Metals and Nitrogenous Compounds in Feed and Food, high variations were observed between the participants' results for the Al concentration in a cocoa powder PT material. This observation was linked to the microwave digestion parameters used by the different participating laboratories. Four parameters were identified and their potential impact on the Al extraction was assessed: (1) Test portion size, (2) reagent(s) used for the digestion, (3) maximum temperature used and (4) digestion duration. This assessment was performed using the same PT material and three certified reference materials: NIST SRM 1566b Oyster tissue, NIST SRM 8439 Durum wheat flour and NBS 1572 Citrus leaves.

This work showed that varying test portion size between 0.2 and 0.5 g did not change recoveries. In contrast, the digestion temperature had a significant impact on the recovery of Al for the NIST SRM 1566b and NIST SRM 8439. The highest recoveries were obtained with maximum digestion temperatures of 240 and 280 ˚C. There was no significant difference between the Al recoveries for digestion times between 20 and 50 min. The reagents used had an effect on the recovery with the use of nitric acid with ultrapure water giving the highest recoveries.

These results confirmed those obtained from the analysis of the PT material by our laboratory and the PT participants. This suggests that a temperature of at least 240 ˚C for at least 25 min is required for a satisfactory microwave-assisted digestion, which is different from the recommendation in the EN (200 ˚C and 20 min). These findings provide important additional information to the EN method and will help the laboratories to improve their protocol for determining aluminium concentration in food samples by ICP-MS.

aluminium, food, feed, ICP-MS, proficiency test, EURL

MDG-ICP-ToF-MS: A Versatile Tool for Quantification in the field of Single Particle ICP-MS Using Isotopic Dilution

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In the interest of exploring their potential in the field of single particle analysis, a Microdroplet Generator (MDG) was coupled to an Inductively Couple Plasma – Time of Flight – Mass Spectrometer (ICP-ToF-MS). Isotopic Dilution Analysis (IDA) was also incorporated for the size determination of three different Platinum nanoparticles samples (50, 63 and 70 nm). The performance of the technique was validated by comparison to traditional size characterization techniques (sp-ICP-ToF-MS, TEM), while the robustness of the technique was proven by incorporating NaCl in the samples' matrix, up to 100 mg/L.

The on-line combination of the two techniques proved suitable for the analysis of the nanoparticle samples, largely due to the higher reproducibility and better characterization capabilities of the droplets produced by the MDG. Usual challenges of the ICP – (ToF-) MS techniques, including transport efficiency determination, or calibration curves, are bypassed through the use of the MDG. Together with the incorporation of ID, the determination of the size of the nanoparticles was enabled. In addition, due to the ID technique, matrix effects as severe as 100 mg/L NaCl were successfully tackled, paving the path for the multielemental analysis of a wide variety of samples (e.g., environmental), making this a suitable technique in potential ecotoxicology studies.

single particle, isotopic dilution, microdroplet generator, ICP - ToF- MS

Au et.al., Journal of Analytical Atomic Spectrometry 2022, 37 (6), 1203-1207,

Au et.al., Algal Research 2020, 49, 101964

ICP-MS determination of Rubidium, a useful technique as a water leaks tracer in drinking water systems

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Water losses due to leakage is an important problem for drinking water supply companies because of three main reasons:damage in buildings and installations, the cost of the water itself, and sustainability considerations of the natural resources with special repercussions in the drought conditions typically of the Mediterranean Area. For this reason, when a leak is detected, it is urgent to find out its origin. Once the possibility that the leak consists of wastewater has been rejected (appearance or simple chemical analyses is usually enough), if not has an easy identification, then three main options have to be considered: drinking water network, relative clean wastewater (depurated water or similar), infiltration of rain water or natural water (groundwater source). Classical chemistry of major elements determination and/or generic characteristic of water such as pH, conductivity etc are not useful techniques for the mixed waters with unknown origin.More complex studies such as Isotopic studies with ICP-MS technique for different elements, such as Sr-87/Sr-86, U-235/U-238,1,2, etc. have showed to be useful in this field. However, high resolution instruments necessary for this purpose, are not today usually available for quality control laboratories in the water sector. In the present work, the determination of Rb by ICP MS has been demonstrated that a very useful for distinguish different type of water and especially effective tracer in water leaks, in a rapid and single determination necessary to make decisions in this type of problems.The validation study performed shows that ICP-MS is a suitable technique for the analysis of rubidium in different water matrixes, in terms of accuracy, precision and sensibility. On the other hand, it has been shown that is very specific tracer to water origin identification depending on the Rb concentration found. Therefore, depending on Rb concentration of water leak, we can identify as; 1)Drinking waterfrom Barcelona Metropolitan Area Network2,5– 5 µg/L Rb. 2) Wastewater entering and output from Wastewater Treatments Plants around Barcelona Metropolitan Area 8 – 20 µg/L Rb 3) Natural rainfall water infiltration and groundwater from Barcelona Metropolitan Area 0,3– 1 µg/L Rb

ICP-MS, water distribution system, water leak, rubidium

Diaz et.al., European Winter Conference on Plasma Spectrochemistry. February 2011 Zaragoza, Spain.

Diaz et.al., Afinidad -Barcelona- AFINIDAD LXXI, 567, Julio -Septiembre (LXXI):567

Evaluation of the use of selenium nanoparticles and selenized yeast extracts to treat cell ferroptosis using single cell strategies

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In recent years, an iron-dependent non-apoptotic cell death pathway has been proposed, called ferroptosis, which plays a very important role in a wide variety of diseases. The mechanism of this type of death is associated with an increase in the production and accumulation of reactive oxygen species (ROS) through the Fenton reaction. One characteristic of ferroptosis is the iron-dependent lipid peroxidation, which can be inhibited by the key Se-dependent regulator of ferroptosis glutathione peroxidase 4 (Gpx4), radical-scavenging antioxidants and specific inhibitors of ferroptosis, such as ferrostatins and liproxstatins, as well as iron chelation [1, 2]. Some recent studies show that pharmacological selenium supplementation, even in the absence of nutritional deficiency, has an unexpected ability to drive adaptive transcription to counteract ferroptosis (and other stresses) and specifically protect neurons.

Therefore, in this work we intend to study the protective effect of Se through cell treatments with Se nanoparticles (SeNPs) and yeast extracts rich in this element (SELM-1) after inducing ferroptosis with erastin as a model molecule. For this purpose, commercial SeNPs with an average size of 20 nm were characterized, as well as a Se-enriched selenized yeast extract (SELM-1), using different techniques such as single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) and transmission electron microscopy (TEM). In addition, the toxicity of both these and erastin, as an inducer of apoptosis, was studied in Hep-G2 liver cancer cells. Likewise, the levels of cellular incorporation of Se from the different sources in liver cells were evaluated using single cell ICP-MS strategies. Preliminary results showed a more effective incorporation of Se from the yeast extract than from the synthetic nanoparticles. Also, a monitorization of the presence of ROS and lipid peroxidation in the presence of erastin and erastin + Se was carried out to study the protective effect of this element.

Ferroptosis, selenium nanoparticles, selenized yeast, single cell ICP-MS

I. Ingold et al., Oncotarget 9 (2018) 32.

J. Li et al., Cell Death & Disease 11 (2020) 88.

Development of ICP-MS method for studies of gadolinium accumulation of in human cell lines

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Rare earth elements have recently become extremely crucial to new technologies, agriculture and medicine. One of the most prevalent lanthanides in medicine is gadolinium. It is mainly used as a magnetic resonance imaging contrast agent in the form of its thermodynamically and kinetically stable low molecular weight complexes. However, several examples of use in therapy can be also given. Recently, a review of various ligand (s) / Gd3+ coordination systems that have been tested as anti-cancer agents was published [1]. Among them some naturally occurring organic ligands were also noticed. For a better understanding of the mechanism of anti-cancer action and transport in the body, it is important to have reliable methods for determination of Ga in various biological materials.

In this work, the ICP-MS method for determination of Gd(III) and its complexes with caffeic acid in cancer cells was developed. Initially, the interference studies were performed using QQQ-ICP-MS spectrometer. Interferences were eliminated by means of collision-reaction cell. Solution stability of Gd(III) complexes in culture medium was studied. As the therapeutic application of Gd(III) complexes relies upon maximising Gd accumulation within the mitochondria of the target tumour cells, in vitro cellular uptake studies were performed. The uptake of Gd(III) ions and complexes of Gd(III)/caffeic acid by breast cancer cells was studied using developed method. It was found that accumulation of Gd(III)/caffeic acid complexes was significantly higher than Gd(III) ions.

gadolinium, caffeic acid, human breast cancer cells, interference elimination

Chundawat et al., Polyhedron 207 (2021) 115387

Rotational, vibrational and excitation temperatures of low-pressure nitrogen plasma

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Last few decades, nitrogen plasma has been used in various applications such as surface modification and nitridation processes, and it studied theoretically and experimentally in massive. Even though, they still have kept attracting industry and scientists due to their unique physical/chemical properties. For example, their rich reactants (N, N+, N2+) role as primary agents responsible for synthesize the nitride film through the implantation and/or adsorbing [1]. The nitride film shows the high-permittivity property with good adhesion, it is crucial to the fabrication of the ultra large scale integration in the semiconductor industry. In addition, due to a negligibly small super-elastic collisional cross section between vibrationally excited nitrogen molecule and neutral, nitrogen show extremely high vibrational temperature and high chemical reactivity [2]. It helps to overcome the reaction energy barrier, and is important for various processes such as N2 fixture to be performed with high energy efficiency [3].

To control the plasma, diagnostic of the plasma properties such as radiation temperature and radical density but also the ambient conditions (e. g. gas temperature) is imperative. However, the diagnostic tools for analyzing nitrogen plasma are not facile or practical.

In this study, we suggested a novel measurement method of excitation temperature of molecular nitrogen based on the synthetic spectra method and investigate the change of radiation temperature with various input RF power (10 W – 900 W, at 0.3 mTorr) in low-pressure nitrogen plasma. As a result, the vibrational temperature Tvib and excitation temperature Texc show a reciprocal relation.

nitrogen plasma, low-pressure plasma, radiation temperature, synthetic spectra, optical emission spectroscopy

Lim et.al., Jpn. J. Appl. Phys, 45, 15, p. 413 (2006)

Zaplotnik et.al., MTAEC9, 45, p. 199 (2011)

Bogaerts et.al., ACS Energy Lett, 3, p. 1013 (2018)

ICPMS/MS dteremination of Cr, Ni and Zn bioacumulation in cells of Green Alga Desmosesmus Subspicatus and their toxicity

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The bioaccumulation studies solved so far were mainly carried out with the aim of using the bioaccumulation potential of algae for the removal of toxic metals from the environment (bioremediation), but they are not aimed at detecting the accumulation of toxic substances in one cell of algae and thus the possibility of introducing a toxic substance into the food chain. The issue of connecting ecotoxicological tests and bioaccumulation determinations of toxic elements in algae with direct analysis using ICP-MS/MS was directly resolved in (1), so the proposed work follows up the knowledge obtained by this study. The method for the analysis of the bioaccumulation of Cr, Zn and Ni in the unicellular algae using ICP – MS/MS was optimized. Cr, Zn and Ni were selected as elements originating from transport; specifically, Ni is not naturally present in cells.

First, 72-hour ecotoxicological tests were carried out on the green algae Desmodesmus subspicatus with selected toxic compounds ZnCl2, NiCl2.4H2O and K2Cr2O7 in concentration series of the toxicant, which were chosen to include inhibition of algal growth in the range of 0-90%. At the same time, the change in concentrations of the basic mineral elements K, P and S was monitored. Based on the obtained results, a concentration of toxic compounds of 0.3 mg/l was selected, both for individual compounds and for their mixtures. For this concentration, 96-hour ecotoxicological tests were performed and the accumulation of toxic elements was monitored at time intervals of 48, 72 and 96 hours. The determination of cell density was calculated after the end of the ecotoxicological tests under a microscope, the samples were filtered through the 0.22 µm membrane filter catching the cells. All samples, blank filters and the CRM were digested in a microwave system, together with the filtered solutions were analysed using 8800 ICP – MS/MS. The resulting values of the content of elements in algal cells were recalculated per one cell. Results represents the amount of elements adsorbed on the surface of the cells and accumulated directly in the cells, which made it possible to assess the relationship between sample toxicity, accumulation of pollutants and a change in the content of selected elements in algal cells.

ICPMS/MS, toxicological test, bioaccumulation, elements, transport, algae

Bucková et. al., Journal of Applied Phycology, 2022, no. 7TH CONGR.

Single Cell- and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry Techniques for Studying the Uptake of Gadolinium Based Contrast Agents in Chlamydomonas reinhardtii Algae and Arabidopsis Thaliana

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Magnetic resonance imaging (MRI) plays a crucial part in medical diagnostics. Approximately 40% of all MRI examinations utilize Gd3+ as a paramagnetic ion due to its contrast-enhancing abilities. Therefore, gadolinium (Gd) is complexed within either a linear or macrocyclic ligand that is either ionic or non-ionic. It was determined in recent years that the linear gadolinium-based contrast agents (GBCAs) can lead to nephrogenic systemic fibrosis and also deposition of a small amount of Gd within the brain, which led to their ban in Europe in 2017.

For the most part GBCAs are not retained in the body and are excreted rapidly, which in turn releases them into the environment. Wastewater treatment plants only eliminate a small percentage of the GBCAs which means these complexes end up in our drinking water and surface waters, especially in the more densely populated regions. To further understand the potential uptake into our ecosystem, two different experiments were designed. First, the species-dependent uptake of GBCAs into Chlamydomonas reinhardtii algae which was investigated by single cell-inductively coupled plasma-mass spectrometry (sc-ICP-MS). This is a fairly new technique that introduces cells one at a time into the ICP-MS to get metal distributions, or in this case Gd, from cell populations. The second study investigated the uptake of free Gd3+, linear GBCAs, and macrocyclic GBCAs in Arabidopsis Thaliana by laser ablation-ICP-MS (LA-ICP-MS). LA-ICP-MS is a technique that can be used for imaging and in this case is used to determine Gd distributions within the leaf that can help determine the amount of exposure and potential uptake paths.

Single Cell ICP-MS, Gd-based MRI contrast agents, LA-ICP-MS

Mass spectrometry methods for Sr-90 determination in environmental samples

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Radioactive Sr-90 (T1/2=28.8 y), produced by nuclear fission processes, is then released into the environment through events like nuclear accidents or the testing and use of nuclear weapons.

Although the alkaline earth metal Sr has no biological function in the human body, it can accumulate in bone formation because its biochemical similarity to Ca. This allows Sr-90 to give a long-term radiation dose. Therefore, from the viewpoints of public health and environmental radiation protection, the precise and reliable detection of Sr-90 in various environmental, biological, and radioactive waste samples is essential.

Radiometric methods have primarily been used for Sr-90 analysis, detecting beta particles emitted by the radioactive decay of Sr-90. In contrast to gamma rays, which have discrete energy, beta particles have a continuous energy spectrum. As a result, efficient separation of interfering beta emitter radionuclides prior to Sr-90 measurement with radiometric methods is critical.

Many successful Sr-90 determinations using mass spectrometry instruments have been reported in recent years. Inductively coupled plasma mass spectrometry (ICP MS) and thermal ionisation mass spectrometry (TIMS) instruments have mainly been applied for Sr-90 measurement (1). The main advantages of mass spectrometry over radiometric methods are shorter analysis times, higher sample throughput, and smaller sample intake. However, it can be challenging to use mass spectrometry instruments to analyse low-level Sr-90 in environmental samples. The isobaric interference of Zr-90 brought on by appreciable Zr concentrations in environmental samples (especially in soil samples) is the first crucial point. The peak tailing on the higher mass side of Sr-88 is the second crucial point. The ions scatter during their acceleration even though the mass spectrometry instruments have a reliable ultra-high vacuum condition in the analyser zone. This scattering causes the ion beam's energy to spread, which is visible as a peak tail in the mass spectra.

In this study, Sr-90 determination using thermal ionization mass spectrometry (TIMS) and triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ-MS) will be evaluated for a range of environmental materials.

Strontium-90, Mass Spectrometry, Extraction Chromatography, Environmental Samples

Kavasi et.al., Analytical Chemistry. 91, 2964–2969, 2019.

How high-temperature microwave acid digestion can turbo-charge ICP-OES or ICP-MS analysis of heavy petroleum products

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In recent years more and more requirements evolved to determine metals and trace elements in petroleum products. For simple products like gasoline, dilution with hydrocarbons and analysis by ICP-OES with specialized sample introduction equipment may be applicable at the cost of deteriorated instrument stability and detection limits due to enhanced carbon-based spectral interference. For heavy products like marine fuels, crude oils, tar, pitch, and similar the widely used and standardized method (1)involves multiple and time-consuming steps like burning, charring, fluxing of ashes in a platinum crucible before finally dissolving the salt cake in dilute hydrochloric acid. This procedure typically runs over night and takes up to 1.5 – 2 days.

This contribution shows, how modern microwave assisted acid digestion can help to speed-up this sample preparation process by a factor of ten and more. It addresses the safety concerns of the industry. It considers the special properties and challenges of the samples due to their high carbon and energy content.

It is demonstrated, how a modern microwave digestion system can reduce the throughput time of the sample preparation to 2.5 – 3 hours.

Analytical data will be presented from a 2-step acid digestion of half gram portions of ASTM proficiency testing samples and NIST SRM. Two vessel systems will be compared, a classical closed vessel system with high-speed pressure monitoring of all vessels and a vessel system with SmartVent technology that allows to release excess pressure from reaction gases.

It can be shown, that analytical performance is at least comparable, if not better than for the classical method, with the benefit of large savings on heating energy, reagents, harmful waste, operator intervention, and time.

heavy petroleum, marine fuels, microwave acid digestion

IP 501/05, Energy Institute, London, (2005)

Detection of post-fire soil contamination using inductively coupled plasma-mass spectrometry (ICP-MS) in wildfire affected areas in Greece

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Fires in urban and natural ecosystems cause catastrophic consequences on a global scale. Concern is raised as it has been observed that the remaining materials after the fire, contain metals, including heavy metals in high or toxic levels[1]. The aim of the present research is to investigate the influence of urban fires on the concentration of mobile forms of such elements of concern and heavy metals in surface and in different soil depths. Sampling of soils of pyrogenic origin was carried out in 2022. At least 800 different ground sampling points were selected according to operating standards in the territory of Mati and Kineta (Attica, Greece). Both suffered from wildfires in July of 2018. The heavy metals content of the soil samples was identified after Aqua Regia extraction. Inductively coupled plasma-mass spectrometry (ICP-MS) was used as analytical method[2]. Due to its high sensitivity and low detection limit twelvemetals were measured (i.e. Al, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sn, Hg, Pb). Certified Reference Materials (CRM) were used for the method development. The results were evaluated using the Dutch List, a collection of values and regulations related with the contaminated soils[3].

ICP MS, heavy metals detection, soil quality

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Poster - Mo 17 Applications

Multielement quantification of intrinsic elements in single cells of snow algae by SC-ICP-ToF-MS

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Trace elements are essential in cells accomplishing various biological functions, such as structural and catalytical in proteins and enzymes. In general, cellular trace elements can be quantified with elemental analysis via bulk analysis, providing information on the average contents of specific elements in cells. However, these methods neglect heterogeneity and varied time dynamics within the cell population, thus biological variability is disregarded. On the other hand, chemical analysis of single cells is an expanding research area that has become increasingly important to reveal the mechanisms of various physiological processes (1). In this framework, ultra-sensitive and accurate methods to quantify trace elements in single cells are scarce and urgently required. Recently, ICP-ToF-MS has substantially advanced allowing (quasi) simultaneous multielement detection of a complete elemental mass spectrum which is perfectly suited for detecting short transient events as those occurring in single cell analysis and therefore can offer multielemental fingerprints of individual cells. Snow algae are a set of freshwater microalgae found in the extreme habitats of persistent snow and glacier fields. In appropriate locations, they can build up massive blooms resulting in a visible pigmentation of the snow (2). The growth of snow algae has been proposed as a key role in climate change as they can decrease the albedo and therefore accelerate the melting of snow and ice fields (3). Many environmental factors impact the extent of snow algae growth and snow algae blooms are more common in the snow containing high amounts of nutrients.

In this work, we have developed an analytical method for multielemental quantification (Ca, P, Mg, Cu, Fe, Mn, and Zn) in single cells of snow algae (Chloromonas remiasii, Raphidonema sempervirens, and Microglena sp.) trying to figure out more information about their ability to grow at lower temperatures and extreme conditions. The algal events were identified by the fingerprint elements at the identified point of time. The next step is to test the feasibility of separating different algae species by means of multivariate analysis, based on the previously defined fingerprint elements.

snow algae, ICP-ToF-MS, single cell

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Poster - Mo 18 Applications

A promising tool for elemental analysis — the role of multinebulizers

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The development and characterization of new liquid sample introduction systems based on nebulizers is still a field of continuous innovation with an open end in elemental analysis. These new nebulizers should generate an aerosol with good characteristics not only from model solutions with well controlled matrix, but also from samples, usually with complex matrix. Nevertheless, ICP-based techniques commonly suffer from some limitations related to matrix effects, caused by non-spectral interferences, and the compensation of matrix effects has a special interest for analysts.

Recently our research group has introduced a new multinebulizer [1]. This presentation will show new possibilities of multiple nebulizers (i.e., multinebulizers), handlingsamples, standards and reagents in an easy way. Examples of applications to the analysis of typical complex matrix samples will be presented, among them, on-line calibration methodologies and chemical vapor generation.

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Multinebulizer, On-line calibration methodologies, Chemical vapor generation, Inductively coupled plasma optical emission spectroscopy (ICP-OES)

García et.al., JAAS, 2020, 35, 265–272.

The effect of Farnesol and Tyrosol treatment for the intracellular metal content of Candida auris

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Nowadays, alternative treatments using quorum sensing molecules (QSM) are increasingly attractive, especially for difficult-to-treat multidrug-resistant pathogens such as Candida auris.Metals are essential for the survival of pathogenic microorganisms, as well as to maintain their virulence. Recent transcriptomic data have demonstrated that farnesol treatment affected the transcription of iron homeostasis-related genes, as well as the iron, manganese, zinc, and copper contents of C. auris [1]. Based on these data, the purpose of our experiments was to measure the changes in intracellular metal content induced by farnesol (FAR) and tyrosol (TYR) treatment with ICP-OES technology in C. auris.

The fungal pathogen was treated with FAR and TYR for 2 and 4 hours, after that the metal contents of the samples were measured with ICP-OES following atmospheric wet digestion. Spectrophotometric measurements demonstated that adding FAR and TYR to preincubated cells resulted in a remarkable growth inhibition which was further confirmed by changes in measured dry cell mass. From the results of the elemental analysis we calculated the average metal content of the samples. 2 hours of FAR treatment caused a reduction in intracellular iron, manganese, and zinc content compared to untreated control cells, whereas the level of intracellular copper showed increase. TYR exposure of the same duration resulted in a decrease in the intracellular contents of the four elements. After 4 hours of FAR and TYR treatment we experienced similar results except for the intracellular manganese content.

Presents study indicates that FAR and TYR affect the growth and intracellular metal content of C.auris. Our results suggest, that these QSMs may be promising candidates in alternative treatment regimens against the multidrug-resistant microbe.

ICP-OES, elemental analysis, analytical spectrometry

Jakab et.al., mSphere. 2021; Oct 13:e0071021.

Evaluation of Indium and Tantalum Secondary Cathodes for Silicon Carbide Analysis Using the Nu Astrum GD-MS

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High purity silicon carbide analysis can prove challenging due to the inertness of the material and the risk of contamination during sample preparation. Even using GD-MS, the material cannot be analysed using standard techniques because of its low conductivity. The Nu Astrum GD-MS allows direct solid phase analysis of silicon carbide using secondary cathodes made from high purity tantalum and indium. The efficacy of the tantalum and indium secondary cathodes was compared for different silicon carbide samples, with varying contaminant levels and particle sizes.

Tantalum “spoon” pin samples were used as a secondary cathode and support for the silicon carbide samples then analysed under standard conditions. 7N Indium shot was used as a secondary cathode by pressing the shot into discs and then pressing the sample into the surface. Qualities considered were ease of sample preparation, availability of materials, matrix intensity, limits of detection, common interferences, and the suitability of the Nu Astrum as the machine of choice for silicon carbide analysis.

GD-MS, Silicon Carbide, Semiconductor, High Purity, Glow Discharge, Magnetic Sector,

Determination of total iodine using ICP-MS in Israeli bottled and tap water: method development and application

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Reliable iodine determination in drinking water samples has gained importance in the last few decades, mostly due to intensive use of both desalinized water that lacks several important nutritional elements, and bottled mineral water.ICP-MS is a sensitive method for iodine determination that must be performed under alkaline conditions because of the volatile nature of some iodine species. However, in water samples with high pH (>10), slow precipitation of calcium (Ca) and/or magnesium (Mg) carbonates leads to clogging of the ICP-MS nebulizer.

We propose preventing this precipitation by adding the chelating agent ethylenediaminetetraacetic acid (EDTA) at 0.1% to a 2% ammonium hydroxide matrix. This concentration of EDTA sufficed for most drinking water samples studied, as long as a 1:1 molar ratio of EDTA to Ca+Mg concentration in the water was maintained. The limit of quantitation of the developed method for iodine was <0.1 ug/L (ppb).

The average iodine concentration in various brands of bottled mineral water sold in Israel was relatively low (7.67 ± 6.38 ug/L). Regular consumption of either desalinated water or bottled mineral water may induce iodine deficiency in Israeli consumers. Therefore, continuous follow-up of the iodine status in both tap and bottled water is strongly recommended.

Totally 18 tap water samples were taken from different Israeli cities or villages (from households and non-residential premises) from North to South. Also, 13 desalinized water samples from 3 desalination plants were analyzed. The range of total iodine content in tap water was 0.2-19.9 ug/L, whereas in desalinized water – <0.1 – 0.85 ug/L. Total iodine was correlated positively and significantly with Na, K, Mg, and S, but in most cases not with Ca.

iodine, ICP-MS, alkaline matrix, bottled water, desalinized water, tap water

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The elemental analysis if the mummies of Vác, Hungary

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Present study consideres the elemental analysis of bone remains received from the Hungarian Natural History Museum. During routine restoration of the Dominican church of Vác in 1994, workers discovered a crypt that had been bricked up for over 200 years with naturally mummified bodies placed in coffins. The primary artifacts were studied by inductively coupled plasma optical emission spectrometric (ICP-OES) method that was tested previously on the bones found at the earth coal mine of Bükkábrány, Hungary. According to our preliminary results the technique is suitable for the quantitative measurement of bone remains.

Samples were photo documented and weighed prior to sample pre-treatment process, which was carried out by wet digestion at high pressure and temperature. As expected, Ca and P were found in the highest concentration and no significant different occurred regarding the macroelements. However, the microelements showed statistically different results among the groups: the levels of Mn and Ba for instance were remarkably higher compared to the others, which can indicate dietetic habits based on vegetal nutrients.

In case of the separately evaluated metals (Al, Fe, Pb, Zn) we experienced significant divergence between the samples: the female bones of Vác pointed higher concentration values than the male ones, especially for Fe, Pb, Zn. The complement of the Pb detected in the remains probably originate from occupational disease in default of protective pieces of equipment. There was an overconcentration of Al and Fe belonging to bones originating from the lignite mine, which can be explained by burial traditions, environmental effects or diagenesis. Results of present work highly contribute to the investigation of the mummies of Vác, supporting the interdisciplinary science of anthropology.

Acknowledgements

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Hungary, mummies of Vác, ICP-OES, elemental analysis, anthropology

Application advantages of a HR-array ICP-OES for the trace analysis of copper ore

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Nowadays, the demand for precious metals and specifically for platin-group metals (PGMs) has increased with the significant growth of economy. Chalcopyrite (CuFeS2) is the world's most important copper ore. During the extraction of copper, the ore is concentrated using flotation and smelting processes. Resulting waste matter named slag is separated and often contains high amounts PGMs. Thus, copper ore, slags and copper concentrates are usually analyzed for being a potential source of these valuable elements.

The determination of these elements by ICP-OES is drastically hampered by the emission spectra of matrix components. Iron is an extremely line-rich element emitting over 9300 ICP spectral lines in the range from 200 to 400 nm – copper more than 1400. In this regard, an ICP-OES with high spectral resolution circumvents the often required need to compromise on the choice of emission lines allowing for a reliable determination of trace concentrations.

Here we present the application advantages for trace analysis in copper matrices originating from an ICP-OES instrument with high-resolution (HR) optics (2 pm @ 200 nm), intelligent torch design and high plasma robustness. Additionally, the benefits of the implementation of powerful software tools (ABC, CSI) for background correction and correction of spectral interferences are demonstrated.

HR ICP-OES, copper, mining

Direct analysis of trace elements in seawater using ICP-MS with versatile reaction modes

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The determination of trace elements in seawater is usually considered to be challenging for ICPMS due to the high total dissolved solids (TDS) in this matrix. The high concentrations of matrix components in seawater, such as sodium, magnesium, and chloride ions, may form polyatomic spectral interferences and complicate the determination of elements, such as As, Co, V, Zn, Cu, and Fe. Even for elements like Cd, Sn, and Pb that are less affected by spectral interferences, the low ppt concentrations in seawater make them difficult to determine with good accuracy and precision. Both NexION® 2000 ICP-MS and NexION 5000 Multi-Quadrupole ICP-MS are equipped with Universal Cell Technical (UCT), which allows for samples to be run in Standard, Collision with Kinetic Energy Discrimination (KED), and Reaction with Dynamic Bandpass Tuning (DBT) modes. Here, we reported a direct analysis procedure using online dilution with a combination of liquid dilution and gas dilution. A variety of reaction/collision gas modes were applied to demonstrate the versatility of the method. The accuracy of the method is validated by the analysis of seawater certified reference materials NASS-7, CASS-6, and MX014.

Seawater, TDS, AMS dilution

Cryogenic cave carbonates by high resolution LA ICP TOF MS imaging – from understanding genesis to documenting ancient anthropogenic air pollution

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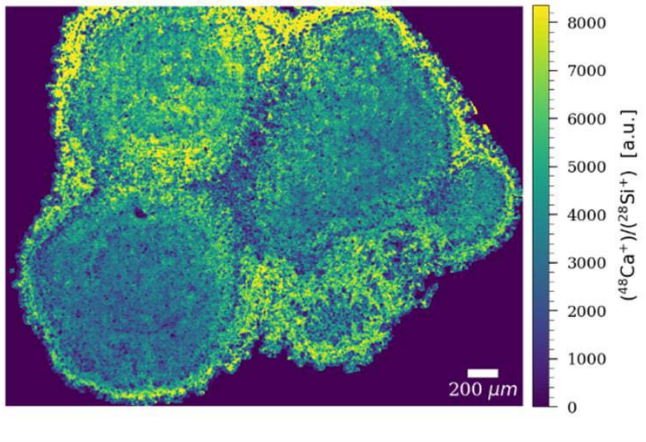
The mechanisms responsible for the formation of cave carbonates (commonly found in speleic environments where the ambient temperature is or was below freezing at the time of formation) are well documented and linked to the water becoming increasingly saturated in ions as it reaches the freezing temperature where it achieves supersaturation and precipitates carbonates [1]. Cryogenic carbonates are good indicators of ambient temperatures and temperature-related processes at the time of their formation and because they can be dated they represent reliable proxies for paleoclimate studies. Due to their extreme formation mechanisms they can be used as proxies to study carbonates formed in similar conditions in the solar system [2].We present elemental distribution data for cryogenic cave carbonates from the Scărișoara Ice Cave, Romania. The samples were analyzed using LA-ICP-TOF-MS instrumentation and the main goal was to identify potential chemical signatures that could be used for rapid and reliable identification of cryogenic carbonates. Additionally, since the cave is in the proximity of a gold/silver mining region which was active since before 100 AD we have investigated the ability of cryogenic carbonates to document air pollution linked to mining activities



cryocarbonate, laser ablation, Time of Flight, air pollution

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High Accuracy Standard Addition ICP-MS Analysis of Elemental Impurities in Electrolyte Salts Used for Lithium-Ion Batteries

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The lithium-ion (Li-ion) battery industry is thriving due to demand for portable electronic devices and a surge in the use of batteries for electric vehicles (EVs). Li-ion batteries currently provide the best combination of cost, capacity, charging speed, and lifetime, and electrolyte composition is a key factor in battery performance. The salts used in Li-ion battery electrolytes include lithium hexafluorophosphate (LiPF6), lithium tetrafluoroborate (LiBF4), and lithium perchlorate (LiClO4). Imide-based Li salts such as lithium bis(fluorosulfonyl)imide (LiFSI) are also used as electrolyte additives to increase battery lifetime at high temperatures. Electrolyte performance is strongly affected by the presence of elemental impurities, which must be monitored in the Li salts in order to ensure quality control of the electrolyte and the final battery product. Electrolyte producers and battery manufacturers therefore require accurate analytical methods to determine a wide range of elements in lithium salts. ICP-MS is the preferred technique for trace element analysis because of its high speed, low detection limits, wide elemental coverage, and good selectivity. These characteristics make ICP-MS the ideal technique to meet the increasingly stringent requirements for quality control of components used in Li-ion batteries. In this study, a standard addition ICP-MS method was developed for the analysis of 68 elements in the Li salts, LiPF6, LiBF4, LiClO4 and LiFSI. The analysis was performed using an Agilent 7900 ICP-MS with HF resistant PFA sample introduction system. The analytes included the metals listed in ISO/WD 10655 (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pd, Zn) and a further 56 elements. Method performance was evaluated for all target elements in the four lithium salts. All calibration coefficients were better than 0.995 with a minimum of three calibration points. MDLs for the trace elements were <0.0005 mg/kg based on the solid salt. Spike recoveries for the trace elements were between 80-120% with RSD <10% (n=3). Instrument and method robustness were assessed during the 6 hour analytical sequence, which demonstrated stable quantitative analysis and good QC recoveries with precision less than ±15% RSD. This newly developed ICP-MS method provides high sensitivity and good control of matrix effects for the multielement analysis of lithium salts. The method addresses the need for stricter quality control of Li-ion battery materials as required by electrolyte producers and battery manufacturers.

Elemental impurities, Lithium-ion battery, LiB, Electrolyte, ICP-MS, Standard addition method, MSA

The Development and Future of Lithium Ion Batteries, Journal of The Electrochemical Society, 164 (1) A5019-A5025 (2017)

ISO/WD 10655

Method Development for the Determination of Vitamin B12 in Infant Formulas

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Vitamin B12 (cobalamin) plays a key role in human biological functions and is vital in the neurological development of infants. Traditional methods for vitamin B12 determination include microbiological assays, spectrophotometric, and various chromatography techniques, many of which are limited in sensitivity, specificity, and efficiency. Inductively coupled plasma-mass spectrometry (ICP-MS) is an alternative technique used to determine the content of vitamin B12 indirectly by measuring the complexed cobalt in cobalamins. This study presents the development of a method for the determination of vitamin B12 in infant formula based on sample extraction using sodium acetate buffer, purification on a solid phase extraction (SPE) sorbent, and subsequent analysis of the SPE eluent by high performance liquid chromatography (HPLC) interfaced with ICP-MS. The method development targeted the requirements outlined in AOAC Standard Method Performance Requirement (SMPR) 2011.005 established for vitamin B12 in infant formula. Method parameters including the type, concentration, and pH of extraction solution and chromatographic conditions were evaluated and optimized. Metrics on method performance including linearity, repeatability, reproducibility, and recovery will also be discussed. The newly developed method will be compared against AOAC Official Method 2014.02 to determine vitamin B12 in infant and adult/pediatric formula samples and available reference materials.

Vitamin B12, infant formula, LC-ICP-MS

Elemental fingerprint analysis of (micro) plastics via ICP-MS/MS – A possible tool for source tracing?

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In recent years, microplastics (MPs) – defined as synthetic polymer particles or fibers <5 mm – were shown to be omnipresent in riverine and marine environments as well as organisms. Analysis of environmental MP focusses mainly on the determination of particle size and shape, as well as polymer type using spectroscopic techniques like FTIR imaging. Indeed, the tracing of specific sources and/or plastic types based on current analytical techniques is challenging. Within this context, the analysis of elemental fingerprints in plastics using ICP-MS/MS may be a new, promising tool for source tracing of MPs derived from complex environmental samples.

Therefore, we present a fully validated digestion protocol for different polymers of environmental concern. This digestion protocol is suitable for a broad range of plastics, e.g. six different certified reference materials (CRMs) comprising the polymer types polyethylene, polypropylene, polyvinyl chloride and acrylonitrile butadiene styrene. Recoveries for the certified elements As, Cd, Cr, Hg, Pb, Sb, Sn und Zn) ranged between 95.9% ± 2.7% and 112% ± 7%. Furthermore, mass fractions of 17 other elements are reported.

The digestion protocol was applied to a set of paint and varnish materials, which are typically used as corrosion protection agents in marine environments. Paint and varnish are a major source of MP in the open ocean, due to their widespread use as coatings in shipping or off shore structures such as windfarms1. In total 26 different coatings of various manufacturers were analyzed for their partially high mass fraction of 52 elements (up to 0.10 g kg-1 of As, 3.1 g kg-1 of Cr and 59 g kg-1 of Pb). Statistical data analysis (cluster and principal component analysis) revealed four principal components. The first factor characterized by the rare earth elements (REE), the second by a number of heavy metals (Cr, Mo, As, Pb, Bi, Mn), the third by a number of possible additives (Ag, Pt, Zr, Co, Au, Ti, Nb).

marine environment, environmental analysis, trace metal, coatings, offshore

Hildebrandt et.al., Environmental Pollution, Vol. 307, 119547.

In-Depth Analytics by High-Throughput ICP-MS

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Next breakthrough biotherapeutics require in-depth characterization of high-performance bioprocesses to identify the optimal high producer cell lines and to meet the intended product quality attributes.

For this, we developed a fast and sensitive ICP-MS at-line method for the quantification of more than 11 prioritized and important trace elements in Chinese Hamster Ovary (CHO) cell culture processes. The method is based on a singleQ ICP-MS (iCAP RQ) system with an ESI prepFAST M5 autosampler to increase throughput. To meet the requirement of a high dynamic concentration range for all elements from 0.0001 µM - up to 1200 µM a customized standard is used to ensure the quantification for all elements of interest in the same run.

A highly automated sample preparation workflow including the ESI prepFAST is coupled to the ICP-MS to allow high-throughput data generation for up to 300 samples per night.

The qualified acquired data are semi-automated analysed and transferred to an internal data warehouse platform. By this, ICP-MS analytes are used for the comprehensive joint analysis of the CHO producer clone performance, other process critical parameters, and product quality attributes.

Taken together, the high throuhgput ICP-MS approach is a key element for fast development cycles of innovative biotherapeutic bioprocesses.

Bioprocess Analytics, High-Throughput

Challenges in sample preparation of carbon-rich samples of natural, geogenic and technological origin

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Carbon appears in different allotropes, the most commonly known are graphite and diamonds but also Buckminster fullerene and graphene. Carbon-rich samples can be of biogenic (e.g. biochar) or geogenic (e.g. graphite) origin but can also be the product of technological processes (e.g. nanotubes, carbon black). One general analytical aim is the determination of the trace element content in these materials. The knowledge of the elemental composition is important for the further applications as well as for the identification of the geographical origin using an elemental fingerprint.

The aim of this work is to develop an universal digestion method for the variety of carbon-rich samples required for the elemental analysis using ICP-MS. However, the complete digestion of these samples can be very challenging. In the case of graphite we observed that the digestion efficiency depends on the crystallinity and the grain size (in the case of flake graphite). Although high temperature and pressure are already required for the digestion, the large volume of gases generated during the digestion increases pressure and therefore requires taking control of the pressure quickly to keep the highly exothermic reactions under control. In most cases stronger oxidising conditions are needed since classic acid digestion methods such as microwave digestion or high pressure asher (HPA) digestion methods are not sufficient. A novel microwave-induced oxygen combustion (MIC) approach was tested for the samples with both high crystallinity and flat structure (flake graphite). This new approach appears to be very promising and will have to be validated for elemental analysis in carbon-rich samples of natural and technological origin (1). Alternatively, the direct way of analysing carbon-rich samples was attempted through LA-ICP-MS. Quantification using spiked carbon samples proved only successful for some trace elements (especially rare earth elements).

carbon-rich samples, sample preparation, elemental analysis, ICP-MS

S. M. Cruz et al., Microchemical Journal, 2015, 28-32

Trends in Nebulization Strategies. Multiple Inlet Nebulizer. MultiNeb®

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Innovative multiple inlet nebulizer features result in a promising, robust, reliable, and more economical analytical methodology for the analysis of organic samples and high solids content samples by ICP-OES and/or ICP-MS. The only multiple inlet nebulizer available allows the simultaneous nebulization of two solutions with similar precision and sensitivity to standard high end nebulizers. The MultiNeb® nebulizer produces simultaneous nebulization of different samples/standards in regular spray chambers, easily upgrading ICP system's ability to perform advanced routines based on the simultaneous introduction of solutions, including cold vapor generation, hydride generation, online isotopic dilutions, etc. [1] The Multineb is the only nebulizer capable of mixing two solutions, miscible or inmiscible, at the moment of aerosol formation at the tip of the nebulizer. MultiNeb® also works fine as a regular nebulizer, using just one of its capillaries. It has been demonstrated that the multiple nebulizer MultiNeb® offers satisfactory results for its application in metal determination in petrochemical analysis, lubricating oils or gold determination analysis after fire assay sample preparation by Standard Dilution Analysis (SDA) is proposed [2]. SDA combines the principles of conventional calibration methodologies of internal standard (IS) and standard addition (SA) so it simultaneously corrects instrumental variations and matrix effects. (i) SDA simultaneously corrects for matrix effects (i.e., systematic errors) and for fluctuations (i.e., random errors) due to changes in instrumental parameters; (ii) significantly reduces the time of the analysis as sample needs a minimal pretreatment (i.e. dilution), only one standard solution is required per sample and there is no need of preparing mixtures; (iii) provides ease of operation, since the system setup is simple, MultiNeb® nebulizer is robust and easy to handle (iv) lower organic solvent consumption, as only aqueous standards are used; (v) no carbon deposits on different places of the plasma torch (e.g., injector and/or tulip); and (vi) can be adapted to many analytes and sample types. The automatization of the whole analytical process can also be easily implemented and it is currently under study in our laboratory.

Nebulizer, Simultaneous nebulization, Carbon Interference, Standard Dilution Analysis, Hydrides, Gold determination, Petrochemical, Lubricating Oils, Automatization,

García et.al., Journal of Analytical Atomic Spectrometry, 35(2) 2019.

Jones et.al., AnalyticalChemistry., 2015, 87, 2321–2327.

Elemental analysis of co-produced wastewater from the Danish chalk reservoirs: traces in a complex matrix

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When crude oil is produced, large amounts of water are made along with the raw material. This co-produced water (PW) is highly saline and contaminated by crude oil from the geological formation and the production additives. Thus, it is heterogeneous and remarkably complex. Since this water is being discharged into the sea at most current offshore production sites, reaching “zero harmful discharge” requires stringent produced water management and improved monitoring and toxicology evaluation. This work aims at an elemental characterization for improved environmental impact assessment, facing the analytical challenges of a hypersaline and carbon-rich water sample.

This work presents a workflow for trace elements analysis with ICP techniques of complex aqueous samples. The focus has been on Fe, Co, Ni, Cu, V, Mn, Cr, Cd, Pb, As, Sb, and Se. Furthermore, all trace elements have been targeted in suspended particulate matter (SPM) and characterized using EDX-SEM and ICP techniques. A matrix matching solution for blanks, calibration standards, and quality checks has been implemented to improve plasma stability and mitigate the matrix effect. A hydride generator introduction system has also been adopted to analyze metalloids with a cleaner signal. The presentation will include the initial results of these analyses of produced water from the discharge point of the main production oilfields.

wastewater, petrochemical, traces, seawater, metalloids, metals, matrix matching, hydrides

Improved Workflow and Throughput for Particle Counting and Wear Metals Analysis coupling ICP-OES with a Liquid Particle Counter

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[1]Perkinelmer, Shelton, United States

The lubricant monitoring field is continuing to expand its ability to measure and identify contaminants of in-service oils.Tracking concentrations of wear metals in accordance with ASTM D5185 by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) is standard within the petrochemical industry as a way of identifying mechanical wear and predicting component failure.Additionally, particle counting has been used for years as a tool in lubricant condition monitoring and maintenance programs.Valuable information regarding the state and health of the equipment can be gained by knowing the size distribution of particles within the fluid.In-service oils and other lubricants are monitored for particle size and count similar to how they are monitored for elemental concentration. An increase in the concentration of particles of certain sizes or concentration of key wear metals indicates when maintenance is required. As separate techniques, particle counting and elemental analysis are resource intensive and can be time consuming. Recently a new instrumental technique has been developed which reduces both preparation and analysis time by combining particle counting with wear metals testing by ICP-OES.This new technique can use less than one milliliter of sample volume, which is then diluted with solvent 1:10.As diluted samples are introduced to the ICP-OES, they are tested by an optical particle counting device which is in-line to the sample introduction system.This allows combined analyses to be performed in 45 seconds per sample and provides both particle size distribution data and wear metals analyses into one analysis.

Results will be presented and discussed regarding this new integrated technique with examination of the particle size and wear metal data for typical in-service fluids.

ICP-OES, Particle counting, Wear metal analysis

The acid matrix effects strike back: Evaluation of sulfur, phosphorus and chlorine influence on the analyte emission signal in inductively coupled plasma optical emission spectrometry

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Inorganic acids such as sulfuric, phosphoric and hydrochloric acids are widely employed for sample preservation and for sample decomposition treatments in elemental analysis. These species are a source of non-spectral interferences in plasma-based spectroscopy techniques (ICP-OES and ICP-MS) that can affect aerosol generation and transport, plasma energetic conditions and the excitation/ionization mechanisms [1,2]. In general, acids affect negatively analyte transport to the discharge as well as plasma temperature, thus decreasing analyte excitation and ionization. Nevertheless, Grindlay et al. [2] have reported that the emission signal for atomic lines of several hard-to-ionize elements (i.e., As, Hg, I, P, Se and Te) in ICP-OES is enhanced by sulfur and phosphorus presence. This phenomenon seems related to a two-step mechanism based on sulfur and phosphorus-based charge-transfer reaction followed by an ion-electron recombination process, by which the population of excited analyte atoms raises up and hence atomic emission. No information was provided about sulfur and phosphorus influence on the excitation/ionization mechanisms of easy-to-ionize elements. Thus, an extended study about the influence of these concomitants on the emission lines of different elements is required to better understand acid matrix effects in ICP-OES.

The aim of this work was to revisited matrix effects by several inorganic acids (i.e., sulfuric, phosphoric and hydrochloric acid) on atomic and ionic emission for 42 elements (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, In, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Rb, Rh, S, Sb, Sc, Se, Sn, Sr, Te, Ti, Tl, V, Y, Zn, Zr). To this end, 2388 emission lines (1089 atomic and 1299 ionic lines) were registered in the presence of sulfuric (20 g L-1 S), phosphoric (20 g L-1 P) and hydrochloric (20 g L-1 Cl) acids and results were compared to those obtained operating a 1% w w-1 HNO3 solution. Non-significant matrix effects were registered for most of the ionic lines selected, regardless the acid employed. Matrix effects for atomic emission lines, however, was strongly dependent on both concomitant and analyte wavelengths characteristics. These results suggest that the mechanisms involved on the population of atomic electronic levels are altered by these concomitants.

Acids, matrix effects, inductively coupled plasma, optical emission spectrometry.

García-Poyo et.al., Spectrochim. Acta Part B 105 (2015) 71–76

Grindlay et.al., Spectrochim. Acta Part B 115 (2016) 8–15.

Analysis of polycyclic aromatic hydrocarbons with surface-assisted flowing atmospheric-pressure afterglow mass spectrometry (SA-FAPA-MS)

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Polycyclic aromatic hydrocarbons (PAHs) have carcinogenic and mutagenic properties and continue to be released into the environment. The analysis of PAHs can be challenging and often requires time-consuming separation steps. In this study, the capabilities of ambient desorption/ionization high-resolution mass spectrometry (ADI-HR-MS) [1] for direct analysis of PAHs were evaluated. Specifically, a flowing atmospheric-pressure afterglow (FAPA) [2,3] desorption/ionization source was used to directly probe analytes from thin-layer chromatography (TLC) surfaces without a preceding separation step. The effect of different surface chemistries on the analyte response was investigated.

A large variety of 30 different PAHs and PAH derivates was deposited onto four different TLC surfaces and analyzed with SA-FAPA-MS. Results indicate a clear trend among the different substrates: Cyano- (CN) and dimethyl- (RP2) modified silica TLCs provided significantly higher analyte ion yields compared to reversed-phase C18 (RP18)-HPTLC and normal-phase (NP)-HPTLC surfaces. PAH solutions with≤ 1 µg/mL could be detected on CN-HPTLC and RP2-TLC surfaces. Characteristic mass spectra for all the compounds were obtained in both positive and negative ion mode. Typically, a higher ion yield could be achieved in positive detection mode. Analysis time per dried analyte residue was typically less than 60 seconds. Complete mass spectral imaging of 23 x 23 mm TLC plates could also be performed (60 min). Overall, SA-FAPA-MS is considered a promising rapid screening method for PAHs.

plasma sources, imaging, environmental science, mass spectrometry, ADI-MS, SA-FAPA-MS, PAH analysis

Shelley et.al., Anal. Bioanal. Chem., 2018, 410(17), 4061-4076.

Andrade et.al., Anal. Chem., 2008, 80(8), 2646-2653

Deciphering microbiological influenced corrosion processes on steel with single cell-ICP-ToF-MS

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Microbiologically influenced corrosion (MIC) is a highly unpredictable process dictated by the environment, microorganisms, and therespectiveelectron source. Interaction pathways between cells and the metal surface remain unclear.[1] The development of this novel single cell-inductively coupled plasma-time of flight-mass spectrometry analytical method and a MIC-specific staining procedure facilitate the investigation of steel-MIC interactions. With this it is possible to analyze the multi-elemental fingerprint of individual cells. The detection method revealed elemental selectivity for the corrosive methanogenic archaeal strain Methanobacterium-affiliated IM1. The interface between material and environmental analysis thus receives special attention, e.g., when considering MIC on solid steel. Hence, the possible uptake of individual elements from different steel samples is investigated. Results showed the cells responded at a single-cell level to the different types of supplemented elements and displayed the abilities to interact with chromium, vanadium, titanium, cobalt, and molybdenum from solid metal surfaces.[2] The information obtained will be used in the future to elucidate underlying mechanisms and develop possible material protection concepts, thus combining modern methods of analytical sciences with materials research.

microbiological influenced corrosion (MIC), single cell-ICP-Tof-MS

Little et.al., Corrosion Science 2020, 170.

Olbrich et.al., Metallomics, 2022;https://doi.org/10.1093/mtomcs/mfac083

Spatial positioning of the re-excitation laser focusing spot in an orthogonal double pulse fs/ns-LIBS configuration

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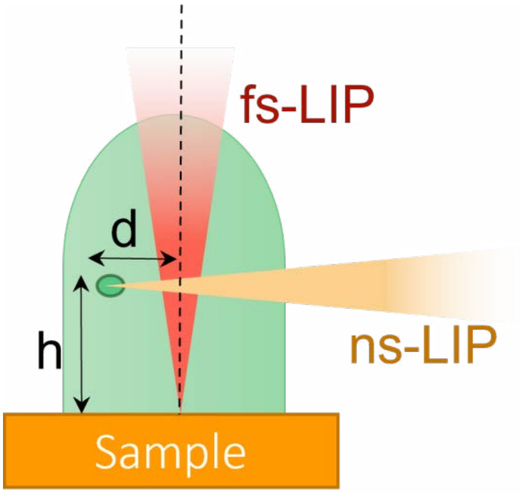
Femtosecond lasers are a useful tool in laser ablation methodologies such as LA-ICP-MS and LIBS, as their ultrashort pulse duration limits thermal effects and preserves ablation stoichiometry, being able to provide remarkable lateral resolutions due to the improved confinement of the of heat-affected region [1]. However, the ultrashort pulse also implies the absence of laser-plasma interaction, resulting in lower excitation temperatures and faster emission decays, which can be an important detriment for spectroscopic analysis. In order to increase emission while preserving the ablation advantages, a double pulse configuration can be implemented to re-excite the ablated matter without further damaging the sample.

In this work, an orthogonal fs/ns-LIBS set-up with a precise positioning system for the reheating laser is presented and a discussion of the effects of changes in the focusing spot position is given, both in terms of height with respect of the sample surface (h) and lateral distance (d) to the fs-LIP (Figure 1). A range of interpulse delay times between ablation and re-excitation lasers is considered throughout the study and fs-LIP plasma diagnostics are carried out in order to provide a better understanding on the observed effects.



LIBS, fs-laser, ns-laser, orthogonal configuration, double pulse, optimization

Singh and Thakur (eds) Laser-Induced Breakdown Spectroscopy (Elsevier, Amsterdam, 2007)

Do We Still Have to Worry about Interferences in ICP-MS?

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[1]PerkinElmer Inc., Shelton, United States

When the first commercial ICP mass spectrometer (ICP-MS) was introduced in 1983, it was of general opinion that this new technology freed analysts from worries about interferences. Many years later, we know that non-spectral and spectral interferences do exist in ICP-MS, but now we have a good understanding of them and over the years, new techniques and technologies have been developed to reduce or eliminate them.

In this poster we will concentrate mainly on spectral interferences removal using a modern spectrometer, such as NexION 5000. The multi-quadrupole technology, in combination with the Universal Cell (UTC) pressurized with pure gases such as O2, NH3, H2 or CH4, can effectively and reproducibly remove interferences leading to improved accuracy, reproducibility and detection limits. The UCT, thanks to its quadrupole design in combination with dynamic bandpass tuning, provides the unique ability of controlling desirable reactions, promoting some weak reactions, rejecting interferences, and preventing side reactions from taking place [1].

ICP-MS, NexION 5000, Spectral Interferences

Badiei et al., “Multimode Cells and Methods of Using Them”, United States Patent 8,426,804 B2, Apr.23, 2013.

Innovative technologies in quadrupole ICP-MS for the determination of ultra-trace levels of As and Se

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[1]Analytik Jena, Saint Aubin, France

Enhancing the analytical performance of ICP-MS instruments is more than ever the key to efficient and reliable routine analysis and result-oriented leading-edge research applications. One of the biggest challenge in ICP-MS is the measurement of arsenic and selenium at ultra trace level, especially in samples containing high contents of chlorine, due to the polyatomic interferences formed in the plasma and the unique isotope of arsenic available.

The new and improved integrated Collision Reaction Cell (iCRC) design of the PlasmaQuant® MS achieves an even greater level of performance in the removal of problematic spectroscopic interferences typically observed with quadrupole ICP-MS. The patented iCRC design works by injecting collisional-helium and reactive-hydrogen gases into the plasma expansion at the skimmer cone tip, removing common plasma and matrix-based interferences that deteriorate the detection limits of important elements like As and Se. The iCRC allows much lower detection limits to be achieved, especially for samples with complex matrices such as hydrochloric acid.

To achieve highest sensitivity and lowest limits of detection for elements measured in reaction gas mode, the patented BOOST technology was used. In BOOST mode, a positive voltage is applied to the skimmer cone allowing to compensate for the loss in sensitivity when using reaction gases.

Nitrogen is a commonly used gas for improving ICP-MS performance by increasing ionization within the plasma, attenuating polyatomic interferences and reducing matrix effects. Particularly for key environmental elements like As and Se that suffer from polyatomic interference and are themselves reported to be only 30-40 % ionized in an argon plasma due to their high ionization potentials.

This work describes the performance of a quadrupole ICP-MS using innovative technologies for the determination of ultra-trace levels of arsenic and selenium.

Nitrogen, Plasma, Skimmer voltage, Arsenic, Selenium, Sensitivity

Plasma propagation through ICPMS interface. Multipin Langmuir Probe measurements of ion beam extraction

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[1]Analytik Jena, Jena, Germany

Typically, quadrupole based ICPMS use classical Compargue Interface having skimmer cone grounded.

Measuring floating skimmer cone potential, we detect +2…+3V under a hot plasma condition. This potential is induced by residual excessive ion concentration in the zone of silence at the tip of the skimmer. It is postulated that the electrons are escaping the ‘zone of silence’ due to the ‘Ambipolar diffusion’ mechanism when the density of electrons (Ne) drops faster than the ion density (Ni) as the plasma expands between the sampler to the skimmer cone. This happens due to higher electron mobility compared to the ion mobility.

We observed that matrix elements can increase plasma potential up to +3…+5V depending on the elements and concentration. This fact alone can explain known ICPMS matrix suppression phenomenon. The main reason for the matrix suppression phenomenon is the additional ion loses due to additional space charge at the skimmer cone tip due to excessive plasma potential.

It has been studied: matrix signal suppression, ion Kinetic Energy Control and ion beam formation.

Experimental device: ICPMS (Analytik Jena) with modified Compargue interface.

Proposed matrix suppression model explains experimental results:

1.Positive skimmer cone voltage reduces matrix suppression.

2.The sensitivity increase x10-100 times is obtained in Collision Cell (iCRC) mode when applying +3…+5V to the skimmer cone.

3.Applying +3…5V to the Skimmer cone increases total ion current extracted from the plasma by a factor of 2 to 3 with unchanged 1mm diameter of ion beam spot, measured by multi-pin electrometer.

The interface details, theory and experimental results will be discussed.

Plasma, ICPMS interface, multipin Langmuir Probe, ion beam extraction, fundamentals

Direct analysis of amino acids with surface-assisted flowing atmospheric-pressure afterglow mass spectrometry (SA-FAPA-MS)

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Ambient desorption/ionization high-resolution mass spectrometry (ADI-HR-MS) enables sample analysis in the native state with little or no sample preparation. Samples can be probed and characterized quickly in less than one-minute analysis time, which is significantly faster compared to classical chromatographic techniques [1].

In this study, thin-layer chromatography (TLC) plates with specific surface chemistries were used as sample support substrates for the direct analysis of proteinogenic amino acids by plasma-based ADI-MS (FAPA, flowing atmospheric-pressure afterglow [2,3]). Analyte ion responses were investigated on different TLC surfaces. Dimethyl (RP-2)- and cyano (CN)-modified silica substrates showed significantly higher intensities for direct amino acids analysis compared to normal-phase (NP)- and reversed-phase-C18(RP-18)-HPTLC surfaces.

Subsequently, the amino acid content was determined by SA-FAPA-MS in both pure-solvent standard solutions and selected real samples (e.g., energy drinks, wine, beer) applied on the aforementioned surfaces. Furthermore, the influence of different dilution solvents on the surface-assisted desorption/ionization process was investigated. The results showed that solvent-surface interactions can affect the signal intensity significantly. Strong diffusion of aqueous sample solutions into the silica-modified surfaces (due to extended evaporation times) resulted in broadened sample spots and reduced signal intensities compared to sample solutions with volatile organic solvents.

plasma-based ADI-MS, SA-FAPA-MS, amino acids, mass spectrometry, plasma sources, imaging, food analysis, sample introduction

Shelley et.al., Anal. Bioanal. Chem., 2018, 410(17), 4061-4076.

Andrade et.al., Anal. Chem., 2008, 80(8), 2646-2653

Methodological platform for the analysis of microplastics in river waters based on single particle ICP-MS

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Nowadays, plastic is a widely used material. As a result, much of the plastic used ends up as waste in the environment, making of it a global problem.It is estimated that around 79% of the plastics produced are discarded to the environment. Rivers are one of these areas. Rivers accumulate an important part of the plastics produced in urban areas derived from wastewater. Wastewater treatment plants (WWTP) can remove around 99% of the plastics present in wastewater1. However, it should be noted that around 80% of the world's wastewater is released untreated into rivers. It is therefore necessary to consider rivers as a sink for microplastics.Due to this environmental threat, in this work it has been carried out a study in different rivers from Spain and France, to know the current situation of these rivers in relation to the presence of microplastics in their waters. A methodological platform based on the use of single particle ICP-MS (SP-ICP-MS), Raman microscopy and Field Emission Scanning Electron microscopy (FESEM) has been used for this purpose. SP-ICP-MS is an element specific technique for particle detection, just providing information about particles containing a certain element, but not about the actual composition of the particles. Therefore, SP-ICP-MS using the 13C isotope 2 was used for a first screening of the samples to detect the presence of particles containing carbon. In addition, Raman and FESEM techniques were used to carry out the confirmation of the nature of the carbon containing particles as microplastics and their visualization, respectively.All the river samples analysed contained plastic microparticles with concentrations over 450 particle per mL. Regarding to their composition, nylon, polypropylene, acrylic rubber and polylactic acid were the particles most commonly detected. Detailed results and sample treatment procedures will be presented.

Acknowledgment

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Microplastic, SP-ICP-MS, Raman, FESEM, River, Carbon, Spain, France, pollution

T. J. Hoellein, et al., Front. Ecol. Environ, 2021, 19, 176–183

F. Laborda et al., Talanta,2021, 221, 121486

Characterization of iron nanoparticles in removal of selected rare earth elements by ICP-MS, AFM and SEM methods

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Over the last decade, zero-valent iron nanoparticles (nZVI) have been the focus of researches in removal of natural water and soil contaminants. Because of their specific surface properties and high reactivity, nanoparticles (NPs) are more efficient in adsorption and reduction mechanisms than iron powder of standard micrometre size. However, nanoparticles tend to oxidize and therefore, their stabilization by surface modifications are widely studied. Chemical modification can improve the dispersion of nanoparticles and their surface activity. Furthermore, modification can enhance mechanical and physiochemical properties of nanoparticles.1 Nanoparticles are studied as an affordable and effective alternative for the removal of contaminants such as toxic metals, organics and microorganisms.2,3 Technologically critical elements such as rare earth elements and actinides are widely used in modern technologies. Due to demanding production technologies and widespread use, these elements are often released in the environment. For this reason, it is quite important to find an effective method for their removal from aqueous systems. Novel approach in recycling of REEs includes the testing of new adsorbent materials such as zero valent iron nanoparticles.

The aim of our study was to characterize bare zero-valent iron nanoparticles and nanoparticles modified with dipicolinic acid. Nanoparticles were synthetized using borohydride reduction of iron ions followed by addition of dipicolinic acid using different molar ratios. The adsorption efficiency of metal ions (Nd3+, Eu3+, Er3+, Gd3+, UO2(2+)) from aqueous solutions was monitored by inductively coupled plasma mass spectrometry (ICP-MS). Nanoparticles were characterized by structural analysis methods such as atomic force microscopy (AFM) and scanning electron microscopy (SEM-EDS). The obtained results show that chemical modification of nanoparticles and adsorption of selected ions on nanoparticles affect their size and structure.

iron nanoparticles, adsorption, REEs, ICP-MS, characterization, AFM, SEM

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Using metal labels for the determination of nucleic acids (DNA and miRNA)

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The high sensitivity of ICP-MS as a technique for the detection of trace metals has opened the door in the last years to their use as labels to allow the specific detection of low abundant biomarkers. These molecules, usually formed by a backbone of C, O, N, P and/or S, can be hardly detected by ICP-MS in their native forms. However, the use of specific reactions with metal-containing labels can boost the detection capabilities of protein and nucleic acid biomarkers. For proteins, direct labelling strategies using macrocyclic metal chelators, such as DOTA or DTPA have been reported. Immunolabelling reactions are much more commonly used due to their high specificity and the availability of metal labels specifically designed to use antibodies as metal tags against their antigens. However, the use of metal labels to specifically detect and quantify nucleic acid sequences by ICP-MS needs slightly different approaches that will be explored in this presentation. Flow cytometry has traditionally used fluorescent tags, such as propidium iodide, as a way of detecting cell nuclei and even quantifying their DNA amount for a wide variety of applications, such as cell-cycle determination, chromosome number determination, apoptosis markers or direct DNA quantification. The use of single-cell ICP-MS analysis in the last years needs new DNA stains that make these applications achievable by this technique, specially with the generalization of the use of mass cytometry. For this aim, metal-based DNA intercalators are commercially available for cell identification. This presentation will discuss the quantitative aspects of a commonly used metal DNA intercalator for DNA quantification at the single cell level by single-cell ICP-MS. Quantification of specific nucleic acid sequences is specially challenging and, in this regard, detection and quantification of micro-RNA sequences (miRNAs) is nowadays gaining importance due to their implication in many physiological and pathological processes, such as cancer and many other diseases. miRNAs are small non-coding RNA sequences of around 20 nucleotides that regulate over 60% of human protein expression and are dysregulated as a consequence of both benign (e.g. in response to physical exercise or stress) and malign processes, such as cancer(1). We have developed a new methodology to detect and quantify miRNAs based on nanoparticle labelling and detection by single-particle ICP-MS that will be presented here.

single-cell ICP-MS, single-particle ICP-MS, DNA quantification, miRNA, gold nanoparticles, metal labelling

J.T. Mendell, Cell, 2012, 148, 1172-1187

Determination of metallic nanoparticles in soils by single particle ICP-MS after a microwave-assisted extraction treatment

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Our current knowledge about NMs impact on human health and the environment is still limited and further research efforts are required to properly understand their effects on human health as well as their fate and behaviour in the environment. To this end, new analytical methods are required for assessing NMs exposure, particularly for complex matrices such as soils [1]. Several methodologies have been proposed for NMs characterization in soils, but they are time consuming and do not fulfill quantitative recoveries [2]. In fact, contradictory reports can be found in the literature, probably due to a lack of control of soil physicochemical properties. A priori, microwave (MW) assisted extraction procedures could be highly beneficious to improve current shortcomings of NMs analysis in soils [3]. To the best of authors' knowledge, this approach has not yet investigated for soils.

The goal of this work was insight into NMs determination in soils samples by means single particle inductively coupled plasma mass spectrometry (spICP-MS) after a microwave-assisted extraction treatment. To this end, five soils samples covering different physicochemical properties (i.e., pH, organic matter, texture, etc.) were selected. Next, the influence of extraction conditions on Au and Pt nanoparticle (NP) concentration number and size have been systematically evaluated. Microwave-assisted was highly beneficial to improve Au and PtNPs recovery without affecting particle size distributions. In general, maximum NPs recoveries were obtained for MW power 800 W, extraction time 15 min and NaOH 0.01 M. Soils texture was critical on Au and PtNPs recovery. Under optimum experimental conditions, quantitative NPs recoveries (80-110%) were achieved for sandy soils but not for clay soils (50%).

Single particle ICP-MS, Metallic NPs, Extraction, Soils, Microwave

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SP-ICP-MS for the caracterization of engineered nanowires and nanorods of different metals

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Traditional therapeutics of cancer show limitations such as drug resistance or several adverse effects. To overcome these limitations and to develop more efficient and less invasive treatments, multifunctional nanosystems can be used as delivery systems. The most important advantages that these nanosystems show are an enhanced treatment efficiency and a decreased drug toxicity by gaining specificity towards tumor cells (1).

One of the most used nanosystems for this purpose are iron nanowires (Fe NWs). These magnetic nanowires bring many advantages over traditional NPs in terms of the application into therapeutics: they show a larger surface area and can be easily (bio)functionalized to enhance their biocompatibility, leading to a more selective intracellular drug delivery while side effects are lowered. Another nanosystem with these biomedical applications are platinum nanorods (Pt NRs) (2). They are used for the latest therapeutic strategy to treat cancer, photothermal therapy (PTT): a minimally invasive platform that induces selective ablation of cancer cells by heat generated in tumor tissue exposed to near-infrared (NIR) light. Pt nanorods are the best potential photothermal therapy agent as they exhibit strong light absorption and efficient light-to-heat conversion.

Since the synthesis of these nanostructures can be rather complex, the first step consists on their structural and quantitative characterization. For this aim, single particle ICP-MS strategies can be applied to obtain information about the synthesis reproducibility and the mass of element per nanorod/nanowire, which is a basic information required for future biological applications.

Nanowires, nanorods, SP-ICP-MS, drug delivery, photothermal therapy.

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The investigation of Au and FexOy nanoparticles in aqua-organic solutions by single particle sector field ICP-MS

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The development of the fields of nanomaterials application is the push for the appearance of innovative analytical methods necessary for monitoring nanoparticles (NPs). In NP, the amount of the element is at the ultratrace level – 10-12-10-15g. Of the modern spectral methods of analysis, only mass spectrometry can provide such a low level of determined amount. The single particle mode (SP) is widely used in combination with quadrupole mass spectrometers (ICP-QMS) and has been adapted to this method. However, the high sensitivity and selectivity of the sector field ICP-MS (ICP-SFMS) open up additional capabilities.

The behavior of gold, magnetite and maghemite NPs in aqua-organic media was studied by single particle ICP- SFMS (ELEMENT XR spectrometer (Finnigan MAT., Germany). We used gold and magnetite (Fe3O4@Na3Cit, Fe3O4@SiO2) NPs synthesized under microwave heating (GEOKHI), as well as magnetite (Fe3O4@SiO2, AllRun, China) and maghemite (Fe2O3@SiO2, DNA Technology, Russia). NPs were characterized by UV-Vis-spectrophotometry, dynamic light scattering and scanning electron microscopy methods.

Based on the experimental data, the optimal conditions for the synthesis of gold and magnetite NPs were chosen; the average value of the limit of determining (LODNPs) the size of gold NPs in the selected instrumental parameters was calculated.LODNPs was 3 nm, this is about an order of magnitude below the limit of detection by the SP-ICP-QMS method with a quadrupole. The measurements of magnetite and maghemite NPs were carried out on the 56Fe in the medium resolution mode. The conditions for determining the size of Fe NPs 10 nm (Fe3O4@Na3Cit) were chosen. LODNPs, the average mass of an element in NPs and the particle number concentrations were calculated. The developed signal processing platform is used to study the behavior of NPs in aqua-organic solutions simulating the composition of biological media.

Nanomaterial, gold, magnetite, maghemite, single particle, ICP-SFMS

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Characterization of biogenic selenium nanoparticles produced by Haloferax mediterranei using single particle ICP-MS

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Selenium nanoparticles (SeNPs) have attracted substantial attention due to their antibacterial, antioxidant, and anticancer properties. Different strategies have been proposed for SeNPs synthesis, but biological methods are particularly advantageous in terms of sustainability and biocompatibility. Haloferax mediterranei belongs to the group of halophilic archaea, one of the predominant microbial populations in hypersaline environments. This microorganism has shown potential industrial applications as a cell-factory for polyhydroxyalkanoates and carotenoids production [1]. Recently, it has also been observed that Haloferax mediterranei produces SeNPs, but limited information is known about the biogenic synthesis procedure and SeNPs characteristics.

Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a powerful technique for nanomaterials characterization and it has already been employed for the characterization of SeNPs produced by different microorganisms [2,3]. Nevertheless, because the high salt content present in culture media employed for Haloferax mediterranei growth (>20% NaCl), the use of SP-ICP-MS for SeNPs characterization is rather challenging due to strong non-spectral interferences. The goal of this work was to develop a methodology for SeNPs characterization in salt rich media by means of SP-ICP-MS. To this end, plasma experimental and cell gas conditions were optimized for SeNPs determination in water and high saline standards. Next, different strategies were evaluated to mitigate matrix effects. Finally, SeNPs produced by Haloferax mediterranei were characterized by the proposed method.

Selenium, Nanoparticles, Haloferax mediterranei, Single particle, ICP-MS

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Detection of silver species in tissues and faeces from animals fed with silver-basednanomaterials by Laser Ablation-Single Particle-Inductively Coupled Plasma Mass Spectrometry

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The excessive use of antibiotics against pathogens can lead to the so-called "antimicrobial resistance". Thus, the investigation of new antimicrobial agents of different origins to replace antibiotics is an urgent need. Silver in its different forms is a potential feed additive acting as an antimicrobial agent1. In this study, different tissues (liver, muscle, kidneys) and faeces samples from "in vivo" experiments were analyzed involving pigs and chickens fed with feeds containing a silver-based nanomaterial at silver concentrations of 20 or 200 mg kg-1. The objectives were to study the fate of the ingested silver, its accumulation in the different tissues and excretion, and whether silver is present in ionic or particulate forms. ICP-MS in conventional mode was used for the quantitative determination of total Ag in the different organs and faeces. Results showed that Ag accumulated in liver (0.15-5 mg kg-1) and kidney (0.4 mg kg-1) but not in muscle. Whereas the major part of silver was eliminated. Differentiation of ionic and particulate silver was performed by ICP-MS in single particle mode, but using a recently developed direct approach based on the laser ablation of the solid samples (LA-SP-ICP-MS). This technique has been used for bioimaging and studying the distribution of the silver species in liver and faeces of pigs and chickens. Ag(I) and AgNPs standards in gelatin were used for calibration and quantification purposes2. The quantification of AgNPs standards by LA-SP-ICP-MS was done using an in-house MatLab script developed by Metarapi et al.3 Laser ablation results revealed a silver concentration of 2 mg kg-1 in livers of pigs fed the diet of 200 mg kg-1 of Ag, whereas for the rest of tissues and diets, silver was below the attainable detection limits. Silver found in pig livers was present in the outer layer of the lobule in ionic form, confirming that silver was absorbed in the intestine in ionic form. LA-SP-ICP-MS analysis of pig faeces confirmed the presence of high concentrations of silver, detecting the presence of particles containing silver with average masses of 520 ag while in the rest of samples only ionic silver was detected. LA-SP-ICP-MS was applied for the first time to the analysis of tissues and faeces of animals fed with silver-based nanomaterials, showing promising result for the differentiation of Ag(I) and AgNPs.

Nanomaterial, Ag(I), Ag nanoparticles, in vivo, distribution, tissues, faeces, LA-SP-ICP-MS

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Single particle ICP-MS analysis using 3D-printed nebulizers and spray chambers

Gyula Kajner[1], Ádám Bélteki[1], Martin Cseh[2], Balázs Vajda[2], Zsolt Geretovszky[2], Enikő Papp[3], Mihály Braun[3], Gábor Galbács[1] ,

[1]Dept. of Inorg. and Anal. Chem., Univ. of Szeged, Szeged, Hungary, [2]Dept. of Opt. and Quant. Electr., Univ. of Szeged, Szeged, Hungary, [3]Nucl. Res., Hun. Acad. of Sci., Debrecen, Hungary

The relatively novel technique of single particle inductively coupled plasma mass spectrometry (spICP-MS) is a powerful tool for the characterization of nanoparticle (NP) or cell dispersions. This technique can provide information regarding elemental or isotope composition of individual particles, as well as the size distribution and particle number concentration (PNC) of their dispersions with great statistical relevance. It has been shown that by utilizing low sample consumption, high transport efficiency nebulizers which facilitate monodisperse droplet formation, coupled with low volume spray chambers, the performance and efficiency of this technique can be further enhanced. The higher sensitivity, lower limit of detections, and decreased sample consumption these accessories provide, come in handy considering the ever-increasing demand for determining the above mentioned characteristics of cell or NP dispersions using lower sample volumes and concentrations [1,2].

In this study we present an alternative, high efficiency, custom sample introduction system which enhances the capabilities of the spICP-MS technique and facilitate analytical applications. The system consists of a high efficiency nebulizer, and a low memory effect, high transport efficiency spray chamber which were both manufactured utilizing a high resolution 3D printer. The geometry of these tools was designed to be compatible with our Agilent 7700X ICP-MS instrument, and our previously reported custom microfluidic chips which can perform sample preparation steps in an on-line manner [3]. The operation of the tools in question were optimized via several hydrodynamic simulations utilizing COMSOL Multiphysics software prior to their production.

The finished design was subjected to experiments examining their operational features and comparing their capabilities to that of the default ICP-MS sample introduction system. Characteristics such as transport efficiency, aerosol droplet size distribution, memory effects, and limits of detection in terms of nanoparticle size and how these properties are affected by the gas flow rates were assessed.

3D printing, Nanoparticles, Nebulizer, Spray chamber, spICP-MS

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Poster - Mo 51 Nanomaterials

Electrochemical cell coupled with ICP-MS as a tool to measure online dissolution of electrocatalysts

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The poster presents the utilization of an home-made electrochemical cell coupled with ICP-MS to study the dissolution of electrocatalysts during the oxygen reduction and oxygen evolution reactions.

This special set-up allows online ppb-range time- and potential-resolved dissolution dynamics of metals. For example, different Pt-alloys could be compared to highlights differences in dissolution mechanism due to the less noble metals.

In addition, several parameters of the set-up were investigated and the impact on the dissolution profile are presented.

Electrocatalysts, Stability, OER, ORR

Microwave digestion and ICP-MS analysis of antimicrobially active microcapsules

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For the purpose of this investigation, a sensitive and rapid inductively coupled plasma mass spectrometry (ICP-MS) spectroscopy was applied in determination of antimicrobialelements if the core/shell of microcapsules. Microcapsules of different sizes (120 and 450 μm) and chemical composition were prepared with zinc and sodium alginate in the shell (with or withouth chitosan), as well as filled with the antimicrobial silver in the core. After preparation, the samples were digested in an microwave oven using 55.55% v/v HNO3 and 44.45% v/v H2O2. Digested samples were transferred to ICP-MS and analysed with aim to monitor the levels of zinc and silver, both being powerful antimicrobial agents. The results show that there is a significant difference in levels of antimicrobial metals between samples prepared with and without chitosan. Whilst Zn levels appeared marginally higher (up to 20 %)in the group of samples prepared without chitosan, compared with the group with it, the Ag content showed larger overall variability (more than 72%). Particularly, smaller microcapsules (120 μm), had the following elemental composition of antimicrobial metals: 98.32 μg/g of Ag and 106.75 μg of Zn. In contrast, three times larger microcapsules (450 μm) contained two times higher amounts of silver (190.98 μg/g) and only 20 % higher amounts of zinc (121.35 μg/g). Nevertheless, after performing the leaching experiments,obtained results proved that the amounts of antimicrobial elements were high enough for efficient antimicrobial activity of newly prepared microcapsules. Therefore such samples can be efficiently applied as antimicrobial coatings on many different items.

ICP-MS; microcapsules; microwave digestion; silver; zinc

A new approach to determining the particle transport efficiency of ablation cells

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Transport efficiency is a fundamental factor in developing an ICP-MS method. The transport efficiency is calculated as the ratio of the analyte amount present on the sample to the amount of analyte reaching the detector. Transport efficiency can be determined for both nebulizer and laser ablation sample introduction systems. Each of these conventional methods has certain limitations, e.g., direct methods do not describe the whole system, but only the nebulization efficiency; indirect methods such as particle size method, and particle frequency method rely on concentrations and sizes of nanoparticles reported by the manufacturer, which may deviate slightly from reality.

This poster presents a new method for determining the transport efficiency of LA-ICP-MS systems. Samples are prepared by precise dispensing of small volumes of nanoparticle suspension using a piezoelectric dispenser and subsequent analysis of the deposited droplets using scanning electron microscopy as a reference method to determine the actual number of nanoparticles. As the next step, IR-LA-SP-ICP-MS analysis is performed. The transport efficiency is calculated as the ratio between the nanoparticles reaching the detector in the ICP-MS system and the number of nanoparticles determined by scanning electron microscopy. Our approach should provide more accurate and robust results than conventional methods for determining transport efficiency.

IR-LA-SP-ICP-MS, Transport efficiency, nanoparticle counting

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SP-ICP-MS analytical parameters for Au, Ag, SPIONs, CeO_2 and ZrO_2 nanoparticle characterization toward Nanotheranostics

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Nanotheranostics aims to perform a premature and non-invasive diagnosis combined with therapy focused on the specific place where the disease is, without affecting the surrounding healthy cells by using nanomaterials[1]. Nanoparticles (NPs) have unique mechanical, optical, magnetic, electric, and structural properties due to their size and surface/volume ratio. Furthermore, at the nanoscale the particles are more bioactive and more chemically active, allowing easy entry into cells and organs.

Nanotheranostics studies are performed using different nanoparticle compositions and size distribution depending on the target disease. Gold nanoparticle (AuNP) is widely used for the diagnosis and treatment of many diseases. Due to their optical properties, they are used as contrast agents and photothermal therapy [2]. Silver nanoparticles (AgNP) are mainly used for antimicrobial and antiviral biomedical applications. On the other hand, SPIONs are used for their magnetic properties. They are used as an FDA-approved contrast agent for magnetic resonance imaging. Cerium oxide nanoparticles (CeO_2NP) are mainly used as antioxidant agents because they have a unique electronic structure that provides multi-enzyme mimetic properties. Finally, Zirconium oxide nanoparticles (ZrO_2NP) have antifungal and antimicrobial properties [3]. In this context, analytical techniques are required to characterize NPs as well as their interaction with cells. Nowadays there are some NPs characterization techniques: SP-ICP-MS, TEM, DLS, NTA, etc.; where each technique provides different information. Particularly, Single-Particle ICP-MS (SP-ICP-MS) not only provides the size distribution and concentration of NPs but also provides the concentration of the dissolved element in the suspension. In this work, methods for NPs characterization by SP-ICP-MS have been developed for AuNP, AgNP, SPIONs, CeO_2NP, and ZrO_2NP and their analytical parameters have been evaluated. For each type of NPs, detection limits have been estimated. Linearity for particle size and particle concentration has been studied. In addition, accuracy and repeatability have been determined for both particle size and particle concentration measurements.

Nanotheranostics, SP-ICP-MS, characterization, AuNP, AgNP, SPIONs, CeO_2NP, ZrO_2NP

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Determination of target proteins in immortalized and primary RPE cells by sc-ICP-MS using metal nanoclusters as labels

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Traditionally, cellular samples have been analysed by conventional nebulization ICP-MS after digestion of the cell, providing information of the whole population as an average (i.e., information regarding individual heterogeneity is lost). However, it is well known that cell populations have a heterogeneous nature and, thus, the study of cell populations on a cell-to-cell basis is frequently required.

The determination of the elemental composition of individual cells can be successfully achieved employing single cell (sc) ICP-MS (1). This technique allows the quantitative study of endogenous elements in cell populations. Furthermore, the combination of sc-ICP-MS with immunocytochemistry makes it possible to determine proteins in individual cells. In this case, the cellular samples are subjected to an immunoassay using an elemental label for detection (e.g., DOTA, MAXPAR, or nanoparticles).

In this work, a biomarker strategy employing metal nanoclusters (MNCs) as elemental labels for the sequential determination of membrane and cytosolic proteins in individual human retinal pigment epithelial (RPE) cells was performed by sc-ICP-MS. The proposed methodology is based on immunoassays in cell suspension using MNCs conjugated to protein specific antibodies for protein determination in individual RPE cells (ARPE-19 and primary human fetal RPE cell lines). For such purpose, NCs of two different metals were evaluated as labels: AuNCs and IrNCs. The metal to antibody stoichiometry in the Au and Ir labelled immunoprobes was determined in order to provide quantitative determination of the target proteins in individual cells.

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Single cell ICP-MS, Metal-tagged antibodies, Nanoclusters, Proteins, RPE cells

Corte-Rodríguez et al. Trends Anal. Chem. 2020, 132, 116042.

Poster - Mo 56 Nanomaterials

Investigation of microplastic size and number changes during simulated UV-degradation using single particle ICP-MS/MS

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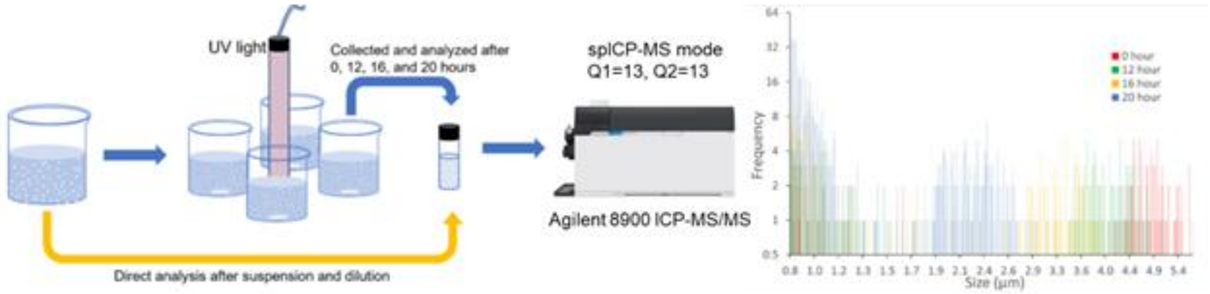
Plastic contamination and plastic contaminating water are concerning issues since plastics never fully degrade but fragment, generating particles in the millimeter to nanometer diameter size range. The full extent of the risks posed by microplastics (MPs) is still unknown, hence the need for reliable particle analysis and particle size analysis methods. Recent studies have shown that spICP-MS can quantify polystyrene (PS) MPs particle sizes and number concentrations by monitoring 13C (1), we further developed the spICP-MS method to quantify the particle number and size of PS MPs during UV-degradation in a lab simulation environment.

The ICP-MS/MS was operated in MS/MS mode to benefit background signal control. The method provided accurate quantification of microplastic particle sizes and number concentrations over a wide size-range covering the submicrometer (0.8 μm) to micrometer (5 μm) scale. The number concentration detection limit ranged from 2.0 × 10^6 to 6.9 × 10^6 particles/L due to the nebulizer efficiency of different sized particles varies significantly (2). The results showed clear fragmentation of PS MPs over time, with the generation of large numbers of nano- and micro-sized particles over 20 hours of UV-light



Microplastics, spICP-MS, size distribution, particle concentration

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Identification of selenoneine and ergothioneine in highly consumed fish and fish-based products

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Selenoneine (2-selenyl-Nα, Nα, Nα-trimethyl-L-histidine), which is a novel Se-containing compound, is the selenium-analogue of the sulfur-containing ergothioneine and it has been identified as a major form of organic selenium in the muscle of tuna, among other tissues (1). Both selenoneine and ergothioneine are not synthesized by humans. However, their dietary intake is of huge significance because they are strong antioxidants and, concerning selenoneine, it is thought to play an important role in the Hg detoxification process (2). Nevertheless, the role of these compounds still remains unknown and new perspectives are needed to be opened. Until now, the vast majority of studies are focus on the identification of selenoneine in fish samples (3). Nevertheless, its simultaneous identification with ergothioneine has never been studied, as well as its presence in highly consumed fish products, such as lump, salmon and trout eggs or surimi and surimi-derived elvers. In this work, the distributions of Se and Hg-containing biomolecules have been investigated by high-performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS) in the water soluble fraction of edible fish and derived products. For this purpose, two size-exclusion chromatography (SEC) columns were employed, having different range of molecular weights separation (3-70 and 100-600 kDa, respectively). In general, Se is bound to lower molecular weight biomolecules than Hg. Furthermore, ICP-MS analysis together with experimental designs were used to optimize extraction conditions of water soluble proteins. Best extraction conditions were found when using ammonium acetate and ammonium formate as extractants. Afterwards, a chromatographic method was developed by high-performance liquid chromatography/electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS), using a reversed-phase C18 column, for the identification of selenoneine, ergothioneine and other organic selenium compounds in the resulting extracts.

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speciation, selenium, selenoneine, ergothioneine, HPLC-ICP-MS, fish-based products

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Analytical approaches to study the metabolism of different arsenic forms in Tilia cordata Mill

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Soil contamination with arsenic poses danger both to humans and the environment. Phytoremediation, the use of plants to remove pollutants, is regarded as a promising and sustainable solution to this problem. Furthermore, dendroremediation (the use of woody plants) is an appealing method because of survivability and easy adaptation of trees, undisturbed growth, and effective phytoextraction of other metals/metalloids.

In order to test the potential for bioaccumulation and transformation of arsenic by Tilia cordata Mill. an experiment was performed. Tree seedlings of this species were grown for 33 days in the hydroponic culture supplemented with different arsenic forms: As(III), As(V), and DMA (dimethylarsinic acid), collected and studied.

The total concentration of arsenic in these plant samples was determined using ICP MS. Arsenic concentration changed through the duration of the experiment. The accumulation of arsenic and its progression varies between the supplemented arsenic forms.There is a significant difference in the arsenic concentration between the organs which highlights the process of upward translocation of arsenic compounds. A series of extraction procedures in diverse sequences using different extractants (water, water-ethanol, SDS) supported with sonication and enzymatic-assisted extraction were carried out and their efficiency was compared. To assess the speciation of arsenic present in the extracts, a HPLC-ICP-MS methods were applied. The use of an anion-exchange chromatography allowed for the separation of inorganic arsenic forms. Changes in the peak heights indicate transformations occurring between them. Additionally, when applying reverse-phase separation with a C-18 column three groups of peaks that represent organic arsenic compounds were detected.

This presentation will discuss the explored extraction procedures allowing to increase significantly extraction yields for As from tree material. In addition, the development of purification methods permitting the discovery of new As metabolites will be shown.

arsenic speciation, extraction efficiency, ICP MS, ESI MS, dendroremediation

Measurement of gadolinium-based contrast agents in wastewater treatment plants.

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Gadolinium (Gd) based contrast agents (GdBCAs) are often administered to patients for magnetic resonance imaging (MRI) to increase tissue contrast. After examination they are excreted through the urine and enter the wastewater system. GdBCAs are not efficiently cleaned up in the wastewater treatment plants and can enter surface water through wastewater effluent. The use of GdBCAs increased over the years, however, there is still a lack of data regarding human exposure. In this study, we investigated the total Gd and GdBCAs content of wastewater influent, effluent, and river water from 2 wastewater treatment plants from Styria, Austria. We found total Gd content to be 0.2 – 0.9 µg/L in the influent and effluent, while in river water it is around 0.05 µg/L. GdBCAs are also found in the influent and effluent with a concentration between 0.2 and 0.6 µg/L.

Gadolinium, MRI contrast agents, speciation

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Determination of the affinity of stripping molecules for Lanthanides (III) by HILIC coupled to ESI-MS and ICP-MS using isotope dilution

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In the energy sector, recycling recoverable materials presents a societal and economic challenge. Concerning the nuclear fuel cycle, selective recovery of minor actinides, americium (Am) and curium (Cm), to partially or totally recycle them is considered a promising strategy by few countries. Am and Cm, although representing only 1% by weight of spent nuclear fuel from current light water reactors, are responsible for much of the radiotoxicity and long-term heat power of final nuclear waste [1]. Several studies are focused on the development of efficient and selective extracting/stripping molecules to set up dedicated treatment processes [2]. The development of analytical methods allowing the online determination of the selectivity of molecules towards the targeted elements, while reducing the consumption of materials, effluent volumes and the time devoted to screening experiments, is essential. To meet this aim, the strategy of this work was based on the simultaneous coupling of a separation technique (HILIC) to electrospray ionization source mass spectrometer (ESI-MS) and inductively coupled plasma source mass spectrometer (ICP-MS) [3]. This powerful approach allowed, online and simultaneously, the structural, multi-elemental and isotopic characterization of the chemical species previously separated. Hence, intensified and quantitative screening of the complexation properties of chelating molecules towards elements could be performed. This approach has been applied to determine the scale of affinity and selectivity of stripping molecules (diamine chelating agent TPAEN, nitrogenous macrocycle NMand triamine chelating agent DTPA) for Sm and Nd used as of analogues of Am and Cm. The HILIC conditions have been optimised to separate the Sm and Nd complexes formed with the three molecules and very good recovery percentages were obtained, between 104-109% for TPAEN, 75-107% for NM and 99-102% for DTPA. A quantification method using isotope dilution was developed and validated, which made it possible to quantify precisely and online the distribution of Sm and Nd in the separated complexes. Hence, these results allowed evaluating an affinity scale of DTPA followed by TPAEN and finally NM for the two lanthanides of interest.

Lanthanides, stripping molecules, affinity, HILIC, ESI-MS, ICP-MS, isotope dilution

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Quantitative determination of Zn and metallothioneins in an inflammatory cell culture model by IDA/IPD-SEC-ICP-MS

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Dietary supplementation with Zn and vitamins has been proven beneficial for the slow-down of age-related macular degeneration (AMD), a prevalent eye disease that affects almost 200 million people in the world, with the highest incidence on the elderly. AMD causes the progressive degeneration of a specific structure of the retina, the retinal pigment epithelium (RPE), which leads to uncontrolled inflammation, the death of photoreceptors and the irreversible loss of vision. The molecular mechanisms through which Zn reduces AMD advance may include the synergic regulation of the metallothioneins (MTs), one of the main cytosolic Zn buffering proteins.

In this study, we established a cell culture model of primary human RPE to investigate the role of the Zn-MTs system against pro-inflammatory stress. First, differentiated RPE cells were supplemented with isotopically enriched 70ZnSO4 using different concentrations (100, 200 and 300 µM) and treatment durations (7, 14 and 21 days). Natural and exogenous (70Zn) zinc were quantified by isotope pattern deconvolution (IPD)-ICP-MS to determine the turnover of the element, while MTs and Zn-MT ratio were determined by size exclusion chromatography (SEC)-IPD-ICP-MS. Optimum concentration of Zn supplementation, i.e., 100 µM ZnSO4, was used for 7-days treatment of differentiated RPE cells subjected to pro-inflammatory stress, where total Zn, MTs and the Zn-MTs system were determined by conventional nebulization or SEC- isotope dilution analysis (IDA)-ICPMS.

This work highlights the applicability of chemometric tools and MS hybrid techniques, combining SEC and ICP-MS for elemental speciation studies in cellular models of relevant diseases like AMD, emphasizing the protective role of Zn against the in vitro inflammation of the RPE.

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Speciation, IDA, IPD, Size Exclusion Chromatography, Zinc, Inflammation, Cellular model

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HBM4EU Study – Assessment of Occupational Exposure to Hexavalent Chromium

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Background

Hexavalent chromium (Cr(VI)) is an important occupational carcinogen. In addition to air monitoring, biomonitoring is commonly applied to monitor exposure to Cr(VI). Within the EU biomonitoring initiative, HBM4EU, we explored the applicability of different biomonitoring methods in the assessment of occupational exposure to Cr(VI) in welding and surface treatment activities.

Objectives

A multi-center cross-sectional study was performed in Belgium, Finland, France, Italy, Poland, Portugal, the Netherlands, Luxembourg and United Kingdom. Harmonized procedures were used to collect biological and industrial hygiene samples. Contextual information was collected using questionnaires. Altogether 602 exposed workers and controls were included in the study. Exposure biomarkers studied included urine, red blood cell and plasma chromium, and exhaled breath condensate (EBC) speciation of Cr(VI)/Cr(III). Urine, blood and plasma samples were analysed by either GFAAS or ICPMS. Analysis of the EBC samples was performed using hyphenated LC-ICPMS, μLC-ICPMS or IC-ICPMS and speciation was achieved using anion exchange columns.

Results

All exposure markers showed highest exposure levels among chrome plating workers. Urinary chromium showed a good correlation with air Cr(VI) in bath platers and welders. Observed low correlations between different exposure biomarkers suggest that these approaches are not interchangeable but rather complementary.

Conclusion

In conclusion urinary chromium showed its value as the first approach for the assessment of internal exposure to Cr(VI). At low exposure levels paired samples are recommended. Chromium in red blood cells and plasma as well as chromium species in exhaled breath condensate were shown to provide additional information when more specific information on exposure is needed.

HBM, chromium, EBC, Blood, urine, biomonitoring

Poster - Mo 63 Speciation

Simultaneous qualitative and quantitative HPLC-ICP MS and ESI MS assessment of selenium and sulfur metabolites in turkey liver

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Selenium (Se) is an essential trace element for higher animals and humans. Supplementation with Se, either in naturally-occurring feedstuffs, as inorganic Se, or as organic Se compounds, results in increasing concentrations of tissue Se.At the same time, selenium is often believed to follow the metabolic pathways of sulphur but according to our best knowledge till now there was no detailed study attempting to assess at the same time the metabolic changes of selenium and sulphur metabolites in the animal samples.

The study consisting of feeding turkey poults with the basal diet supplemented with four different selenium doses (0, 0.4, 2 and 5 µg Se/g diet) was carried out°. The water extracts of turkey liver samples were analyzed in parallel by ICP and ESI MS. The use of the new NexION 5000 multi-quad ICP MS offered a unique opportunity to quantify with accuracy both S and Se and to characterize tissue Se/S accumulation in turkey poults fed different levels dietary inorganic Se on elemental level.The study demonstrated that excess dietary Se up to 2 µg Se/gdid not dramatically impair growth or alter selenoenzyme activity or selenoprotein transcript expression in the young poult. What's more, Se concentration in extrahepatic tissues does not notably rise (less than 2 times) above Se adequate levels (0.4 µg Se/g) with dietary Se supplemented as high as 5 µg Se/g (1).

The presentation discusses the development of the methodology allowing simultaneous identification of low molecular weight selenium and sulphur compounds, present in turkey liver at different supplementation levels. In addition, lack of unspecific incorporation of Se (as selenomethionine) in proteins is demonstrated for both water soluble and insoluble proteins. The developed methodology will allow understanding of mutual dependence of sulfur and selenium metabolic processes such as possible Se metabolism by sulfur metabolizing enzymes, and explain lack of apparent Se toxicity effects on transcription in case of administration of high doses of selenium.

° Partially supported by: NIFA, USDA, 1016808, Multistate NC-1170

selenite supplementation, selenium and sulphur speciation, selenosugars, ICP MS, ESI MS

Taylor et. al.,Poult Sci 2019;98:855-65

Poster - Mo 64 Speciation

Determination of arsenic species in biological samples using IC-ICP-MS

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The Flanders Environment Agency (Flemish Government) is responsible for the monitoring of the state of the environment in de Flanders Region. This involves monitoring of water, air, sediment and biota.

Biological samples consist of fish and mussels. The samples are processed, frozen and pretreated by freeze drying followed by grounding in a ball mill. Before analysis, arsenic species are extracted overnight with a diluted mixture of nitric acid and hydrogen peroxide and subsequential heating in a waterbath at 90 °C for 1 hour. Finally the extract is centrifuged and filtrated over a 0.45 µm syringe filter before analysis. After extraction, inorganic arsenic is convereted to As(V). Certified Reference Materials are treated in the same way.

Analysis is performed using an inert IC-ICP-MS system. The IC system consists of a refrigerated autosampler, a heated column compartment @ 45 °C and an IC-pump. The stationary phase consists of a guard column and an analytical anion-exchange column. As a mobile phase, ammonium carbonate solutions in a concentration of 10and 200 mmol/L are used. Sample injection voluime is set to 25 µL @ 0.4 mL/min flow rate. The IC is coupled with a SQ-ICP-MS system tuned for highest sensitivity @ mass 75. Calibration of the system is performed using 6 reference standards of As(V), AsB, As-MMA, As-DMA and AsC in a range of 0.1 to 25 µg/L.Analytical performance is checked with a procedure blank, independant control standards @ concentrations of 0.5 and 10 µg/L and Certified Reference Materials. The retention time is monitored for stability. Total analysis time is about 6 minutes in which all species are separated using gradient elution.Laboratory performance is monitored by participation in interlaboratory comparison studies.

The expanded uncertainty of measurement at a 95% confidence level (k=2) varies between 24 and 33 %. After validation the method was accredited by BELAC according to ISO 17025:2017 for all species, except the AsC.

Dominant species to be found in the samples are AsB and As-DMA. Inorganic arsenic is only detected in a few samples.

Speciation, arsenic species, biological samples

Speciation of Chromium using µLC-ICP-MS: Method development and validation

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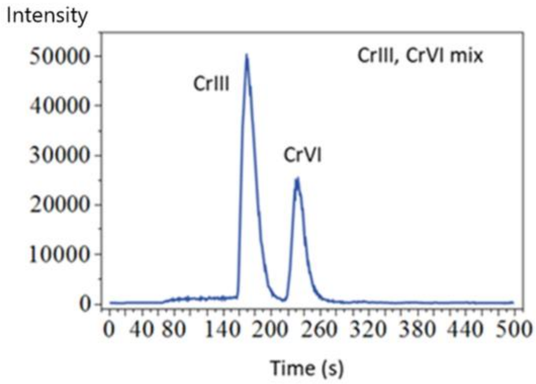
Chromium (Cr) is a transition element that exists in oxidation states ranging from - 2 to +6. The common stable ones in the environment are trivalent Cr(III) and hexavalent Cr(VI) chromium. Cr(III) is an important micronutrient, while Cr(VI) is carcinogenic. The environmental concentrations of both oxidation states are low. Due to the differences in toxicity between Cr(VI) and Cr(III) compounds, speciation of Cr is important. Therefore, an improved sensitive and robust method for the simultaneous determination of Cr(III) and Cr(VI) in environmental and biological samples has been developed. The method uses a hyphenated micro liquid chromatography (µLC) system coupled to inductively coupled plasma mass spectrometry (ICP-MS). The optimised method incorporates a pH adjusted EDTA complexation step to stabilise Cr(VI) and Cr(III). The µLC system uses an anion exchange micro-sized column to separate the Cr species. Cr(III) and Cr(VI) were separated with different retention times at 170 and 230 sec, respectively. The method was validated using a drinking water proficiency testing material sample. The developed method can be used for rapid routine determination of chromium species with high precision and reliability.



Speciation, Chromium, Method development, ICP-MS, Coupling, Analytical chemistry, Toxicity

E Leese et al., Int J Hyg Environ Health, 2017, 220(2 Pt B):415-423

Multielemental speciation analysis of Cd2+, Pb2+ and (CH3)3Pb+ in herb roots by advanced hyphenated technique HPLC/ICP-DRC-MS

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The high risk of including elements that induce toxic effects in the food chain is caused by the poor physiological barrier of plants and the absorption of toxic elements, as well as the development of high tolerance to their high level and a poor reaction to stress initiated by the presence of metals. An important problem in the speciation analysis of lead and cadmium together with their organic and inorganic compounds is the stability of these compounds throughout the analytical process and the availability of appropriate certified reference materials (CRMs), which are necessary for the validation of the analytical procedure. The main concept of the research was to develop and validate the sensitive analytical procedure for the determination of Pb2+, (CH3)3Pb+ and Cd2+ in samples of Chinese herbs. The object of the study were roots in which lead and cadmium accumulate in significant amounts,according to previous studies. The advanced high performance liquid chromatography combined with inductively coupled plasma mass spectrometry equipped with a dynamic reaction chamber – HPLC/ICP-DRC-MS, was applied to the analysis of environmental samples. Separation of species was achieved using a column IonPac CS5A 2x250-mm, and the composition of the mobile phase: 40 mM EDTA, 20 mM TMAH, 20 mM oxalic acid, which allowed for a short analysis time, less than 2 minutes.The method allowed very low levels of LOQ: 0.10, 0.29, 0.30 µg L-1 for Cd2+, Pb2+ and (CH3)3Pb+, respectively. Then, the method was applied to the herbs samples in which the share of contents of the determined species is on average 59%for Cd, and 58% for Pb. The content of Cd2+ in the extracts was in the range 3.3 – 107 µg kg-1, and for Pb2+ 5.1 – 23 µg kg-1,however no (CH3)3Pb+ was detected in the samples.

Acknowledgements

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speciation analysis, herb roots, HPLC/ICP-DRC-MS, validation, Cd, Pb

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A method using HPLC-ICPMS/MS for simultaneous arsenic and selenium speciation analysis in large-scale epidemiological studies

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Arsenic (As) and selenium (Se) are trace elements present in the environment, with Se being an essential micronutrient for the human body to stay healthy, but only when supply is adequate, while As is widely known for its toxicity. Urine is the dominant excretion route for both elements and thus, urinary As and Se speciation are of particular interest for understanding human metabolism and related health outcomes. Urinary speciation of As and Se is influenced by dietary intake and genetic variability and is dominated by methylated arsenicals, arsenobetaine, inorganic As, selenosugars, and trimethylselenonium ion (TMSe). However, particularly for Se species, their individual influence on human health and disease remains largely unexplored. Research indicates that TMSe is a major Se metabolite in some people and genetics predict the ability to produce it in significant amounts. Further elucidation of the metabolic pathways of Se is essential for the understanding of its role in human health. Selenium speciation analysis, especially in large-scale epidemiological studies, remains cumbersome due to the laborious and time-consuming analytical methodologies. We use an already implemented analytical method currently used for speciation analysis of As, for the simultaneous determination of As and Se species in a single measurement. Elemental species separation is performed using ion-exchange high-performance liquid chromatography (HPLC) coupled to inductively coupled plasma tandem mass spectrometry (ICPMS/MS) as elemental specific detector in oxygen reaction mode to remove polyatomic interference. This new approach is robust, faster, and more cost-efficient than the currently utilized methodologies. We also provide preliminary data supporting the first large study examining the effect of individual Se species on long-term health outcomes in the Multi-Ethnic Study of Atherosclerosis, a population-based study of healthy adults across six US cities comprising nearly 7,000 participants, with known health outcomes over almost two decades, rather than total As and Se alone. Our work paves the way to advance the understanding of beneficial or detrimental health outcomes of As and Se exposure and metabolism.

high-performance liquid chromatography, ion-exchange, oxygen reaction mode, tandem mass spectrometry, health, Multi-Ethnic Study of Atherosclerosis

Use of Zeeman AAS for mercury determination in black storks

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Black storks (Ciconia nigra) are migratory birds part of whose population breeds in Eastern Europe, including Latvia. Their numbers in the Baltics region are decreasing, making them endangered species. Similarly to aquatic birds their diet preferences (mainly fish) make them suitable as bio-indicators for mercury pollution assessment . In case of mercury aquatic environment plays a big role, because that's where most of the mercury methylation processes occur. Methylmercury is known to bioaccumulate in the organisms and biomagnify through the food chain. This means that even very low mercury concentrations for example in water can result in high levels of mercury in organisms higher up the food chain. There are few studies on environmental mercury pollution in Latvia.For total mercury concentration measurements we used Zeeman atomic absorption spectrometer (ZAAS) Lumex RA-915M. The use of Zeeman background correction, coupled with high frequency modulation of light polarization and a multipath analytical cell provides high sensitivity and low detection limits. We paired the spectrometer with an attachment for thermal combustion. Such setup allows direct determination of mercury in biological samples without additional pretreatment, with detection limit of 1-3 ng/g. At the moment we are working on research concerning mercury concentration levels in various artefacts of black storks collected from various nesting sites all across the Latvia. Use of non-invasive type of artefacts is important when working with endangered or vulnerable species. Such artefacts include eggshells of hatched or failed eggs and feces [1]. Up to date we have measured several hundred samples. Results show that average concentration of mercury in feces is 100 ng/g, with slight differences depending on location and age of birds (adults or chicks). Mercury levels in eggshells was observed to be in range from limit of detection (2 ng/g) to 100 ng/g, while concentration in shell membranes was higher – some of the highest values reaching 1800 ng/g. Further temporal and spatial analysis of the data of measured mercury concentration will be done, but obtained results prove that the ZAAS method can be applied for analyzing mercury content in the biological samples like feces and eggshells.

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Mercury, atomic absorption spectroscopy, black storks, thermal combustion

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Cell-to-cell heterogeneous association of prostate cancer with gold nanoparticles elucidated by single-cell inductively coupled plasma mass spectrometry

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Understanding the uptake and biodistribution of nanoparticles (NPs) into the cells is essential to evaluate the mechanism of action, efficacy, and safety of nanosystems applied in clinical diagnostics or as drug carriers. The estimation of NPs per cell is typically performed by sampling a known number of cells and measuring the average concentration of NPs. However, this approach is limited and does not provide information on the NP distribution's heterogeneity. Thus, a novel method to quantify the uptake of AuNPs (either internalized or firmly bound to the cell membrane) in individual prostate cancer cells (PC-3) was developed. The method is based on Single Cell Inductively Coupled Plasma Mass Spectrometry (SC-ICP-MS) and allows the accurate quantification of gold concentrations at the attogram (ag) per cell level. The procedure was successfully applied to understand the interaction of AuNPs with PC-3 cells, showing cell-to-cell variances in the ability to uptake AuNPs. By varying the AuNPs concentration from 2 to 32 µg L-1 increased the population of PC-3 cells containing AuNPs from 1.83 to 38.36%, respectively. At the higher exposure concentration, 22.79, 12.83, and 1.79 % of the cells presented 1, 2, and 3 AuNPs/cell, respectively. Moreover, a dose-dependent increase in the number of cells containing AuNPs/cell over the exposure period was observed, although only a tiny fraction (2.2 and 3.8 %) was taken up by cells. The present paper opens new perspectives for further investigations toward understanding NPs–cell interactions, leading to better design of nano-based drug delivery approaches.

Nano-based drug delivery systems, Single Cell, ICP-MS, Gold NPs, Prostate Cancer Cells, NP-cell interaction

Characterization of microplastics using LA-ICP-MS and LIBS

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Due to the growing demand and use of plastics, the disposal and waste of plastic products are getting more important. Even though recycling has gained more and more attention lately, a significant amount of discarded plastic still ends up in the environment. There it undergoes mechanical and chemical alteration and degradation, resulting in microplastics (MPs) formation. These MPs are suspected of releasing contained additives and adsorb trace elements from the environment. Additionally, the particles get overgrown by microorganisms, ingested by biota, and further enter the human food chain. Due to their immense impact on our ecosystems, a better understanding of their fate in the environment and characterization of their changing properties is becoming of significant interest.

In the last few years, the use of SP-ICP-MS for the assessment of particle size of MPs has become very popular. However, the characterization of MPs using solid sampling techniques is less frequently reported.

Therefore, this work investigates MPs of a wide range of commonly used polymers (e.g., PE, PET, PP, PS, PA). Different types of aging procedures were carried out, including exposure to UV radiation and oxidizing reagents followed by soaking in artificial seawater spiked with various heavy metals. Additionally, biological aging was carried out by exposing MPs to freshwater and wastewater, leading to biofilm formation.

LA-ICP-MS and LIBS were used to characterize individual particles and the surrounding biofilm. Therefore, both high-resolution mappings of cross sections and depth profiles were recorded. Here, LA-ICP-MS was used to measure the inorganic constituents of interest, revealing the uptake from the environment (e.g., Pb) in surface-near regions of the particles and the release of additives (e.g., Zn from the bulk of the particles. Additionally, the composition of the formed biofilm was assessed. To confirm the findings, microwave-assisted digestion followed by liquid ICP-MS analysis was carried out. On the other hand, LIBS is used to detect polymer-specific signals (C, H, O, C2, CN) to assess the potential degradation of the polymer particles.

LA-ICP-MS, LIBS, Microplastics, Imaging, Depth profiling

Direct Detection and Characterization of Microplastics by Flowing Atmospheric-Pressure Afterglow Mass Spectrometry (FAPA-MS)

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The increasing and rampant consumption of plastic materials have caused countless litter accumulation in remote environments such as Antarctica, mountain peaks, and deep ocean floors,[1] making them ubiquitous materials. Weathering and breakdown of these plastic materials can lead to the formation of microplastics (MPs).[2] Flowing atmospheric-pressure afterglow (FAPA) is a plasma-based source that belongs to a large group of novel ambient desorption/ionization (ADI) sources, whose features include less sample preparation, no need for chromatography, and the possibility of direct analysis under ambient conditions.[3] These are attractive features that have rarely been applied to MP analysis.

In this work, a feasibility study is presented to detect MPs directly with a FAPA ionization source coupled to high-resolution mass spectrometry (HR-MS). MPs were custom-made by grinding and sieving to yield particles in the µm-range from polystyrene (PS), low-density polyethylene (LDPE), polypropylene (PP), and polycarbonate (PC). The influence of FAPA operating parameters on the mass spectral data was investigated and optimized. Plastic materials and MPs were identified based on characteristic molecules from the starting plastics in the m/z 65–500 range with high mass accuracy. With FAPA-MS in positive ion mode, protonated and oxidized species were detected as the major contributing ions. Differentiation of the MPs was done with principal component analysis (PCA). Furthermore, to explore the influence of thermal desorption on the signal-to-noise ratio, selected materials were submitted to higher temperatures (~450 °C) and directly probed with FAPA-MS. Elevated desorption temperatures were found to induce degradation and enhance fragment ion signals. Lastly, the presence of specific ions in selected materials suggested the presence of plasticizers and additives. Overall, FAPA-MS has the potential to become a fast MS-based method for the identification of MP types in the future.

microplastics, plasma-based ambient ionization, mass spectrometry, instrumentation, FAPA

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Investigation of hydro chemical background concentrations of ground water discharges from rock glaciers in the Austrian alps

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Rock glaciers are periglacial landforms in high alpine regions consisting of a mass of rock with interstitial ice. They are considered as shallow ground water reservoirs in alpine catchments and constitute a precious freshwater resource for downstream regions. Recent global research has been intensively focused on aspects such as geomorphological dynamics, hydrological flow paths, storage capacity and storage/discharge characteristics – in particular with regard to climate change. However, a deeper understanding of the hydrochemistry of rock glaciers is essential for the assessment of their potential as potable water supply.

This work is focused on densification of the hydro chemical background information of ground water discharges from rock glaciers in various alpine regions located in the Eastern Alps of Austria's territory. Analytical tools based on ICP-MS are implemented for the investigation of concentrations of both, inorganic substances regulated in the EU Water Framework Directive and national regulations, as well as hazardous elements and emerging pollutants such as technology critical elements.

Advanced and robust methodologies capable of selectively and quantitatively analysing these elements at naturally occurring concentrations will be developed. The analytical methods investigated will involve ICP-SFMS operated under clean-lab conditions in combination with on-line matrix-separation and analyte enrichment techniques such as solid-phase extraction and cold vapour technique as well as IC-ICP-QMS for redox speciation analysis of iron and arsenic. This combination will provide an improved and valuable set of analytical methods capable of mapping of elements and their inorganic species in the aquatic environment at trace- and ultra-trace levels, which is invaluable for our understanding with respect to the mobilization, environmental fate and eco-toxicological potential.

elemental ultra-trace analysis, redox speciation analysis, geogenic background concentrations, emerging inorganic pollutants, natural water

Evidence of metal particles in cannabis vape liquids and their implications on metal measurement reproducibility

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Recent surveys indicate that cannabis vaping is a popular mode of cannabis use. Cannabis vaping involves the vaporisation of a cannabis vaping liquid or solid via a vaping accessory constructed of various metal or other parts. An increasing number of reports advocate for expansion of regulated metals in cannabis vape liquids beyond As, Cd, Hg, and Pb to reflect the possibility of consumers' exposure to the large number of metal contaminants found in these products. However, the metal analysis in cannabis vape liquids is challenged by poor precision and reproducibility. Herein we present results of 12 metal concentrations in 20 legally purchased and 21 illegal cannabis vape liquids. Cobalt, chromium, copper, nickel, lead and vanadium in several legal and illegal products exceeded the established tolerable limits, in some instances by > 100-fold.Lead mass fraction in 5 illegal samples reached µg g-1 and high levels of nickel (max 677 µg g-1), zinc (max 426 µg g-1) and copper (max 485 µg g-1) were also measured. Significant differences in metal concentrations were observed in cannabis vape liquids originating from two identical devices, although the liquid was of the identical lot. Metal particles were observed by scanning electron microscopy, and laser ablation inductively coupled plasma mass spectrometry confirmed presence of copper, zinc, lead and manganese particles. Co-localised particles containing aluminium, silica, and sodium were also detected. These results identify different metal particles as a possible cause of poor measurement precision and for the first time, provide evidence of metal particles in cannabis vape liquids contained in unused cannabis vape pens.

cannabis, metal particles, ICP-MS, LA-ICP-MS, SEM/EDS,

Analysis of Sr-90 in milk by ICP-MS/MS: new development in sample introduction

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In case of a nuclear accident both Sr-89 and Sr-90 will greatly contribute to the radiation dose to the population through food and water. Radionuclide Sr-89, with a half-life of 50 days is most abundant the first year after a nuclear event. However, it decays quickly and Sr-90, with a half-life of 28.8 years, is one of the most significant radionuclides concerning potential internal radiation dose after this time.

Sr-90 is traditionally analysed using liquid scintillation, a method that is time consuming and therefore not the best suited in case of an emergency, in which rapid analyses are needed in order to meet the demand of data to decision-making. It is therefore of interest to increase measurement capabilities for Sr-90, in order to maintain the control of food and water supply chains over a long period of time.

The latest analytical developments allows the measurement of Sr-90 with ICP-MS/MS, configured with two quadrupoles and a reaction cell (Agilent ICP-QQQ 8900) and coupled to a flow injection sample introduction system (ESI PrepFAST). This technique is being developed at the Swedish Food Agency, with support of other public agencies, for the analysis of milk and will be presented here. The goal of the project is to have, in addition to the traditional measurement methods, a ready-to-use method that can be implemented quickly across the country by several, both public and commercial, laboratories who have ICP-MS/MS analysis capabilities.

The challenge of such a method is to obtain a rapid technique to analyse very low levels (ppt range) of Sr-90 in milk. This work is using a published method as a basis for ICP-MS settings (1) and explores and combines several approaches to obtain the maximal signal intensity and stability for Sr-90. It also includes the optimisation of O2 flow in the reaction cell to both enhance Sr intensities and minimise Zr-90 interferences (2), and will highlight new technical developments for introduction of very small volumes of samples to the instrument.

ICP MS/MS, ICP-QQQ, Sr-90, flow injection, sample introduction, milk

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Method development for mini-column sorption experiments using HPLC and ICP-MS in the context of repository research

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[1]Saarland University, Saarbrücken, Germany

The safe and economically as well as ecologically sustainable storage of HLW (high-level radioactive waste) from nuclear power is a difficult and important issue of our time. An international consensus has been reached on final disposal in deep geological host rock formations using a multi-barrier system based on boreholes in clay rock layers reinforced with sand, clay- and cement-based materials. Therefore, a valid performance verification of the technical components envisaged there, including the construction materials to be used, is required. Cement-based materials and, due to the time period required for a safe repository, their alteration products, such as portlandite and C-S-H phases, are of particular interest. Since the amount of portlandite decreases with time, the performance verification of radionuclide retention at C-S-H phases is essential for a valid safety demonstration. Furthermore, the research project here must be oriented towards the framework conditions of a repository in Germany. For this reason, radionuclide retention at cement corrosion phases under hyperalkaline conditions at medium to high ionic strengths is of particular interest. For this purpose, here batch experiments with subsequent ICP-MS measurements are predominantly used. Due to unrealistic solid-liquid ratios in batch experiments, HPLC experiments with mini-columns have recently emerged as a promising alternative, whereby a possible HPLC-ICP-MS coupling holds great potential for optimising the sorption experiments. Therefore, the development of methods for conducting mini-column sorption experiments and the elaboration of existing methods are in the foreground, whereby the results from the applied methods are always compared with each other and, if necessary, supported by suitable modelling. Although it has not yet been possible to realise a HPLC-ICP-MS coupling with C-S-H phases as adsorbents, it has nevertheless been possible to carry out mini-column sorption experiments and quantify them using ICP-MS. In these first column experiments, results from batch experiments could be reproduced and can even be fitted in a first approximation with simple sorption models.

calcium-silicate-hydrate, adsorption, HLW, HPLC-ICP-MS-coupling

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Using the NexION 5000 for Automated High Throughput Analysis of Rare Earth Elements in Large Batches of Mining Discovery Samples by LA-ICP-MS

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Identifying deposits of rare earth elements (REE) that are economically viable to extract has become increasingly important. Providing rapid and cost-effective means to screen discovery samples for REE content would allow greater resolution and/or greater survey area coverage but would necessitate the analysis of hundreds, if not thousands of samples per day. Acid digestion may require several different approaches, depending on rock/mineral composition and has time and safety implications.

Direct analysis of solid samples via LA-ICP-MS in a high throughput environment has been made possible by synchronizing the NexION 5000 ICP-MS(PerkinElmer) with the sample handling/ablation capabilities of LaserTRAX (Elemental Scientific Lasers) into a single workflow. This work demonstrates the NexION 5000 Multi-Quadrupole ICP-MS as sensitive and robust detector suitable for the routine quantification of ultra-trace impurities and major components in solid matrices.

Here we present, short and long-term performance data, of discovery samples in the determination of major and trace elements. Fused Li-tetraborate bead samples were analyzed by XRF before being transferred to the LaserTRAX/NexION 5000 instrument. Automated data reduction was performed in Xceleri (Elemental Scientific Lasers) synchronised sample ID's with quantitative data, regularly calibrated and performed quality control checks.

LA-ICP-MS

Classification of fermented soybean paste products by inductively-coupled plasma optical emission spectroscopy analysis

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Fermented soybean paste is widely used as food sauces or additives in East Asia. It is called Doenjang in Korea, Miso in Japan, and Huangjiang (or Dajiang) in China. The flavors and tastes of fermented soybean paste vary with production methods and ingredients. The main ingredients are soybean, salt, wheat flour, rice, etc. The commercial fermented soybean pastes circulated in Korean markets are mainly produced in South Korea and China. In this work, the concentrations of Al, Ba, Ca, Ma, Sr, Cu, Fe, Mn, and Zn in 101 products from South Korea and 65 ones from China, purchased in the Korean markets, were analyzed by inductively-coupled plasma optical emission spectroscopy (ICP-OES). The discrimination powers of those elements were investigated and the effective variables, the concentrations of Mg, Sr, and Zn, were selected as latent variables for modeling. The Korean and Chinese products were modeled by two classical algorithms, k-nearest neighbors (k-NN) and partial least squares-discriminant analysis (PLS-DA) using 111 training objects. The PLS-DA model outperformed the k-NN in classification accuracy providing 94.5% correctness for the separate test data set with 55 objects. Our results suggest that the plasma-based elemental analysis techniques can be used as a reliable methodology for screening fermented bean paste products with fake origin labels in combination with an appropriate multivariate data modeling algorithm.

Classification, fermented soybean paste, inductively-coupled plasma optical emission spectroscopy

Biomonitoring for respirable crystalline silica: the determination of Si-containing particles in exhaled breath condensate using single particle inductively coupled mass spectrometry

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Biological monitoring is a useful way of determining overall exposures to chemical substances; however, in the case of respirable crystalline silica (RCS), this has not been possible in conventional biological matrices.Previous research at HSE had shown that it was possible to detect silicon-containing particles in exhaled breath condensate (EBC) samples using single particle inductively coupled mass spectrometry (spICPMS) .Recent method developments and improvements have meant that that it is now possible to detect silicon-containing particles in exhaled breath condensate (EBC) samples using an spICPMSMS (Agilent 8900) withparticle size measurement range of >100 -2000 nm.

This optimised spICPMSMS method was used to determine Si-containing nanoparticles in EBC samples from a range of UK workers with potential RCS exposures.Control EBC samples were also collected for comparison.In addition the EBC was standardised by collecting the same volume of exhaled air (50L) from each volunteer.Static air/bulk samples were also collected to allow particlesize characterisation and the concentration of RCS to be determined in each workplace.These samples were further characterised using a range of analytical techniques to determine the crystallinity of the RCS and airborne particle sizes

This improved methodology offers a viable biomonitoring method for a range of workplaces and has the potential to inform on the efficacy of respiratory protective equipment and control measures in the workplace.Challenges with this measurement remain with high dissolved backgrounds and non-spherical nanoparticles causing issues with the analysis.

Silica, RCS, biomonitoring, exposure, single particle

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Elemental Profiling of Herbal Dietary Supplements by ICP-MS method: classification by multivariate statistical tools

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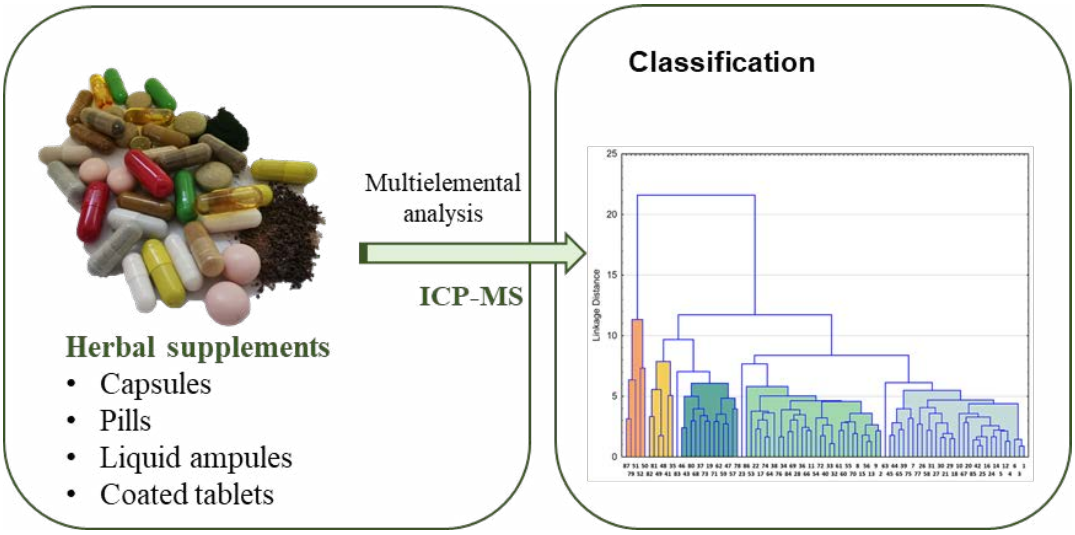
[1]Faculty Of Science, University of Zagreb, Croatia, Zagreb, Croatia, [2]Croatian Institute of Public Health, Zagreb, Croatia

Herbal supplements, which can be produced in the form of capsules, powdered pills, liquids and oils, contain a complex matrix. The plasma-based techniques (ICP-OES, ICP-MS) allow multi-elemental throughput in a variety of sample matrices. They are capable of collecting large sets of elemental composition data, which enables the construction of a large database for sample profiling.

The aim of this study is to determine elemental profiles of different formulations of representative herbal supplements from Croatian market. The contents of twenty-four elements in eighty-seven samples of different herbal dietary supplements were determined. The elements Co, Fe, Na, Se, Tl, and Zn were established as the marker elements. Multivariate PCA analysis showed the successful discrimination of Se and Zn-enriched supplements. Recognition of similarities in sub-clusters of samples was achieved by hierarchical cluster analysis. It allowed visualization of the exceptional elemental profile of several mixed-herb supplements. Distinctive features of herbal dietary supplements with peculiar influences of botanical, environmental and/or production conditions on their elemental profile were highlighted.



herbal dietary supplements, ICP-MS, elemental profiling, multivariate statistics

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Stroke differential diagnosis in serum and nasal exudate by HPLC-ICP-MS and Fe isotopic composition via MC-ICP-MS

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Stroke or cerebrovascular accident (CVA) is one of the main causes of death worldwide. There is also a high morbidity associated with this pathology, ending up with a percentage at about 50% of survivors chronically disabled1. CVA can be classified as ischemic (caused by a blood clot) or hemorrhagic (produced by broken blood vessels), both causing a decrease in the blood flow to the brain. This organ is highly immunoprotected by the blood-brain barrier, so the access of direct clinical parameters associated with the CVA is rather limited. Therefore, blood tests are typically used to help in the diagnosis (together with head computerized tomography and magnetic resonance imaging for instance). The recent description of a lymphatic drainage from the brain to the nasal mucosa paves the way to investigate nasal exudate to provide information about CVA.

In this context and aiming at the search of potential biomarkers for differential diagnosis of CVA, we have investigated potential differences in the protein profile of Fe, Cu and Zn between patients diagnosed both with ischemic and hemorrhagic stroke. For such aim, size exclusion HPLC-ICP-MS analysis was performed using two types of biological fluids: serum (most common fluid using for diagnosis) and nasal exudate (as a potential source of direct information from the brain). In addition, high precision Fe isotopic analysis has been also pursued, first by developing a single-step isolation procedure and next aiming at obtaining Fe isotopic composition by MC-ICP-MS using both biological fluids.

Acknowledgements: This work was financially supported through project AYUD/2021/51289 (PCTI Program of the Government of the Principality of Asturias and FEDER Program of the European Union) and PID2019-107838RB-I00/Agencia Estatal de Investigación (AEI)/10.13039/501100011033) in Spain.

Stroke, iron, ICP-MS, HPLC-ICP-MS, isotopic analysis,

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Accurate and Reliable Analysis of Food Samples using ICP-MS

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Food is subject to regular analysis for potentially harmful contaminants, including screening for pesticides, typical contaminants and also toxic metals. This task is commonly fulfilled by analytical testing laboratories, often specialized particularly in the analysis of foods, which turn over a large number of different sample types to provide rapid answers to manufacturers and regulatory authorities.

For elemental analysis, the use of inductively coupled plasma mass spectrometry (ICP-MS) is widespread due to the outstanding detection limits that can be achieved. Although ICP-MS is known as an analytical technology unaffected by matrix effects, this may still be an issue when testing large amounts of potential different sample types. Matrix effects could be observed when samples contain differing amounts of major elements, or when the digestion procedure may result in different acid concentrations. Although internal standardization provides a means to account for the changing responses, due to the stringent QC requirements applicable in regulated laboratories, even small differences in the samples may cause the need to isolate a particular sample, dilute and re-run, which creates additional labor and cost for the laboratory.

This presentation will highlight how ICP-MS can be used for the high throughput analysis of food samples using automated dilution of the samples with argon gas directly in the instrument. The method was fully characterized and initially validated using a certified reference material as well as spiking experiments, and has proven to provide accurate and reliable results.

Food analysis, ICP-MS

Strategies and approaches for particulate matter (PM) analysis in air

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[1]PerkinElmer, Toronto, Canada, [2]PerkinElmer, Rodgue, Gemany, [3]PerkinElmer, Sear Green, UK

Atmospheric aerosols, or particulate matter (PM) are one of the main sources of climate change. However, the mixing state of aerosols and the influence of particle composition on particle size isn’t well known. The main objective of this work is to develop a method to analyze these aerosols on a single particle basis using inductively coupled plasma-mass spectrometry. A comparison between urban particulate matter collected in Montreal will be compared to aerosols from pristine locations, identifying elemental markers for anthropogenic aerosols and particles of natural origin.

The GED may help me get a more accurate measurement of atmospheric aerosols by minimizing the sample preparation. A minimal sample preparation is important to ensure the size and the composition of the particles arent’t altered before analysis. Also, with the GED, we could eventually monitor the PM number concentration and composition in Montreal in real time by injecting air directly from outside.

GED, Particles, Air quality

Rapid classification of post-fire soil contamination by heavy metals (Pb, Cr, Zn) using Laser Induced Breakdown Spectroscopy (LIBS).

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Fire events are becoming more frequent in occurrence, especially in Wildland-Urban Interface (WUI) areas, and larger in terms of areal coverage. Changes occurred during fire, have attracted the scientific interest for the unquantified risk of post-fire metal concentration in soil [1]. Fire can affect a range of physical and biogeochemical properties of soil and is able to both release and redeposit metals on the soil surface. Metals in the environment, particularly Cr, Cd, Cu, Hg, Mn, Ni, Pb, Zn and As are of great environmental and human health concern due to their toxicity, environmental persistency and tendency to bioaccumulate [1]. High-sensitivity spectroscopy techniques such as FAAS, GFAAS, ICP-OES and ICP-MS are applied to measure the concentration of heavy metals in soil samples [2]. Their disadvantage is that first the solid sample must be transformed into solution where the metal content is determined [2]. These analytical techniques are precise, but they are also time-consuming and expensive with consecutive laboratory analysis. In this study, Laser Induced Breakdown Spectroscopy (LIBS) [3] is proposed as a low-cost technique for the rapid classification of post-fire soil samples, regarding their heavy metals contamination level (Cr, Pb, Zn). The soil samples origin from the WUI areas of the Mati and Kineta (Attika, Greece) after the wildfires of 2018. LIBS provided data support for the in situ soil pollution assessment. Based on the Dutch soil Intervention values, classification of the soil samples was performed. The contamination level of soil samples was classified as in the range of the 'Soil Remediation Intervention Values (SRIV)' indicating when the functional properties of the soil for humans, plant and animal life, is seriously impaired or threatened or in the 'Target Values (TV)' meaning that there is no contamination, and no remediation is needed. Samples that their contamination level was found in the 'SRIV area', were subsequently analyzed by the precise quantitative ICP-MS technique. Thus, LIBS was used as a qualitative rapid, low-cost screening method that reduces the number of samples that need to be tested with quantitative techniques and proved to be a significant tool with great benefits.

LIBS, soils, post-fire, classification, heavy metals, Pb, Cr, Zn, ICP-MS, Laser-Induced Breakdown Spectroscopy, Pollution Assessment

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Cadmium accumulation in organ tissues after inhalation of cadmium-based nanoparticles

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Cadmium and its toxic effects are a very current issue at this time, as poisoning by this element can cause serious health problems or death. Long-termed exposure to cadmium can lead to cancer and adverse effects on organ systems (skeletal, reproductive, cardiovascular, central and nervous etc.). Cadmium is transported through the bloodstream and is found in a wide range of tissues. We monitor the distribution of cadmium in organ tissues. We also monitor whether the distribution of cadmium in the tissues will affect the content of biogenic elements (copper, zinc, iron etc.) [1]

The distribution of the elements was monitored in the organ tissues of mice that inhaled either clean air or air contaminated with cadmium nanoparticles. The mice were sacrificed and their organs were removed. The organs were placed on a microscope slide in the form of a thin cryosection, which was analyzed by laser ablation in combination with inductively coupled plasma mass spectrometry (LA-ICP-MS). Distribution maps of cadmium and other elements of interest were created from the measured data. In my poster, the distribution maps of the organs of mice that inhaled clean air and mice that inhaled air contaminated with cadmium nanoparticles are compared.

mass spectrometry, laser ablation, cadmium, nanoparticles, organ tissues

Rafati Rahimzadeh et.al. Caspian J Intern Med. 2017 Summer;8(3):135-145.

LIBs-LIBS: A story about fluorine

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[1]University of Münster, Münster, Germany, [2]Elemental Scientific, Inc.,, Omaha, USA, [3]Elemental Scientific Lasers, Bozeman, USA

Lithium-ion batteries (LIBs) are the key energy storage device of the 21st century due to their high energy density. They are used frequently in electrical devices like smartphones as well as in the automobile production. Even though lithium-ion batteries have been used for decades, little is known about the composition of the solid-electrolyte interface (SEI layer) and cathode-electrolyte interface (CEI layer), which readily form on the anode and cathode surfaces, respectively, upon charge and discharge. Lithium hexafluorophosphate is a constituent of lithium-ion battery electrolyte that tends to decompose under formation of toxic compounds like organofluorophosphates (OFP's). Because the SEI and CEI layers are prone to the accumulation of degradation products; it may be hypothesised that OFP's accumulate in both layers. However, detection of fluorine and fluorine-containing compounds remains a challenge due to the high ionisation potential of the element, making detection problematic using conventional methods, like ICP-OES and ICP-MS.

In this work, laser-induced breakdown spectroscopy (LIBS) was used to detect fluorine on various electrode surfaces. Lithium-ion batteries were prepared using SMGA5 and NMC622 electrodes and fluorine-containing electrolyte with the additive fluoroethylene carbonate (FEC). The three cells were then charged and discharged to 3.6V, 4.2V and 4.8V. Using a 193 nm laser, the samples were analysed for C, H, O, P, Li and F using two different detection configurations based on multi-channel CCD and ICCD detectors, respectively. Although fluorine accumulates on the surface without the additive, it was found that most of the fluorine on the surface arises due to FEC. It was further determined that with increasing cycling voltage, the fluorine intercalates deeper into the SEI layer. Additionally, phosphorus, fluorine, and carbon signals correlate well on the electrodes, indicating that fluorine-containing organic substances accumulate in both SEI and CEI layers.

By using LIBS, it is possible to determine fluorine on lithium-ion battery electrode surfaces and create depth profiles showcasing the trends regarding intercalation of different elements into the graphite layer. By using imaging techniques, fluorine distribution and its relationship with major elements like phosphorous and carbon could be illustrated.

laser-induced breakdown spectroscopy, imaging, elemental analysis, fluorine, batteries, lithium-ion batteries

2D elemental mapping of micrometeorites via LA-ICP-ToF-MS

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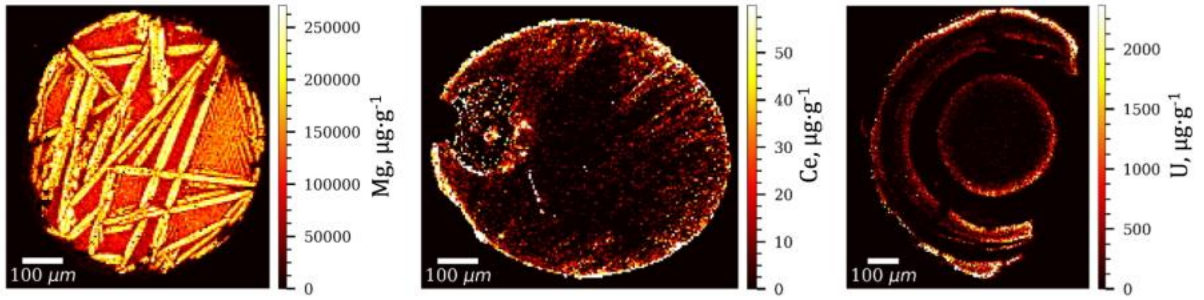
Micrometeorites, tiny extraterrestrial particles, largely produced by collisions of celestial bodies, which survived atmospheric entry, fall on Earth at a rate of 40000 tons annually, and can be retrieved on the Antarctic. Micrometeorites represent a valuable source of information on the chemical evolution of the Solar System. Their microscopic size (50-2000 μm) warrants the use of novel in situ mapping techniques of elemental analysis. Hyphenated with a low-dispersion laser ablation (LA) system, ICP-ToF-MS allows for 2D mapping at several hundred hertz, with each laser shot recorded as a single pixel, and for quasi-simultaneous rapid acquisition of almost the entire periodic table.

In this contribution we present approaches for and results of high-resolution multi-element 2D mapping of micrometeorites cross-sections via LA-ICP-ToF-MS. Quantitative data for each pixel was obtained through a combination of multi-point calibration - via a set of natural glass reference materials - and 100% oxide normalization to account for ablation yield variations. Detection limits down to a few ng/g were attained while only using a 5x5 μm square laser spot. Analysis of the elemental images of micrometeorites allows to recognize and isolate melts of different composition, complimenting petrographic observations.



Laser Ablation, Imaging, LA-ICP-ToFMS

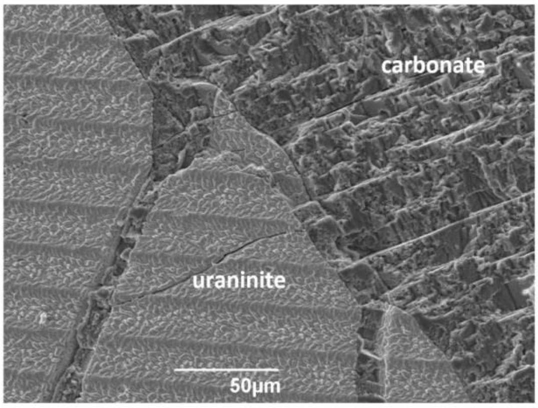
Sample structure and sample surface property as important parameters for LA-ICP-MS imaging

Markéta Holá[1], Zita Salajková[2], Jakub Ondráček[3], Martin Kubeš[4], Vojtěch Wertich[4], Viktor Kanický[1]

[1]Department of Chemistry, Faculty of Science, Masaryk University, Brno, Czech Republic, [2]Istituto Italiano di Tecnologia, Rome, Italy, [3]Institute of Chemical Process Fundamentals of the ASCR, Prague, Czech Republic, [4]Department of Geological Sciences, Faculty of Science, Masaryk University, Brno, Czech Republic

The astonishing advancement of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method in recent years has increased their potential for many applications in different areas. This progress is remarkable especially in imaging techniques. Imaging is performed by scanning ablation mode by a set of adjacent line scans covering a defined sample area. Using optimized conditions an image of element (isotope) distribution is obtained. The final spatial resolution depends mainly on the size of ablation spot and scan speed. Other parameters are crucial for the method success, for example for the detection limits or analysis time (hence price), such as dwell time, number of measured isotopes, area measured, repetition rate or data evaluation procedure.

Another aspect that affects the accuracy and sensitivity of the LA-ICP-MS imaging method is the structure and properties of the sample itself, especially its surface. The sample surface can be modified in various ways and thus can affect laser-sample interaction, aerosol formation, fractionation processes and therefore the measured intensities of the analytes by LA-ICP-MS.



Ablation craters of line scans on the polished thin section of U-mineralisation.

The interface of two mineral phases of the analyzed sample - uraninite and carbonate and a very clear difference in the ablation process of both mineral phases.

LA parameters:

LSX-213 G2+ 213 nm, spot size 20 µm, 8 J cm^{-2}, 20 Hz, 20 µm^{-1}

Laser Ablation, LA-ICP-MS, surface topography, imaging, fractionation

Salajkova Z., Hola M. et al., Talanta, 2021, 222, 121512

Precognition - a new feature in iolite to improve imaging quality

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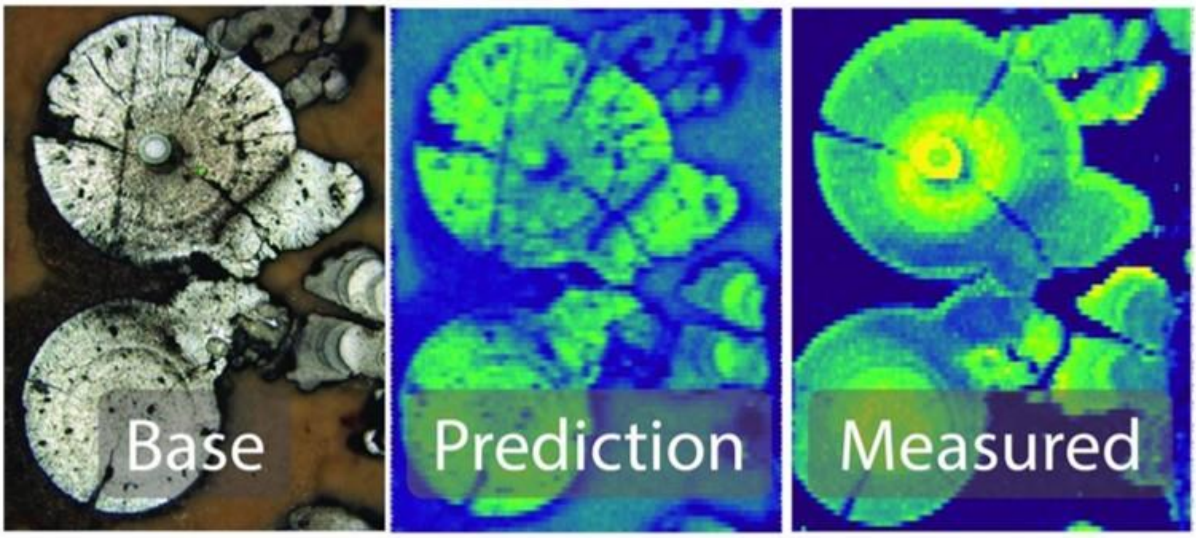
[1]Elemental Scientific Lasers, Huntingdon, United Kingdom, [2]Sheffield Hallam University, Sheffield, United Kingdom, [3]Elemental Scientific Lasers, Bozeman, United States, [4]Elemental Scientific Lasers (iolite), Melbourne, Australia

Selecting parameters for LA-ICPMS imaging is a challenging tight-rope walk between sensitivity, resolution and imaging speed. All too often parameters are selected based on educated guesswork and, unfortunately, this can lead to poor quality imaging where regions of interest cannot be resolved from one another, signals cannot be measured above background, or aliasing obscures any useful data.

Precognition is a new iolite-powered feature within ActiveView2 that uses multiple methods to predict imaging quality before a precious sample is ablated. First, the proposed pixel size is overlaid onto an optical image of the sample and adjusted to ensure features of interest are adequately resolved. Precognition also uses a test piece of data to calculate whether the ICPMS integration times are set correctly to observe signals above baseline and maximise imaging speed.

Here, we will directly compare images taken based on parameters intuitively derived by the user with an image taken after Precognition has been applied to demonstrate the improvement in image quality.



iolite, precognition, imaging, laser ablation

Imaging of coralline algae by LA-ICP-MS

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Climate change and observed melting of arctic ice covers lead, inter alia, to the fluctuation of carbonates in arctic seas what influences marine organisms with carbonate skeletons. Coralline algae are an example of such organisms what makes them an interesting climate status indicator. Numerous examples of their analysis using LA-ICP-MS technique can be found in the literature (1,2), but so far, no matrix-matched standards enabling quantitative analysis have been developed. Moreover, published works are devoted to the analysis of long-lived specimens and no images presenting the elemental distribution in algae have been published.

Performed studies included the method development of the preparation of standards based on the main ingredient of algae skeleton- calcite, optimization of the ablation conditions and imaging of coralline algae deposited on high impact polystyrene plates which were gathered from Spitsbergen. As part of the cooperation, analyzed samples were obtained from the Institute of Oceanology of Polish Academy of Sciences.

laser ablation, imaging, inductively coupled plasma mass spectrometry, coralline algae

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Quantitative study of neurodegeneration-related proteins at the single-cell level by LA-ICP-MS using specific gold-labelled immunoprobes and a fully matrix-matched calibration

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The study of biological processes is highly limited by the high heterogeneity of biological samples, especially regarding cells. Therefore, new analytical methodologies need to be developed that allow the determination of elements and biomolecules at single-cell level to gain a detailed understanding of these processes [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-1α 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.

quantification, proteins, cells, laser ablation, matrix-matched standards, bioimaging

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Diffusive gradients in thin films (DGT) combined with LA-ICP-MS for elemental mapping of localised aluminium corrosion

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Multi-elemental mapping based on the combination of passive, non-destructive Diffusive Gradients in Thin films (DGT) with LA-ICP-MS enables in situ visualisation and quantification of chemical processes occurring at reactive interfaces. For the last nearly 30 years, DGT has been applied primarily for environmental analysis. Recent studies opened a new perspective for understanding corrosion processes as part of materials science [1].

In this study, a novel application of DGT LA-ICP-MS for the in situ multi-elemental mapping of localised corrosion is presented on the example of aluminium. DGT Polyacrylamide- and polyurethane-based binding gels with homogeneously distributed iminodiacetate (Chelex 100) and TiO2 (Metsorb) binding phases were applied to Al specimens composed of Al and other trace elements (e.g. Fe, Cu, and Zn). The DGT-Al setup was immersed for 24 and 72 hours in a NaCl solution (w = 1.5%, pH = 4.5) at room temperature. The binding gels were evaluated and analysed by LA-ICP-MS. The DGT-Al setup was further optimized in order to minimize crevice corrosion in the DGT – Al interface. Quantification was done by linear calibration using DGT standards with known analyte mass loadings. Imaging was complemented by SEM/EDX microscopy of the metal surface.

The first results obtained on elemental fluxes showed a high flux of Al after 24 and 72 hours, with a similar distribution pattern to the original corroded metal surface. However, the Fe flux after 72 hours showed a more localised release of the corrosion products.

The obtained results show that DGT in combination with LA-ICP-MS enables in situ mapping of Al, Fe, Cu, and Zn metal solubilisation, and the DGT flux provides quantitative information about the spatiotemporal reaction dynamics of corrosion processes.

Mapping, DGT, Aluminium, Pitting corrosion, LA-ICP-MS

Wagner et al., Analytica Chimica Acta, vol. 1212, p. 339910, 2022

Sodium accumulation and distribution in floral organs of tomato

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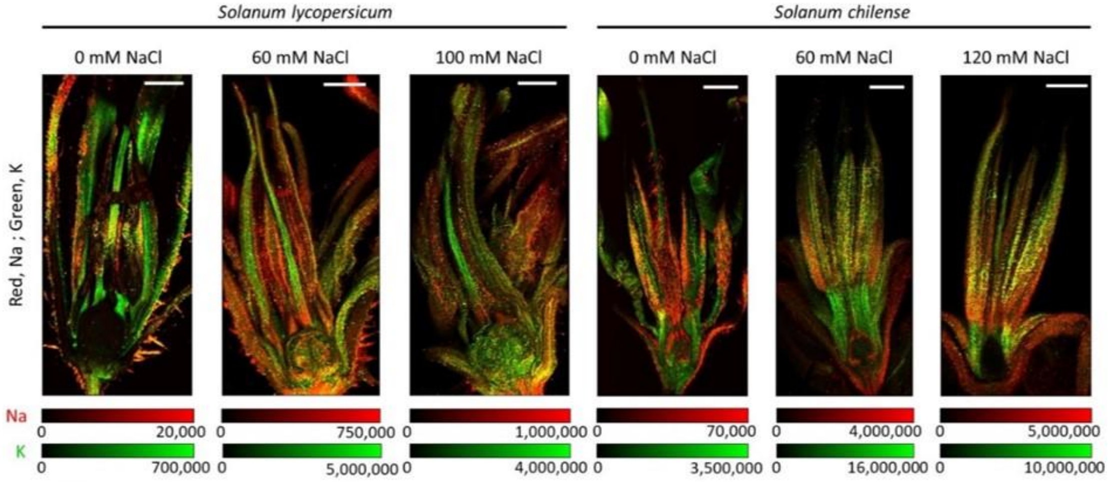
Salinity is a growing global concern that affects the yield of crops, including tomato (Solanum lycopersicum). Its wild relative, Solanum chilense, has been reported to be salt tolerant. Salt tolerance of these two species was evaluated. Plants were exposed to increasing NaCl concentrations from seedling stage to fruiting. Salinity decreased the number of inflorescences in both species but the number of flowers per inflorescence and sepal length decreased only in S. lycopersicum. External NaCl supply decreased the stamen length and pollen production, but increased pollen viability in S. chilense. Although the fruit set was not affected by NaCl supply, fruit weight and size decreased in S. lycopersicum only. There was more Na in inflorescences and fruits of S. chilense than of S. lycopersicum. Concentration and localization of Na and K differed in floral organs of the two species as revealed using LA-ICP-MS. In S. chilense Na was mainly located in male floral organs, while in S. lycopersicum in non-reproductive floral organs. Results confirmed that S. chilense is more salt tolerant than S. lycopersicum and indicated that differences could be related to dissimilarities in Na distribution and transport in flowers (1).



salinity; inflorescences; ion localization

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

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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 induced breakdown spectroscopy (LIBS) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) utilizing a new 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 F which was detected and quantified by LIBS, while Mg, Mn, Zn, and Sr were measured by LA-ICP-MS. This information 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 LIBS-ICPMS allows for high-resolution elemental mapping in a timely manner, making it possible to look at larger data sets.

LIBS-ICPMS, Shark Teeth, Fluorine, Imaging

Pb isotopic ratio determination in recycled plastic samples by MC-ICP/MS: An Analytical feasibility

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Plastic recycling is one of the main challenges of the energy transition. Plastics are widely used in many fields (automotive, packaging, and housing) and generate a huge quantity of waste. As mechanical recycling is typically accompanied by degraded plastic properties, chemical recycling is needed to develop a circular economy, in which monomers and oligomers can be re-polymerized following purification and used in similar applications as the virgin polymer equivalent, which is produced from fossil fuels.

Inorganic elements for coloring and heat stabilization (oxides of Ti, Zn, Co, and Pb), flame retardant synergic species (Sb_2O_3) or other stabilizing purposes (organometallic compounds of Ba, Sn, and Zn) is usually used in the plastic industry [1]. During the plastic life cycle, from the formulation to the recycling process and possible fate in the environment, the isotopic signature of the elements can be modified and need to be determined to access to the evolution of inorganic elements during the life cycle of the plastic (recycling plastic content, purification, environment accumulation, …).

Nissen et al. [2] published a methodology to determine $^{208}Pb/^{206}Pb$ et $^{207}Pb/^{206}Pb$ isotopic ratios in polyethylene (PE) from different providers but the accuracy and precision obtained by ICP-QMS were not sufficient to discriminate the samples. To our known knowledge, there is no methodology to investigate heavy elements isotopic ratio in recycled plastic samples. The aim of this work is to develop a complete methodology to measure the isotopic ratios for plastic containing heavy elements using MC-ICP-MS. For the analytical feasibility, the study is only focused on the Pb isotopes determination. After a MAWD (microwave-assisted wet digestion) method to mineralize the sample, the purification step using ion exchange resin (AG1-X8) was optimized with a virgin PP spiked with a Pb isotopes standard (NIST 981, $^{208}Pb/^{204}Pb = 36.724 \pm 0.009$ [3]). Elution profile of Pb and interfering elements during the purification step were analyzed by ICP-QMS prior to MC-ICP-MS analysis. After this crucial optimization, a PE EC 680 certified at 11.3 mg/kg of Pb and one real PP waste sample containing Pb and coming from mechanical recycling were chosen to validate the developed methodology.

plastic recycling, MC-ICP-MS, isotopic ratio, lead

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Importance of Analyte-matrix Separation in U-Pb and Pb-Pb Dating Systems

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Dating is nowadays widely used method combing geology and analytical chemistry. It provides useful geochronological information in specific areas. Inductively coupled plasma mass spectrometry (ICP-MS) is still one of the common methods used for elemental and isotope ratios analysis. [1] The dating principle assumes that the age of a sample can be calculated from the ratio of two or more isotopes present in the sample. To determine the isotope ratios, the sample preparation is crucial in order to eliminate interferences and improve accuracy. [2]

Besides ore mining, manual separation, sample digestion and dissolution, the critical step in the preparation procedure is analyte-matrix separation. Uranium and lead are usually separated from sample matrix by the principles of ion exchange chromatography using previously developed procedures or new approaches can be introduced. In this study, series of U and Pb standard solutions have been used to optimize the separation procedure using commercially available resins. Different eluting agents were tested. After the method optimization, uraninite samples were analysed. For elemental and isotope ratio analysis, solution method ICP-MS has been used. Results will show the importance of separation process in sample preparation phase and its influence on final isotope ratio.

ICP-MS, solution nebulization, ion exchange chromatography, dating, uraninite, isotope ratio

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Development and validation of MC-ICP-MS based methods for Ni isotope analysis to study plant hyperaccumulation

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Hyperaccumulating plants typically accumulate particular trace metals in their biomass without showing symptoms of toxicity. Metal concentrations in the aboveground biomass of hyperaccumulators often exceed background levels of regular plants 100-1000 times and may reach >10 g kg-1. Metal mobilisation mechanisms in the rhizosphere by hyperaccumulating plants are still mostly unexplored. Hyperaccumulation of Nickel was observed to lead to isotope fractionation (1). Consequently, studying the difference (Δ60Ni/58Ni) of Ni isotope compositions between bedrock, soil, plant material and plant exudates may be a powerful tool to study and further understand metal mobilisation processes by Ni-hyperaccumulating plants.

Special attention needs to be paid to the critical steps of the analytical protocol and understanding the fundamentals and tuneable instrument parameters of multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS)to assure accurate Ni isotope ratio measurements with low bias from the true value and low uncertainty. In this study, a microwave-assisted digestion protocols using tetrafluoroboric acid (HBF4) was investigated, as well as a two-step isolation protocol separating iron (Fe) and Ni using Bio-Rad AG MP-1 and AG 1-X8 anion exchange resins respectively (2). The MC-ICP-MS used (Nu Sapphire, Nu instruments, Wrexham, UK) offers the application of a hexapole collision/reaction cell (CRC) to remove spectral interferences. The MC-ICP-MS was further optimized for simultaneous measurement of 58Ni – 64Ni target isotopes, 57Fe for interference correction on 58Ni and 65Cu/63Cu as a ratio for instrumental isotopic fractionation correction based on the regression model. The IAG MUH-1 certified reference material was used to validate the digestion and isolation protocols as it closely resembled the soil and rock samples. The HBF4 digestion demonstrated ~100 % Fe and Ni recovery, and the isolation protocol has shown ~95 % Fe and Ni recoveries even in presence of high boron contents as a consequence of the digestion. The CRC allowed to remove the 40Ar18O+ interference on 58Fe/58Ni using H2 and He gases but further investigation is needed to fully remove the 40Ar16O1H+ interference on 57Fe (3).

Ni isotopes, Isotope analysis, Mass spectrometry, Method development

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Isotopic fingerprints of «non-traditional» elements for authenticity and geographical assessments of food and beverages

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Authenticity and traceability of food are an area of a high priority since they link directly to the quality. However, more and more food and beverage are subject now to misdescription or adulteration and thus poses an increased risk for customers and producers. The new advanced analytical approaches, notably, stable isotope analysis of non-traditional elements such as strontium (Sr), lead (Pb), and boron (B) combined to trace element profiles make a decisive contribution to geographical provenance assessment. These isotopic signatures are indeed influenced by geological scenes, anthropogenic, agricultural, and environmental impacts, or even production processes.

Sample preparation methods are developed and optimized regarding matrix specification of each sample, notably, appropriate ion exchanging resin needs to be applied for a reliable analyte purification (satisfactory yield >80%) prior to MC-ICP-MS analysis. Isotope measurement was performed by MC-ICP-MS with a precision down to 0.003% (2RSD, Sr), and 0.02% (2RSD, Pb) in the conditions of wet or dry plasma respectively. Boron isotopes in wine were determined using quadrupole ICP-MS with a precision down to 0.5% (2RSD).

An integral review of these isotopic and elemental markers shows great potential in reliable authenticity assessment of foods and beverages, especially for those within a limited geographical area of production and standardized processes. The efficiency of geographical provenance determination using this approach was confirmed by its successful application to different food and beverages such as red wines and champagnes, products labeled IGP from France (rice from Camargue and dry-cured ham from Bayonne), French mineral bottled waters and tea samples from wide-worlds origins.

The obtained results build on and extend the previously developed database and aimed to investigate and develop a conceptual and practical framework that promotes a valid indication approach to deal with fraudulent practices in the food sector.

Isotopic analysis, Strontium, Lead, Boron, Food authenticity, Geographical origin

Strontium isotope ratio as marker of wood provenance

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Determining the date and provenance of wooden structures and artefacts is paramount to establish their specific historical and socio-cultural contexts. Different approaches can be used to study wood provenance, but most of them are based on tracers controlled by climatic factors. The analysis of strontium isotopes in wood offers an interesting opportunity to discriminate wood sources according to geological parameters. When using Sr isotopes as a provenance tracer, the assumption is that tree inherits a Sr isotope signature that reflects the geological history of the region where it grew (1). Soils generally share similar ^{87}Sr/^{86}Sr values with their substrate (2). However, soil can exhibit a considerable variation within a given geologic zone, since minerals within the rock weather at different rates and hence contribute unevenly to bioavailable strontium in soil. Other major sources of variability in bioavailable strontium in soil are ground and stream waters, wind-transported dust deposits, as well as sea spray in coastal zones and rainfall (3). Therefore, for predicting the isotopic composition of trees growing in a specific location, it is necessary to analyse the topsoil and groundwater responsible for most of the Sr uptake. The scope of the present study was to test strontium isotopes as a tool for accurate determination of the growing site for a specific tree (Norway spruce). For this purpose, ^{87}Sr/^{86}Sr ratios in wood, water and soil samples were determined. Samples originated from an area with different underlying geology (limestone, andesite and metamorphic schists), located in Romania – known as one of the major exporters of sawn wood. In order to examine variability of ^{87}Sr/^{86}Sr ratios in the last 50 years, ten different sections of wood cores, each representing five years of growth, were analysed. The results from the present study are a starting point for creation of ^{87}Sr/^{86}Sr isotope ratio maps (isoscapes) for Romania that will help the delimitation of homogenous areas with unique geochemical signatures.

^{87}Sr/^{86}Sr, isotope fingerprinting, wood signature, surface and ground water, soil

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Pb isotope ratios to link environmental sources with high blood Pb concentrations in children in Georgia

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Lead (Pb) is a potent neurotoxin, and has been a global public health concern for many years. A recent national survey of Georgia identified that 41% of children aged 2-7 years had blood lead concentrations (BLCs) greater than the blood lead reference value (BLRV) of ≥5 μg/dL. For this work 36 children from Georgia that had previously been identified as having a BLC > BLRV were recruited. In addition to a blood sample from each participant, environmental samples including spices, paint, soil, dust, flour, tea, toys, milk and water were collected from each household and investigated as potential sources of Pb exposure. Total Pb concentrations of these environmental samples were determined using ICP-MS. This identified that many spice, paint, dust and soil samples were above Georgian reference values. The Pb isotope composition of the blood and environmental samples from three households were determined by ICP-MS. As blood Pb inherits its isotope composition form the source of exposure this can be used to identify the most likely source(s). This isotope fingerprinting approach identified that some spice and dust samples were the most likely sources of Pb to the blood whilst soil and paint samples were isotopically distinct from the blood Pb. This data highlights the contribution that Pb isotope ratio analysis can make to Pb surveillance in cases or regions where high BLC's are identified and which may then be used to inform intervention measures and improve health outcomes.

Lead isotope ratios, Blood lead concentrations, Environmental tracing, blood lead concentration

Preparation and characterization of deuterated co-polymers as potential hydrogen isotope calibration standards for laser ablation-based spectroscopy

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Hydrogen isotope analysis has always been a valuable tool in biology and environmental science, but recently the research interest for has been rekindled by the progress of hydrogen fusion-related nuclear projects. Some of these projects, such as our plasmonics-related NAPLIFE initiative [1], are already laser-based, while others require laser-based analytical techniques for assessing fuel retainment in construction materials. Laser induced breakdown spectroscopy (LIBS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) are two prominent, laser ablation-based spectroscopy techniques which can advantageously used to target the analytical task of hydrogen isotope analysis in solid samples [2, 3]. These techniques require reliable calibration standards with known and controllable hydrogen isotope content. One of the possibilities for having such standards is the preparation of polymers from deuterated monomers. We synthesized photo-copolymers for the above purpose from partially deuterated methyl methacrylate and diuretic-methyl acrylate mixed in various proportions. Different photoinitiators, excitation light sources and illumination times were tested for their efficiency until the use of Irgacure 784 in combination with LED excitation at 520-525 nm was chosen. The degree of conversion was monitored by Raman spectroscopy. In order to boost the light absorption of the polymer at potential laser ablation wavelengths (e.g. 266, 532 or 1064 nm), the use of various additives including carbon micro- and nanoparticles, organic molecules, metallic complexes were investigated. A detailed characterization of the mechanical, optical and laser ablation properties of the polymers was also performed. The partially deuterated polymers were also subjected to LIBS measurements, which showed good signal-to-noise ratio, well-resolved hydrogen isotope peaks (protium and deuterium) in the spectra and well defined, reproducible ablation craters. The deuterium signal showed a good correlation with the design composition in the sample series. In summary, we consider our production method fit to create calibration standards for the LIBS or LA-ICP-MS quantification of hydrogen isotopes.

Acknowledgments
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LIBS, LA-ICP-MS, isotop ratio measurement, reference material

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Stable isotope analysis as a critical tool on the advancement of mercury and selenium interaction in biota. New insights on mercury demethylation mechanism.

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Mercury (Hg) exhibits both, mass dependent and mass independent fractionation. This singularity has been exploited on the study of biological samples to obtain simultaneous information about the (pollution) sources and the fate on living organisms of this element. Hg is a globally distributed pollutant largely present in aquatic ecosystems in its most neurotoxic chemical form: methylmercury (MeHg), that bioaccumulates and biomagnifies through the aquatic food chain. Hg fate and its detoxification mechanism in biota remains unclear. The role of selenium (Se) as toxicity antagonist as been evoked, based among others on the formation of tiemannite (HgSe), considered the end-product of MeHg demethylation. This study reports for the first time HgSe nanoparticles species-specific (Hg) isotopic characterization (δ202Hg, Δ199Hg) in seabirds and corresponds to the largest characterization of this compound in biota. A large set of Antarctic Giant Petrels, the main scavengers in the Southern Ocean, exhibiting Hg and Se levels up to 1000 µg/g was investigated. The Hg isotopic signature in key tissues as brain, liver and kidney was compared with the Hg species specific corresponding to the HgSe (δ202HgHgSe, Δ199HgHgSe). Results reveals that no isotopic fractionation appears to be induced during the HgSe NPs biomineralization step from the precursor-demethylated species. In contrast, a shift of ~3 ‰ δ202Hg could be associated to the cleavage of the C-Hg bond (MeHg detmethylation). Selenoneine (SEN) was first identified (HPLC-ICPMS, ESI-MS/MS) in this wild avian species as the major Se specie in all tissues and blood. The high levels of SEN in the brain (85% of total Se), and its rapid decreased (from 68 to 3%) with the increase of Hg content in the liver suggest that this selenometabolite might be playing a key role in the Hg detoxification pathway. Simultaneously, Se isotopic composition (HG-MC-ICPMS) was characterized in key internal organs of seabirds. The variation of the Se isotopic pattern between organs (3-5 ‰ δ82/78Se) as well as the first-time species-specific Se isotopic characterization in HgSe NPs (1-6 ‰ δ82/78SeHgSe) provide unique information regarding its interaction with Hg.

mercury, selenium, isotope ratio, seabirds

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Comprehensive (geo)chemical characterization of the Austrian-Slovenian Mur/Mura River catchment

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The international project “MURmap”, co-funded by the Austrian Science Fund (FWF, I 5491) and Slovenian Reasearch Agency (ARRS, J1-3023) aims to shed light to the processes between geosphere and anthroposphere interactions in the fragile system of the Mur/Mura River. The potential of combined element fingerprinting, and isotope tracer approaches to elucidate natural and anthropogenic processes are investigated by determining the (1) natural geochemical background of the catchment area and (2) the main tributaries, (3) historic and recent anthropogenic influence on the environment of the Mur, as well as (4) transfer of chemical elements between solid and liquid phases.

Therefore, water, suspended particulate matter (SPM), alluvial and stream are sampled at different seasons/water regimes (water and SPM: May 2022, August 2022 and February 2023). In addition, long-time series based on regular sampling of water at selected locations will provide time-resolved data to e.g. monitor extreme weather phenomena.

Here, the project is presented in detail along with results from the first sampling campaigns focussing on elemental analysis (incl. REEs and TCEs), single particle analysis and selected isotope ratio patterns (B, Sr, Nd, Pb). An analytical focus was set on developing fully validated methods based on ICP-MS/MS (PerkinElmer Nexion 5000, Agilent 8900) and MC-ICP-MS (Nu Plasma HR and Nu Sapphire).A clear correlation of geological catchment and elemental as well as isotopic signatures can be seen for all matrices (water, SPM, single particles and sediment) with a few hot-spots that are particularly interesting as they reflect potential historic and recent anthropogenic influence.

Natural tracers such as Ca/Sr mass fraction ratios indicate a change from metamorphous and crystalline to carbonate host rock along the river from Austria to Slovenia. Single element peaks at specific locations (e.g. As or Au) could be linked to ancient and historical land use within the area, such as As , which was mined from 14th to 19th century in the very upper part of the Mur River catchment. Nanoparticle fraction of chosen elements (Fe, Ti, Nb, Nd, Pr, La, Ce) match with the element distribution measured in water.

environmental analysis, element analysis, isotope analysis, mass spectrometry

A second anchor Fe isotope reference material based on high purity Fe metal for the exhausted IRMM-014

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Iron isotopes are used in a variety of fields from e.g., geologic question to medical applications. Measurements of iron isotopes are usually performed as delta measurements to an artificial based delta zero standard. In the case of Fe isotopes is that delta zero standard IRMM-014, a pure Fe metal. Unfortunately, that conventional delta zero reference material defining the δ^{56}Fe scale is out of stock and therefore unavailable. To overcome that situation and fulfill the need for laboratories that measure Fe isotope on a regular basis we will provide a set of solutions with IRMM-014 and a second anchor point for Fe isotope ratio measurements that is based on a pure Fe metal. This new second anchor point, a high purity Fe from BAM, will be calibrated against IRMM-014 and can be used as bracketing standard or as reference value for stable Fe isotope measurements.

We are in the good situation that BAM ordered a large stock of IRMM-014 several years ago. That stock of IRMM-014 Fe cubes and IRMM-014 Fe wires will be dissolved in 6M HCl in a large quantity. The new anchor point, the high purity Fe metal, that is commercially available at BAM, is a pure Fe metal with only trace amounts of impurities. The high purity BAM material will also be dissolved in 6M HCl in large quantity. Several aliquots of both solutions will be measured on the Neptune Plus MC-ICP-MS to define this second anchor point with a low uncertainty. Further will we send several aliquots of both solutions to different laboratories to also measure this second anchor point of high purity Fe on the δ^{56}Fe scale.

We will report the values of that study on BAM high purity Fe and will provide a guide for scale conversion to the IRMM-014 scale and for uncertainty calculation to use that new anchor point instead of the exhausted IRMM-014.

Fe stable isotopes, reference material

Kr and polyatomic Ar interference removal for transition metals and Sr using the collision/reaction cell of the Nu Instruments Sapphire dual path MC-ICP-MS

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"Isotope ratio measurements of transition metals are impeded by isobaric interferences from polyatomic Ar species such as $^{14}N^{40}Ar$ = ^{54}Fe and ^{54}Cr, $^{16}O^{40}Ar$ on ^{56}Fe, $^{23}Na^{40}Ar$ on ^{63}Cu, or $^{24}Mg^{40}Ar$ and $^{14}N_2{}^{40}Ar$ on ^{64}Zn and ^{68}Zn, respectively. Impurities in the Ar gas used can further impose isobaric Kr interferences on Sr isotopes. Here, we demonstrate the removal of these isobaric interferences using the collision/reaction cell of the Nu Instruments Sapphire dual path MC-ICP-MS for isotope ratio measurements of Cr, Fe, Cu, Zn, and Sr.

Removal of Ar-based interferences for transition metal measurements is facilitated via addition of a He-H_2 gas mixture to the collision/reaction cell. Copper and Zn isotope ratios were acquired simultaneously using 500 ng/mL Cu and Zn concentration standard solutions, and Zn was used to correct for fractionation of $^{65}Cu/^{63}Cu$. Internally corrected and standard-bracketed $\delta^{66}Zn/^{64}Cu_{86}$ (internally corrected with $^{68}Zn/^{66}Zn$) = 0.000 ± 0.037 and $\delta^{68}Zn/^{66}Cu_{64}$ (internally corrected with $^{66}Zn/^{64}Zn$)= 0.000 ± 0.036 (2σ SD; n = 94), with measured Zn isotope ratios following a mass-dependent fractionation line. Zinc-corrected $\delta^{65}Cu/^{63}Cu_{86}$ (internally corrected with $^{68}Zn/^{66}Zn$) = -0.001 ± 0.033 and $\delta^{65}Cu/^{63}Cu_{64}$ (internally corrected with $^{66}Zn/^{64}Zn$)= 0.000 ± 0.028 (2σ SD; n = 94). Concentration mismatching of up to 10 % produces only negligible deviations < 20 ppm for Zn-corrected Cu isotope ratios. Chromium and Fe isotope ratio measurements are currently in progress.

Strontium isotope ratio measurements use a He-O_2 gas mixture to effectively remove Kr on ^{84}Sr and ^{86}Sr while preserving mass-dependent isotope fractionation for the measured Sr isotope ratios. The external repeatability of repeated measurements using wet (250 ng/ml) and dry plasma (50 ng/ml) is better than 25 ppm (2σ SD) for internally normalised $^{87}Sr/^{86}Sr$, and repeated measurements of the NIST SRM 987 yield an average $^{87}Sr/^{86}Sr$ of 0.710254 ± 0.000016 (2σ SD; n = 30)."

Collision/reaction cell, MC-ICP-MS, Sapphire, dual path, isotope ratio, interference removal

Evaluation of the new MC-ICP-MS/MS Neoma. Is it the game changer ?

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In the last two years, a new generation MC-ICP-MS (Neoma) was launched by ThermoFisher Scientific and is now available in two different configurations, i.e., with and without a MS/MS option. This presentation will focus on the MS/MS settings which was installed in 2022 as an upgrade of our standard Neoma. We can now compare the performances of the instrument against our Nu500 NP1 and Neptune + on well-known applications like Copper and Zinc isotopes analysis or Sr and Ca with and without laser ablation.

The MS/MS mode of the Neoma was used to measure the isotopic ratios of selenium, copper, and iron for the three configurations. The 40Ar+36Ar, 40Ar+38Ar, and 40Ar+40Ar isobaric interferences on 76Se, 78Se, and 80Se can be resolved using O2, 40Ar+23Na on 63Cu, and 40Ar+14N, 40Ar+16O on 54Fe and 56Fe using H/He. For example, the 40Ar+23Na interference correction (with He) on 63Cu was studied with the addition of Na until a ratio of 100 x Na vs Cu.

MC-ICP-MS, Copper, interference

On-line Species-specific Isotopic Analysis of Sulfur by Hyphenation of Capillary Electrophoresis with Multicollector-ICP-MS

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A method was developed[1] for a species-specific isotopic analysis of sulfur via on-line hyphenation of capillary electrophoresis with multicollector ICP-MS (CE/MC-ICP-MS). Instrumental mass bias was corrected by external correction with multiple-injection sample-standard bracketing approach. The isotope ratio measurement results obtained with the newly developed on-line CE/MC-ICP-MS method were compared with the results obtained via traditional MC-ICP-MS measurement. The traditional off-line method involved an analyte/matrix separation by anion exchange chromatography to separate sulfate ions from other sulfur species. By comparing the on-line results with the off-line ones, the most suitable data evaluation method was identified for the processing of the transient signals. The repeatability for the sulfate-δ34S value was 0.57‰ (2SD) and thereby only twice higher than the obtained with off-line measurements (0.30‰). The application of the method on real samples was accomplished by the analysis of naturally present sulfate in river systems.

River water sulfate, Sulfur isotopes, Species-specific isotopic analysis, Multiple-injection sample-standard bracketing approach

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In-situ Rb/Sr by LA-MC-ICP-MS/MS: Thermo Scientific Neoma MS/MS

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The introduction of ICP-MS/MS instrumentation in the last decade, such as the Thermo Scientific™ iCAP-TQ™ and Agilent Technologies™ 8800 and 8900, has seen the development of many new analytical methods. One such analytical method, which has been of great interest to the Geoscience community, is in-situ Rb/Sr dating by laser ablation (LA-) ICP-MS/MS [e.g., 1,2]. However, Rb/Sr dating has traditionally benefited from the significantly higher isotope ratio precision which can be achieved by using a multicollection-based detector, such as within MC-ICP-MS or TIMS. A natural conclusion which could be generated from these previous statements is that in-situ Rb/Sr dating may be best realized by an instrument combining the excellent precision of isotope ratio measurements from MC-ICP-MS with the full analytical versatility of established ICP-MS/MS designs.

In-situ Rb/Sr dating has already been reported for two prototype MC-ICP-MS/MS developed by Thermo Fisher Scientific™: Proteus MC-ICP-MS/MS [3] and Vienna MC-ICP-MS/MS [4]. The Vienna MC-ICP-MS/MS was built upon the experiences collected from the preceding Thermo Scientific Proteus, borne from a cooperation between the University of Bristol and Thermo Fisher Scientific, introducing a ground breaking novel pre-cell mass filter design. While both Proteus and Vienna were highly successful for in-situ Rb/Sr analysis, with Proteus providing a hundred-fold increase in sensitivity and 25 times improvement in Sr isotope ratio precision over single collector ICP-MS/MS instrumentation [4], neither prototype was made commercially available. Here we report on the analysis of in-situ Rb/Sr using the first commercially available MC-ICP-MS/MS, the new Neoma MS/MS MC-ICP-MS, an upgrade option for the latest Neoma MC-ICP-MS platform. The larger detector array, wider dispersion, seamless laser-instrument software integration, all combined with its unique MS/MS technology: the Neoma MS/MS dramatically improves precision and accuracy of in-situ Rb-Sr, revolutionizing in-situ geochronology.

MC-ICP-MS/MS, Rb/Sr, Neoma MS/MS, geochronology

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Spatial resolution 87Sr/86Sr isotope ratio determination of cave bear teeth using LA-MC-ICP-MS

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The $^{87}Sr/^{86}Sr$ isotope ratio determination in tooth tissue, which is an important biological archive, is widely used for studies about provenance, habits, and mobility of ancient animals and humans. Sr isotope ratio analysis by multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS) in such matrix can be done in solution by dissolving the sample, or directly on a solid sample by the use of laser ablation (LA). In the first case, very accurate data can be obtained, since all interferences on Sr isotopes are removed during the preparation of the sample solution. The result is an average value of the bulk sample that lacks spatial resolution. Contrary, with the direct introduction of the solid sample by LA a high spatial resolution of Sr isotope data can be obtained. Unfortunately, the accuracy and precision of these data can suffer due to the possible unresolved isobaric interferences.

In the present study, we optimized LA and MC-ICP-MS parameters to obtain high quality spatial data for $^{87}Sr/^{86}Sr$ isotope ratio in teeth of cave bears with low Sr content (around 100 mg/kg). For better spatial resolution and accurate Sr isotope ratio results, the rapid response sample transport system coupled to LA was used. The influence of isobaric interferences on the precision and accuracy of $^{87}Sr/^{86}Sr$ isotope ratio determination and modes to eliminate them were studied on reference materials with different calcium carbonate matrices, such as ECRM-752-1-NP, JCt and SPLT-NP-B01 and home-made pellets from NIST SRM Bone Meal. After optimal ablation and measurement parameters were obtained and correction equations set, the method was applied to canine teeth samples from adult cave bears that lived in the last glacial period in the Alpine region (Würm glaciation). The specimens found in the Divje Babe I Cave (Slovenia) were estimated to be 50 – 60,000 years old. The growth of permanent canines begins around the first year of life, and the formation of annular dentin increments in the teeth continues until the death of the animal. For each year, annual increments were visible in the cross section. By analysing all the profiles with LA-MC-ICP-MS, we approximately followed the growth direction trying to observe possible seasonal variations in the Sr isotopic composition.

$^{87}Sr/^{86}Sr$, LA-MC-ICP-MS, method optimisation, teeth, cave bear

Analytical strategy for characterization of spent UO2-Gd2O3 nuclear fuel samples by mass spectrometry

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In the framework of the REGAL Program (Rod-Extremity and Gadolinia AnaLysis), coordinated by SCK CEN, the Belgian Nuclear Research Centre, CEA participates into the phase II of this Program (starting in 2021), as a second laboratory for precise isotopic analyses.

The LANIE laboratory, which is specialized in high precision elemental and isotopic analyses by mass spectrometry of radioactive samples, has done analyses on irradiated UO2-Gd2O3 nuclear fuel samples. Gadolinium, and more particularly its isotopes 155 and 157, is a burnable poison that plays an important role in the optimization of fuel campaign durations in current and future nuclear reactors in France and abroad. Unlike boric acid, which is present in the moderator, gadolinium is introduced directly into some fuel rods at specific positions in the fuel assembly in the form of a mixture of UO2 and Gd2O3 oxides. The quantity of gadolinium in a reactor cannot be controlled in real time. Its isotopic composition evolves strongly as the absorbing isotopes are consumed by nuclear absorption reactions. Its effect on the reactivity decreases until it becomes almost negligible when all the isotopes 155 and 157 have been consumed. The evolution of gadolinium isotopes must be finely modelized by neutronic codes in order to correctly calculate the evolution of nuclear reactor cycles.

The analytical strategy previously developed on simulated fuels was applied and validated on gadolinia fuels and the calculated concentrations and isotopic ratios measurements of the different radionuclides of interest (U, Pu, Nd, Gd) could be determinated by isotopic dilution and TIMS-MC or ICP-MS-MC measurements.

Other samples remain to be analyzed in the same way and a “cross-checking” using the results obtained during phase I of the REGAL Program will be done between SCK and CEA..

The results obtained will allow the improvement of neutronic codes which are key simulation tools for the operation of existing and future nuclear power plants with a maximum level of safety as well as for the reprocessing processes of spent fuel.

nuclear fuel samples, gadolinium, isotopic measurements, isotopic dilution, ICP-MS-MC, TIMS-MC, mass spectrometry, radiochemistry

Evaluation of the affinity and selectivity of biomimetic peptides towards uranium by HILIC-ESI-MS/ICP-MS

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Understanding and limiting the impact of uranium (U) on man requires the characterization of the interactions of UO_2^{2+}, the chemical form of U in vivo, with target biomolecules that are unknown until now. In this context, biomimetic peptides, designed specifically to mimic the coordination sites of UO_2^{2+} in proteins, are very useful chemical tools todetermine the parameters responsible for UO_2^{2+} affinity towards its target proteins and further develop selective decorporating agents.

The aim of this work is to develop a dedicated analytical method to determine in a single step and at physiological pH, the affinity and selectivity of multi-phosphorylated biomimetic peptides for UO_2^{2+}. The strategy was based on the simultaneous coupling of hydrophilic interaction liquid chromatography (HILIC) to electrospray ionization mass spectrometry (ESI-MS) and inductively coupled plasma mass spectrometry (ICP-MS). Firstly, different sets of UO_2(peptide) complexes were successfully separated using different polar stationary phases, being the first HILIC separations of UO_2^{2+} complexes reported in the literature. A dedicated method had been developed for identifying the separated peptide complexes online by ESI-MS and simultaneously quantifying them by ICP-MS, based on U quantification using external calibration. The effect of several structural parameters of the peptides, such as the number and position of phosphoserine (pSer) residues but also their cyclic/linear structure, on UO_2^{2+} affinity were determined. Results showed that the tetra-phosphorylated cyclic peptide (pS1368) exhibited the highest affinity for UO_2^{2+} in comparison with its linear homologue and with cyclic peptides containing lower number of pSer, while the position of pSer had very little influence on this affinity. Following the same approach, the selectivity of pS1368 was determined in the presence of endogenous cations as potential competitors in biological media. pS1368 was the most selective towards UO_2^{2+}, underlying its potential as a promising decorporating agent of this element in vivo.

UO_2^{2+}, biomimetic peptides, metals, affinity, selectivity, HILIC, ESI-MS, ICP-MS

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Measurement of organofluorines in ski waxes with non-target HPLC-qTOF-MS/ICP-MS

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Per and polyfluoroalkyl substances (PFAS) are common additives in ski waxes for their water repellent characteristic. Abrasion of ski wax leaves PFAS on the snow surface, which upon melting, can migrate the soil, taken up by plants or go into the groundwater. However, little is known about concentration and species of PFAS in the ski waxes. In this study we analysed different, commercially available ski waxes using non-targeted HPLC-qTOF-MS/ICP-MS to understand more about what kind of PFAS can be left behind in the environment after skiing.

PFAS, skiing, speciation, fluorine

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Development and validation of a novel method for Hg speciation analysis in food by HPLC-ICP-MS within the 3rd (French) Total Diet Study

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3rd (French) total Diet Study (3rd TDS). TDSs are endorsed by the World Health Organisation (WHO) and Food and Agriculture Organization of the United Nations (FAO) and they are one of the most efficient tools for national assessment of chemical contamination of food prepared as consumed. This allows estimating human dietary exposure after matching contamination data (occurrence) with the consumption patterns based on samples representativeness. TDSs provide valuable scientific information to national authorities in order to address the risk for the general population in terms of food chemical hazards and permitting to protect the public health on a long-term basis.

An effective separation of Hg2+ and MeHg species was achieved in less than 7 min using a peptide mapping RP column. The development was carried out using an experimental design for the HPLC separation and the sample extraction. In the latter case, two extraction approaches, employing a closed microwave system and the use of a heating block, respectively, were compared.

The method was validated based on the accuracy profile approach according to the NF V03-110 French standard, which takes into account the simultaneous assessment of the accuracy and precision of the method. The accuracy profile is an expression of the combination of the systematic (trueness) and the random error (repeatability and/or intermediate precision) for a series of analyst's levels in various matrices in range of concentrations called validity domain. For this purpose, five measurement series were repeated in duplicate on (5) different days, over a timespan of two months for constructing the accuracy profile.

This method was proved to be robust and suitable for the routine determination of MeHg and Hg2+ in fishery products with satisfactory analytical performances in order to assess the risks related to the consumption of this type of foodstuffs.

Hg speciation analysis, food, microwave extraction, HPLC-ICP-MS, experimental design, Total Diet Study

Simple methods for the determination of Arsenic speciation by Hydride Generation and Plasma Atomic Emission Spectrometry

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Arsenic is found in nature in different chemical forms with variable toxicity. Inorganic arsenic compounds are more toxic than organic ones, and As(III) is more toxic than As(V). The main concern about arsenic is the contamination of groundwater that affects many different countries around the world. Some bacteria can be used to prevent or decrease arsenic toxicity by modifying arsenic speciation into less toxic species. It is, then, important to find reliable methods to quantify total arsenic and arsenic species in water and exhausted culturing media to understand the capacity of bacteria to modify arsenic speciation.

Hydride generation (HG) is a selective sample introduction method that decreases matrix effects and increases sensitivity by forming hydride gas. GH requires a reductant, usually sodium borohydride, acid medium, and in some cases a prereductant. Different prereductants and acidic conditions allow the differentiation between species. [1]

In this work, we develop different arsenic speciation methodologies in water and exhausted liquid media samples using HG coupled to two different plasma based atomic emission spectrometers. The first one is an inductively coupled plasma atomic emission spectrometer (Agilent 5100 ICP-OES) and the second one is a new microwave induced plasma atomic emission spectrometer (Agilent 4200 MP-OES). With the first instrument (ICP-OES) we use a classic VGA77 as HG, meanwhile, with the MP-OES, we use a Multiple Sample Introduction System (MSIS), which is a simple and easy-to-use hydride generation system. [2]

Different methodologies using these devices and instruments are studied in order to clarify the behaviour of four different arsenic species: Arsenite, Arsenate, MMA (monomethylarsonic acid) and DMA (Dimethylarsenic acid). The more useful methods for the determination of the arsenic speciation are applied to spiked water and used to assess As speciation in grown bacterial cultures. A mathematical strategy is developed, combining calibration equations of each method to determine the concentration of the four species. Good agreement is obtained for the spiked samples for the four arsenic species in both matrix samples.

Arsenic speciation, Hydride Generation, ICP-OES, MP-OES, Bacterial cultures, Natural Water

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As species immobilization in the mining-contaminated soils using soil remediation

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We explore the possibility of using horticultural compounds, such as, coconut and pine husk, cellulose, and nanocellulose for arsenic species immobilization in severe mining-contaminated soils. Arsenic species in plants and soils from Pejão mining region are extracted with a 1 molL-1 of KNO3 remediated with horticultural compounds and further HPLC-ICP-MS measurements conduct. The results show that arsenate is the main specie in all the soils analyzed and that in some samples arsenite and methylated species could also be detected. The determination of the ''pseudototal'' arsenic in these soils, obtained by applying extraction with aqua regia (ISO Standard 11466), is also carried out. The results of laboratory demonstrate that horticultural compounds drastically reduce the arsenic species content in the environment.

soil, Arsenic, Species

Development of HPLC-ICP-MS method for the speciation analysis of nano and dissolved forms of silver in biological samples

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A rapid growth in the commercial application of silver nanoparticles (AgNPs) has been observed mainly due to their wide spectrum of antimicrobial activity (e.g. food contact materials, cosmetics, anti-odour sportswear, socks, disinfecting sprays, toothbrushes, water filters). Therefore, it is certain that the exposure to silver among humans and in the environment will increase. The unique reactivity of silver nanoparticles increases the possibility of their dissolution into ionic forms. Therefore, analytical methods are required for the simultaneous determination of silver nanoparticles and silver ions in different matrices (consumer products, environmental and biological samples).

The application of high performance liquid chromatography (HPLC) for the separation of nano and dissolved forms of silver with post-column ICP-MS detection is presented in this work. The Nucleosil C18 column (7 µm particle size, 1000 Å pore size, 250 × 4.6 mm) was used for the chromatographic separation. Special attention was paid to optimizing the composition of mobile phase to ensure the stability of both silver species. The developed HPLC-ICP-MS method is characterized by low limits of detection: 2.0 pg/mL Ag(I), 3.1 pg/mL 10 nm AgNPs, 2.2 pg/mL 30 nm AgNPs and good precision (0.08 – 0.3% for retention time and 0.2 – 4.5% for peak area). The method was successfully applied for the studies on the transformation of silver species in water – green algae environment.

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silver nanoparticles, HPLC-ICP-MS, speciation

Copper speciation in human serum of hepatobiliary cancer patients by conjoint liquid chromatography and inductively coupled plasma mass spectrometry

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Copper (Cu) is essential trace metal for all living organisms. Its concentration in the plasma of a healthy human population ranges between 500 - 1000 ng/mL. Most of the Cu is firmly bound to the ceruloplasmin (Cp), (around 90%), while the rest is exchangeable Cu, weakly bound to albumin (HSA) and amino acids [1]. Due to important physiological functions and the role of Cu in various diseases, it is necessary to quantify the concentration bound to Cp and the exchangeable fraction. According to available literature data Cp can be potentially used as a biomarker for cancer diagnosis and prognosis [2]. More detailed information can be obtained when Cu bound to Cp in human serum is determined. In the present study, Cu speciation analysis was applied to determine Cu-Cp in the serum of twenty hepatobiliary cancer patients in order to investigate the possibility of using Cu-Cp as a potential biomarker in neoplastic diseases. The results were compared to the Cu-Cp content of twenty healthy individuals.Cu-Cp was determined based on our previously developed analytical method [3]. Conjoint liquid chromatography (CLC) on short-bed convective interaction media (CIM) monolithic disks was used to separate the Cu bound to low molecular mass (LMM) species and the Cu bound to Cp and HSA in human serum. Two immunoaffinity CIMmic albumin depletion (α-HSA) disks and one CIMmic weak anion-exchange diethylaminoethyl (DEAE) disk were assembled in a single housing, forming a CLC monolithic column. The separated Cu species were quantified by post-column isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). To check the significancy of the differences in the Cu-Cp, Cu-HSA and total Cu concentrations between the populations of cancer patients and healthy individuals, a Student's t-test at a 0.05 level of significance was applied. The obtained data suggested that Cu-Cp can be used as a potential biomarker in cancer diagnosis.

Copper speciation, biomarker, hepatobiliary cancer, conjoint liquid chromatography, monolithic disks, isotope dilution

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Lipophilic arsenic compounds in cultured Chlamydomas sp. compared to Laminaria saccharina

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The rich biochemistry of arsenic especially in marine environments is by now well known. This element is present not only in water-soluble compounds, but also in lipophilic compounds. In fish lipophilic arsenic is present predominantly in form of hydrocarbons and fatty acids. Macroalgae of the order Laminariales and Fucales contain beside As-hydrocarbons also As-containing phospholipids. Algae of these two orders were predominantly studied so far. In marine microalgae and plankton samples arsenic-containing phytols were also detected. Lipophilic arsenic compounds in fresh-water / terrestrial environments have not been reported extensively. Partly this may be to blame on the generally lower arsenic concentration in terrestrial / freshwater organisms. Here we report on a study of arsenic species synthesised by a wide-spread freshwater / soil microalgae family. Chlamydomonas is a group of freshwater/soil microalgae often used for studies, especially C. reinhardtii is used very often and also available in a variety of well-defined genetic mutants. Culture of different strains of this algae under environmentally relevant background concentrations of arsenic showed that the algae not only absorb arsenic but metabolise inorganic arsenic to a variety of methylated arsenicals. Lipophilic arsenic compounds were dominant and included As-containing phospholipids and As-phytols, but no As-hydrocarbons or As-fatty acids, both of which were identified in marine microalgae (Dunaliella tertiolecta) and macroalgae.

arsenic, microalgae, lipophilic arsenic

Determination of methylmercury and inorganic mercury in human hair samples of individuals from colombia by ID-GC-ICP-MS

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Mercury (Hg) is a toxic substance of major public interest due to its increasing emissions to the atmosphere by both natural and anthropogenic sources, such as the amalgamation from artisanal small-scale gold mining (ASGM). In the course of ASGM activities, not only harmful vapors are released to the atmosphere, but Hg residues enter to aquatic ecosystems, where part of them are transformed into methylmercury (MeHg). This MeHg is biomagnified through the trophic chain, being fish consumption the main route of Hg exposure for humans (1).

Colombia stands out as one of the world's leading gold-producing countries, as a great part of its rural population is involved in mining-related tasks. Hg uses in artisanal gold mining are well widespread in Colombia, thus the country is the most mercury polluting per capita. Hg species-specific determination in indigenous population samples provides a general exposure view, either from Hg burning vapors or from consumption of contaminated fish. Most studies of human exposure to Hg are focused on the determination of total mercury (THg) in different biological biomarkers such as blood, hair, or urine. However, the determination of inorganic mercury (Hg(II)) and methylmercury (MeHg) along with THg can provide useful information on the exposure sources (2).

In this work, MeHg, Hg(II) and THg concentrations were determined in 96 human hair samples of individuals, mostly non-directly occupied in ASGM tasks, from six different Colombian regions: five Andean regions (Nariño, Chocó, Antioquia, Bolivar and Sucre) and one Amazonian region (Vaupes). The determination of Hg species was done by gas chromatography coupled to inductive plasma mass spectrometry (GC-ICP-MS). Sample quantification was carried out by isotope dilution analysis with a double tracer to obtain accurate and precise results and to correct for interconversion between species during the sample preparation procedure (3).

mercury, methylmercury, inorganic mercury, isotope dilution, GC, ICP-MS, hair

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Ultra-trace analysis of (^{57}Fe)transferrin in cell media using SEC-ICP-QMS

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Iron is an essential micronutrient that is required by all cells. Although mammalian iron metabolism is in general well characterized, surprisingly little is known about the transfer of iron from the body of a pregnant woman to that of the developing fetus. This topic is largely understudied due to the lack of appropriate analytical methods, which allow to assess the total amount as well as the chemical form of iron that is transported from mother to child. In this contribution we aim to investigate the potential of isotopically labelled (^{57}Fe)transferrin in combination with (size-exclusion chromatography) inductively coupled plasma quadrupole mass spectrometery ((SEC)-ICP-QMS) for the quantification of ^{57}Fe and isotopically labelled (^{57}Fe)transferrin in cell media. Our preliminary studies show that very low analyte concentrations, a high iron background and the lack of intact apo-transferrin standards for ^{57}Fe labelling represent major challenges to the determination of isotopically labelled (^{57}Fe)transferrin in relevant cell experiments. Consequently, we aim at addressing these points by the use of an inert and metal-free HPLC system (NexSAR™, Perkin Elmer, USA), optimized instrumental conditions and the analysis of further commercially available apo-transferrin standards. The developed analytical method has high potential to be used in in vitro as well as in vivo models and thus investigate the transport mechanism of iron from mother to child.

speciation analysis, enriched stable isotopes, human metabolism

A Comparison Revue of SEC/AF4-ICP-MS Hyphenation: Speciation and Quantitation of Polydimethylsiloxanes at Trace Levels

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Polydimethylsiloxanes (PDMS) are worldwide the most often used silicon-based polymers, because of their outstanding properties. Routinely used ICP methods [1] revealed the ability to quantify ultra-trace levels of PDMS as silicon in volatile and non-volatile organic solvents. But the drawback of ICP is that it is only suitable for the determination of total silicon; distinguishing between different silicon components is not possible.

A combination of size-exclusion chromatography with ICP-OES overcomes this gap and provides a highly flexible separation of organosilicon compounds according to molecular weight [2]. This suitable method was transferred to ICP-MS combined with different size separation systems like SEC and asymmetric flow field-flow fractionation to investigate the possibilities and limitations offered by these tools for the separation, characterization, and detection of organosilicon compounds with the intention to further decrease the LOD and to expand this investigation to a greater molecular size range.

This work presents a comparative view on SEC and AF4 combined with ICP-MS with respect to separation power over different molecular weight PDMS compounds under consideration of sensitivity, selectivity, and robustness. The work leads to application related recommendations, as depending on the nature of components of interest, the two techniques have advantages and disadvantages. The experiments show that the use of SEC-ICP-MS is preferred with respect to selectivity, robustness, ease of use and because of the flexibility in terms of selectable organic eluents. Especially when compositions are expected to have molecular weight distributions ranging from low to medium mass averages and their components mainly have linear structures. In contrast, higher sensitivity can be obtained using AF4-ICP-MS, because of the high-volume injection possibility (900µL), especially when branched molecules with high mass distributions are expected.

Both separation techniques combined with ICP-MS offer the possibility to separate different molecular mass compounds, silicon and non-silicon-based, and generate valuable information about sample compositions. ICP-MS shows a clear advantage compared to ICP-OES regarding the addressable concentration range of Si (ppb – wt%).

Speciation, Quantification, SEC, AF4, ICP-MS, ICP-OES

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In-situ study of temperature related changes in polymers using LIBS

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The influence of elevated temperatures on the properties of polymers is of great interest for almost all practical applications. Depending on the type of material, polymerisation temperature might influence the final properties of the product. For other polymers, the investigation of high-temperature degradation is of more interest. And for some products, both might be true.

To study temperature related changes in polymers using LIBS (Laser Induced Breakdown Spectroscopy) we have implemented a heating chamber, facilitating temperatures up to 1000°C and different atmospheres, in our commercially available LIBS instrument. Polyimides, which are a type of high-performance polymer, designed to use at temperatures near the expected limits for purely organic materials, were chosen as a sample material. In this work, in-situ measurements during fabrication and for degradation studies were carried out using temperatures up to 400°C. Elemental lines as well as molecular emission bands were used to monitor changes in the polymer structure.

LIBS, polymers

kHz LIBS-Imaging: Building the future of elemental imaging

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Laser-induced breakdown spectroscopy (LIBS) is a versatile analytical tool for studying the elemental composition of any kind of samples, such as solids, liquids, or gases. LIBS imaging is now established as a very attractive and popular technique for qualitative and/or quantitative spectrochemical characterization of specimens of interest for a wide range of applications. In recent years, the implementation, i.e., spatially resolved surface analysis, LIBS-imaging, is becoming one of the reference elemental imaging tools [1].

Today, LIBS technology can achieve a spatial resolution of 10 µm, which means 10^6 spectra per cm^2 . On the other side, the most commonly used laser frequencies are in the order of 10 - 100 Hz.As a consequence, to measure a large sample brings new issues to consider and one of them is the duration of data acquisition, as it can reach 2.5 hours per cm^2 (10 µm resolution). Consequently, when large areas are analyzed by LIBS-imaging, reducing the analysis’ duration is at the cost of, either the resolution or the inspected area.

In this work, we demonstrate the proof of concept of the use of kHz laser in a LIBS instrumental system to carry out elemental imaging analysis over geological samples. The use of kHz allows to optimize the analysis duration; we achieve to measure one cm^2 in less than 20 min while keeping the 10 µm resolution. Moreover, the reduction of the measurement time by 1 order of magnitude renders LIBS-imaging attractive for news types of applications where duration is a critical factor, such as in industry or non-stable samples. A critical analysis of the obtained results is presented, as well as the advantages and drawbacks of the use of kHz laser for elemental analysis by LIBS.

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LIBS, Imaging, kHz LIBS,

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Hyphenation of a high-speed laser ablation system to Quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for imaging applications

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Laser Ablation (LA) coupled with ICP-MS is a well-established way to directly analyze solid samples. The main advantages of laser ablation include the ability to avoid lengthy and potentially contamination prone sample preparation protocols and the ability to obtain information about the spatial resolution of an analyte in a sample.

The interest in so-called mapping techniques has increased in recent years, calling for laser ablation systems to develop methods to improve sample transfer and therefore speed of mapping experiments. New laser-ablation systems dedicated to high-speed mapping are commercially available and can be easily coupled to quadrupole ICP-MS for such applications.

With the improvement in sample transfer and washout times from laser ablation systems, the time available to analyze discrete packets of sample from a laser pulse is drastically reduced. The limit for lateral resolution using a sequential ICP-MS, such as a quadrupole ICP-MS, is dependent on the dwell times chosen for each measured m/z channel. This has a direct impact on the signal-to-background ratio achievable for each m/z channel; therefore, a direct impact on the final image contrast for each mapped m/z channel.

In this poster, the authors chose a Granite thick section containing a range of elements in localized crystal distributions to demonstrate the ease of coupling to a commercially available high-speed mapping laser ablation system, ease of dwell-time optimization for best signal-to-background ratio and image contrast across all scanned elements, and finally fast analysis times from sampling to image.

Laser Ablation, Imaging, Fast Washout, Image Contrast

LA-ICP-OES for high-precision analysis of Sr/Ca paleo-seawater temperature proxy in corals

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The Sr/Ca ratio of coral carbonate is a widely used proxy for reconstructing paleo sea surface temperatures (SST).Living Porites sp. colonies build skeletons that can span more than 300 years and, hence, represent valuable archives for past climate conditions, even in very remote areas of the tropical oceans where no instrumental records exist.[1] Subfossil Porites corals provide records of seasonal to interannual variability in time windows spanning the Past Millennium, the Holocene and even the Past Interglacial. Such paleo-temperature data sets are urgently needed for validating models that are developed for predicting the future of Earth climate. Sr/Ca directly compares to the temperature where coral carbonate crystallized from seawater. Consequently, a small uncertainty of Sr/Ca ratio determinations accomplishes temperature estimates with high resolution. We routinely determine Sr/Ca by liquid sample introduction ICP-OES with measurement uncertainties of ~0.05%rel. (1SD) which correspond to temperature uncertainties of ~0.1°C. Here, simultaneous 'multi-collector' data acquisition is the gold standard for a high precision determination of elemental/ isotopic ratios and superior to instruments with sequential data acquisition like ICP-MS. MC-ICP-MS instruments do not have the dispersion needed for a simultaneous analysis of Ca and Sr. Conventional Sr/Ca analysis is based on micro-drilled coral carbonate powder with a spatial resolution of ~1 mm allowing for monthly to bimonthly SST estimates. This approach is extremely time-consuming and labour-intensive given sample numbers of 3-4,000 samples for a typical temperature record of ~300 years from a large Porites coral colony. Direct solids micro-analysis utilizing laser sampling has a huge potential for increasing sample throughput. Published data for Sr/Ca by LA-ICP-MS, however, do not have the quality that is needed for high resolution temperature reconstructions. We couple a 193nm excimer laser (ESL imageGEO193) with a large format fast-washout two-volume ablation cell (ESL TV2) to a simultaneous ICP-OES instrument (SPECTRO Arcos II MV) in axial viewing mode. This is the only ICP-OES instrument with transient data acquisition as needed for laser ablation signals. A series of coral-carbonate nano-particulate powder pellets ('nanopellets')[2 3] with variable Sr/Ca ratios is used for intensity ratio calibration. We will report on figures-of-merit of this setup for high-precision Sr/Ca analysis by LA-ICP-OES.

simultaneous ICP-OES, transient mode, 193nm excimer laser, two-volume cell, Sr/Ca, corals, intensity ratio calibration, nanopellets

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Study of the beryllium spectral line shape using Laser Induced Breakdown Spectroscopy

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Beryllium is a naturally occurring element in metal-poor stars and has been chosen as the element to cover the first wall of ITER (International Thermonuclear Experimental Reactor).Erosion of beryllium under transient plasma loads will determine the lifetime of the ITER first wall, so the presence of Be dust particles in plasma should be monitored. In addition, the Be deposits on other fusion reactor components should be studied by, for example, a calibration-free LIBS method. This method requires determination of the plasma parameters, which can be derived from the parameters and shape of the Be spectral lines. The study of the Be lines shapes was performed using spectra recording of the plasma emission due to interaction of the fourth harmonic Nd:YAG laser radiation at 266 nm, pulse energy 70 mJ at 10 Hz repetition rate with the BeO target. The target made from BeO ceramics was rotated by the motor in the low-pressure chamber. The 1:1 image of the plasma plume was projected by optical mirrors on the entrance slit (20 μm wide) of a 0.5 m Ebert-type spectrometer with an iCCD camera operated in the image mode and controlled using a pulse generator (DDG 535, Stanford ResearchSystems) triggered optically by the plasma. The plasma emission was accumulated over 160 ablation events to exclude the influence of shot-to-shot fluctuations in the signal. The acquisition gate width was 100 ns. Since previous studies have shown some discrepancies between obtained line shape parameters and theory2, the main task was to enable spatially and temporally resolved measurements of Be lines of interest, which was readily achievable with the used experimental setup. Careful inspection of the ablation and plasma creation process provided insurance that the dust-free environment is indeed obtained in the experimental setup. This is a quite important aspect since dust can have a significant influence on the line shape parameters. Knowledge about its impact on the line shapes will be highly beneficial in the future, where large amount of ITER-related dust is expected to be formed and interfere with the plasma and its emission. Further improvement of this study is the possibility of testing the less obvious influence of self-absorption on the line shapes and intensities. This was achieved using the setup with the lens and flat mirror3.

beryllium, LIB S, spectral line shapes, plasma diagnostics, plasma fusion reactor

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Direct metal analysis by new Galvano-mirror fs-LA-ICP-MS using 100%-normalization method with NIST612 glass CRM as calibration standard

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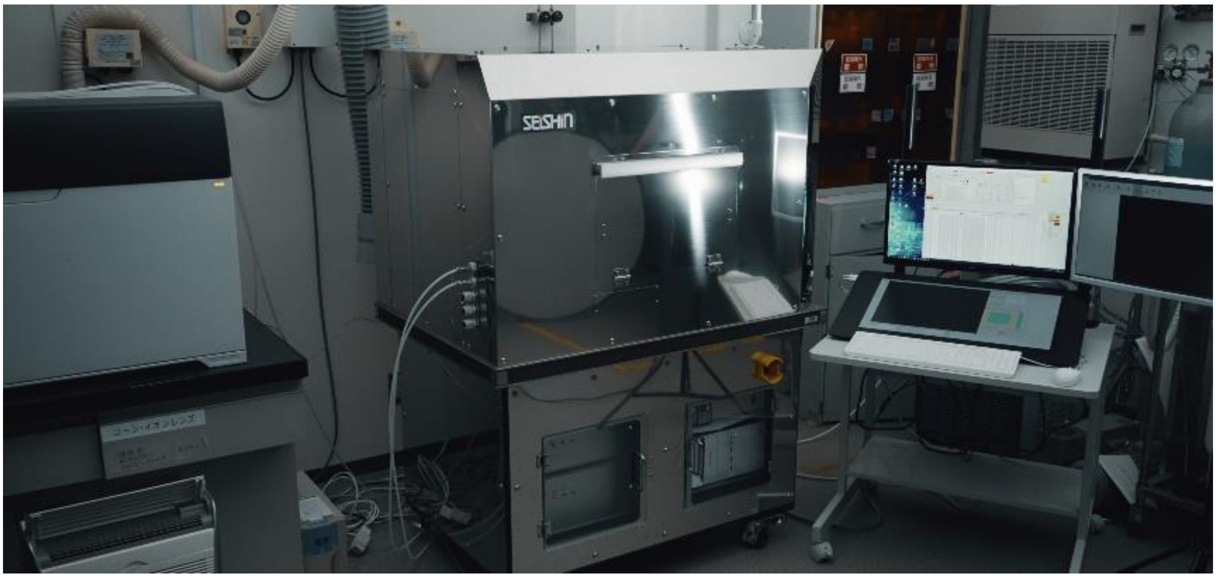
A demonstration of quantitative solid direct analysis by new LA-ICP-MS will be presented. The demonstration used ICP-MS coupled with the latest femtosecond laser ablation system (fs LA-ICP-MS) and 100% normalization method. The combination solves the difficulty to find calibration standard in LA-ICP-MS, allowing simple but accurate quantitative solid analysis. The fs-LA is a new LA system by SEISHIN (Kobe, Japan) which features high repetition rate pulse up to 60khz and fast scanning by Galvano mirror. The improved elemental fractionation by the fs-LA and the 100% normalization method allows us to use NIST glass CRM as calibration standard for metal analysis. The details of the technique and the demonstration result will be presented.



LA-ICP-MS, Solid Analysis, Laser, high purity metal, metal analysis

Laser ablation ICP-MS quantitative analysis of selected lanthanides adsorbed onto zero-valent iron nanoparticles

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Nanosized zero-valent iron (nZVI) has become one of the most important engineered nanomaterials and has been an object of numerous studies for their potential application as an environmental remediation agent.1 One of the pollutants that have gained large importance in recent years are lanthanides due to their application in many modern materials and systems (e.g., electronics, optics, catalysts).2 Therefore, a method for their recovery from environment, as well as analytical method to assess its efficiency, is needed. However, due to their chemical and physical similarities, as well as the fact that they usually occur in mixtures with other lanthanides, make their determination rather difficult and complicated. Quantitative analysis of lanthanides was done in the past by atomic absorption and atomic emission spectrometry, however numerous coincidences and interferences in their optical spectra would render application of these methods for lanthanide determination very difficult and time consuming. Currently all forms of inductively coupled plasma mass spectrometry (ICP-MS) have been employed in determination of lanthanides in various samples due to its great sensitivity, high precision and accuracy, wide linear dynamic range and limited interferences. ICP-MS has mainly been applied to aqueous samples, while solid samples traditionally require often tedious sample dissolution procedure during which original sample is destroyed and may become contaminated due to addition of dissolving reagents. Laser ablation (LA) as a sample introduction method for ICP-MS allows for direct analysis of solid samples, with no or minimal sample preparation procedure and is virtually non-destructive. In addition, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) can be utilized for sample microanalysis, elemental mapping and depth profiling, expanding the analytical applications of ICP-MS. The aim of this work is to assess applicability of LA-ICP-MS to quantitative analysis of selected lanthanides in iron-rich matrix (i.e., nZVI particles). Particles are synthesized by reduction of iron(III) salt by sodium tetrahydroborate in aqueous solution and used for sorption of lanthanides from pH-adjusted standard solution. After that nZVI are deposited onto a surface of silica-coated glass plate and their composition determined by LA-ICP-MS. As a quality check, the lanthanide solution after sorption is analyzed by ICP-MS with solution nebulization as a means of sample introduction.

iron nanoparticles, lanthanides, LA-ICP-MS, quantitative analysis

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Improving the Quantification of Carbon, Nitrogen and Oxygen with Fast Flow GD-MS

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Sector Field Fast Flow Glow Discharge Mass Spectrometry (FF-GD-MS) is routinely applied for the direct analysis of a wide range of materials.Especially for aerospace, electronics and photovoltaic industries, quality control at high sample turnaround is required, for example for nickel super alloys producers or high purity copper refineries.

There is an increasing interest of analysis where beneath metals and metalloids also carbon, nitrogen and oxygen need to be quantified with one single technique. Here we show results of a newly developed CNO kit. It improves the quantification of carbon, nitrogen and oxygen with the Thermo Scientific™ Element™ GD Plus GD-MS significantly.

Glow Discharge, Carbon, Nitrogen, Oxygen

Nd:YAG vs. fiber lasers, or Laser induced breakdown spectroscopy with widely different pulse profiles and repetition rates

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Laser induced breakdown spectroscopy (LIBS) is a dynamically developing atomic spectroscopy method, which is capable of quick multielemental analysis of solid liquid and gas samples with little to no sample preparation. Its quick advancement is partly due to the constant technological progress of the pulsed laser sources, better beam parameters, higher and more stable pulse energies are available every year. One of the most popular, modern laser sources in the industry are fiber lasers, which are widely used for cutting, welding, marking, etc. of workpieces. Indistrial fiber lasers usually employ a fused silica optical fiber doped with rare earth metals as an active medium (amplifier) and the end-on pumping is achieved by a fast semiconductor laser [1]. These sources can provide continous or pulsed emission, and their pulse repetition frequency (PRF) is much higher (kHz-MHz range) compared to that of typical solid state lasers (PRF of a Nd:YAG is usually 1-20 Hz). They are robust, have a long life span (tens of years) and require little maintenance. Due to recent developements in this field, the pulse energy of these lasers now reaches the several mJ range, accompanied by ns duration pulses, which brings up the possibility of their use in LIBS [2]. The elongated beam profile and high pulse repetition rate of the fiber laser are very unique properties, which might can be advantageously used for LIBS purposes. Our research group have already demonstrated the benefits of utilizing high repetition rates in the range of tens of kHz. By the usage of two consecutive laser pulses with very short inter pulse delay the signal was significantly increased, and the detection limit was lowered [3]. In this current study we are comparing a TRUMPF Trupulse nano 5020 fiber and a Quantel Ultra 100 laser sources, which have 40-2000 and 6 ns pulse lengths, respectively. We compare their ablation properties, as well as their plasma temperatures, and emission characteristics as well. We also tested the effects of applying different atmospheric conditions on the plasma parameters.

LIBS, fiber laser

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Depth-resolved analysis of technologically relevant materials by simultaneous LA-ICP-MS & LIBS measurements

Maximilian Podsednik[1], Silvia Larisegger[1], Michael Nelhiebel[1], Stefanie Taibl[2], Philip Klein[2], Jürgen Fleig[2], Ahmed Bahr[3], Helmut Riedl[3,4], Paul Heinz Mayrhofer[4], Andreas Limbeck[2]

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To meet the challenges of the 21st century, like global warming and increasing energy consumption, tremendous progress in material science has been essential for the last decade. To optimize technology relevant for energy production and storage (e.g., solar cells, fuel cells, and batteries) and systems exposed to high temperatures, corrosive milieus, or mechanical impact (e.g., machining, aerospace industry), novel high-performance materials are inevitable. To establish a correlation between composition and function, a fast analytical characterization is necessary since crucial material properties are determined by the elemental composition from the bulk stoichiometry down to dopants present with lower contens or unwanted impurities.

For the spatially resolved characterization of high-performing materials, direct solid sampling methods like LA-ICP-MSor LIBS can be used as analytical techniques. While LA-ICP-MS is more suited for the analysis of trace elements, LIBS offers the possibility to analyze elements like O, H and N, which are not accessible for LA-ICP-MS.

In this work, a method for simultaneous LA-ICP-MS & LIBS measurements is presented. To demonstrate the capabilities of this setup, a depth-resolved analysis of the challenging element oxygen in ceramic and coating materials has been performed. LIBS with ICCD detection provided sufficient sensitivity for oxygen analysis, while all other sample constituents were measured using ICP-MS, enabling accurate determination of changes in sample composition. The application of a 193 nm excimer laser system enabled fast measurements with a depth resolution in the order of 100 nm only, showing the potential of this method to provide depth-resolved information about overall differences in stoichiometry and oxidation behaviors.

LA-ICP-MS, LIBS, depth profile analysis, oxygen-distribution

Poster - Tu 64 LA & GD

Laser Ablation Split Stream (LASS) Analysis in Economic Geology: Insights into Metallogenesis, Silesia-Cracow MVT District, Poland

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Laser ablation split stream (LASS) analysis in the geosciences has rarely been applied outside of petrochronology. Here, we demonstrate its application toward a deeper understanding of ore-forming processes in the Silesia-Crakow (SC) District, Poland. SC is a classic Mississippi Valley-Type ore system composed principally of sphalerite, galena and marcasite-pyrite ore minerals. These sulfides were analyzed in-situ from several deposits using a Teledyne Cetac Analyte Excite[a] 193 Nm laser system. The laser stream was split between a quadrupole ICP-MS (Thermo ICAPQ-RQ[a]) and a multi-collector ICP-MS (Nu Plasma 3[a]). Signal strength was optimized using the internal flow meters of each instrument. The LASS analysis allowed simultaneous analysis of a suite of mostly chalcophilic trace elements (V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Mo, Ag, Cd, In, Sn, Sb, Pt, Tl, Pb) and S isotopes (^{32}S,^{33}S, ^{34}S). Enhanced sensitivity[1] provided high quality analyses down to 20 micron laser spot size; a critical requirement in complexly-zoned sulfides. This allowed coupling of chemical/isotopic information with textural information to provide a relative temporal context for sulfide precipitation. For instance, from examination of complex textures in sulfide speleothems, some of the S was present as gaseous H_2S in karst cavities implying that the ore metals carried in chloride-rich fluids and ligands were geochemically decoupled. In addition, the ability to accurately calculate $\Delta^{33}S$ has allowed the recognition of unexpected mass independent fraction with implications for the source of at least some of the S.

[a] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government..

Laser ablation, split stream analysis, economic geology, sulfur isotopes, chalcophile elements

Pribil et.al., 2022, 2023 European Winter Conference on Plasma Spectrochemistry.

Implementation of a new heating stage for in-situ LIBS analysis of temperature induced processes

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Temperature-induced and temperature-dependent processes in solid materials are vital for many technological application fields. In related research, samples are often treated in an oven at a defined temperature for a specific time and analyzed ex-situ after cooling the sample to ambient temperature. This approach can be prone to errors for multiple reasons. The observed process can continue further during cooling, and rapid cooling could change the sample properties and lead to stress or cracks. Moreover, further reactions can occur if the sample-surrounding atmosphere is not controlled (humidity, traces of corrosive gases, oxygen). Thus, for concerning applications, in-situ analysis is indispensable.

Laser Induced Breakdown Spectroscopy (LIBS) is a powerful technique for direct solid analysis, offering elemental information of the entire periodic table and the possibility of spatially resolved measurements - analytical capabilities which make LIBS perfectly suited for the characterization of processed, aged or degraded samples. However, commercial LIBS instruments only allow operation at ambient temperature, permitting solely the ex-situ investigations mentioned before.

This work presents the development and application of a newly implemented heating stage for in-situ LIBS, enabling measurements at temperatures up to 1000 °C while the chamber atmosphere can be changed as required. This combination allows the investigation of a large variety of scientific questions.

The versatile applicability is demonstrated in different examples by the in-situ acquisition of time-resolved results. The scaling of copper under synthetic air was monitored at different temperatures by measuring the oxygen signal of the growing oxide layer. Exploiting the capability of LIBS to obtain also molecular emission, e.g., C_2 or CN, the imidization reaction of precursers to a polyimide film was monitored at different temperatures. Finally, the interdiffusion of metals in layered systems was investigated using depth-resolved analysis.

in-situ LIBS, heating stage, material characterization

Development of LA-ICPMS method for elemental characterization of PM samples and its application to ambient samples from Ljubljana

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Particulate matter (PM) consists of various particles suspended in the atmosphere and it is an air pollutant harmful to humans and the environment. Its elemental composition is regulated by national authorities (e.g. EU directives 2004/107/EC and 2008/50/EC) and routinely monitored by collecting PM on quartz fiber filters and analyzing it with inductively coupled plasma mass spectrometry (ICPMS). Since PM is a solid material, a pre-treatment with acid microwave digestion (MW) is required, which is a source of many drawbacks (e.g. produces a lot of toxic waste, is time-consuming, provides the possibility of sample contamination or loss of volatile elements, etc.) [1]. Furthermore, the prescribed method does not provide a complete digestion of all PM matrixes and is certified only for four elements (i.e. As, Cd, Ni, Pb). To overcome those drawbacks, we developed a new method, using laser ablation (LA) coupled to ICPMS, which determines elemental concentration directly from solid samples [2]. We optimized instrumental parameters, determined the sampling procedure, and investigated the homogeneity of the samples. The calibration presented an issue since the matrix-matched standard with certified elemental composition is not commercially available [3], therefore, in-house standards were produced by characterizing ambient PM samples with instrumental neutron activation analysis (k0-INAA). The resulting method was proven sensitive and accurate and could determine at least 20 elements in a single run.

The developed method was later used in the project studying the impact of PM pollution on cultural heritage. A large number of samples from different seasons were analyzed and based on their elemental composition, the major sources (e.g. traffic, biomass burning, crustal dust, marine source, secondary sources) and their contributions to PM pollution were identified..

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Determination of trace elements and Sr and Pb isotope ratios in Arctic resuspended soils by tandem ICP-MS and MC-ICP-MS

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Mineral dust emission and transport can occur at high latitudes, strongly impacting the Earth's radiative budget and particularly snow albedo. Even though the Arctic region is not often considered as a relevant dust source, there are many geophysical processes that can produce mineral dust, and, in a context of arctic amplification, the relevance of high latitude dust (HLD) sources is quickly increasing, because of the progressive exposure of ice-free areas. Although there is still a lack of knowledge concerning HLD sources and their impact, previous studies have shown how the dust produced there affects the high Arctic (>80°N), contributing to both the radiative forcing effect in the atmosphere and changing the albedo of the snow. Apart from the local contributions, the mineral dust formed in the HDL sources, is also subjected to long-range transport (Meinander et al., 2022). In this work, we have characterised both potential HLD source areas through the resuspension of soil samples and potential receptor areas through filtration of snow samples. The potential HDL sources considered are Iceland, Alaska and Svalbard Island (Norway), while the second ones, were obtained filtering snow, firn or ice sampled on different glaciers also located in Svalbard. Resuspension of the soil the filters was achieved via an innovative system, composed of a resuspension chamber connected to an aerosol sampling system, has been used. The filters loaded by soil resuspension were digested and characterized from a chemical point of view, quantifying 31 trace elements (TEs) using tandem ICP-MS. Moreover, the Sr and Pb isotope ratios were measured on the whole set of samples using a MC-ICP-MS unit at the A&MS Lab at Ghent University. Specific TEs can be used to recognize different patterns in dust originating from regions characterized by a different geological composition. Furthermore, isotope ratio determination is considered as a robust and reliable tool for tracing the origin of particulate matter. The analyses of two different isotopic systems is useful in order to differentiate eventual dust sources characterized by overlapping signatures for one of the two elements.(Bazzano et al., 2021; Conca et al., 2019) The proposed methodology is therefore promising for tracing dust emission and transport in the high Arctic and potentially to reconstruct past circulation patterns by investigating the dust composition in ice cores.

HLD sources, mineral dust, trace elements, Sr & Pb isotope ratios, Arctic, Tandem ICP-MS, MC-ICP-MS

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From offshore wind to green Power-to-X products – how ICP-MS can help to monitor potential emerging chemical emissions

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In order to combat climate change, the share of renewable energy production must increase drastically. Offshore solutions are gaining more and more importance and the number of offshore wind farms is growing steadily. As of 2021 28 GW of offshore wind energy was installed in Europe and 55.9 GW worldwide. The UN set the goal to even expand the global offshore wind capacity to 380 GW by 2030. Moreover, recent activities are aiming also for the production of green hydrogen and secondary chemical products such as ammonia, methanol and synthetic fuels – called Power-to-X products–within offshore regions.

However, the impact of these offshore constructions – wind turbines and production platforms – on the marine environment remains unclear in many aspects. In fact, little is known about potential chemical emissions from corrosion protection systems such as galvanic anodes composed of AlZnIn alloys or coatings, used to protect offshore structures. The anodes are designed to corrode instead of the structural steel, resulting in the continuous emission of metals (e.g. > 250 kg Al-anode material per pile and year) into the marine environment.

The presentation will give an overview over potential emission sources of offshore renewable energy production and will then go through the process of tracer identification, method development and application to sample sets of seawater, sediment and biota with ICP-MS based techniques to study the potential unwanted side effects of renewable energy production.

For the identification of tracers anode material and wastewater from different Power-to-X processes were analyzed using ICP-MS techniques. Tracers for galvanic anodes such as In and Ga were regularly determined in seawater and sediment samples from offshore wind farms since 2016. Local accumulation of the tracers Ga and In was found in seawater in a wind farm cluster, indicating the release of anode material into the marine environment. In general, the concentrations in seawater ranged between 0.01 ng/L and 0.27 ng/L for In and between 1 ng/L and 5 ng/L for Ga.

seawater, sediment, marine environment, technology-critical elements, environmental analysis

Fast extraction approaches for the multi-element analysis of dried matrix spots (DMSs) via ICP-MS

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Many novel clinical specimens offer the possibility to easily produce dried matrix spots (DMSs), such as dried blood spots (DBSs) dried urine spots (DUSs) and dried plasma spots (DPSs), to mention the most relevant ones, thus making it possible for any patient to prepare such DMSs home and send them to the lab by ordinary mail. Most of these new devices can be prepared using only a minimal (e.g., 10 µL) volume, which can be perfectly established with high reproducibility and practical independence from the physical properties of the target fluid, which are key requirements when quantitative analysis is aimed at [1].

This work discusses simple and efficient approaches to extract the target trace elements from such samples, prior to their multi-element analysis via quadrupole-based ICP-MS, thus offering a methodology that can be readily applied in clinical labs. Challenging issues related with contamination issues and approaches to minimize them will be addressed.

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DBS, blood analysis, tandem LIBS LA-ICP-MS

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NANODELIVERY SYSTEMS FOR CISPLATIN: EVALUATION IN COMPLEX CELL SYSTEMS LIKE SPHEROIDS AND ORGANOIDS

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Over the last few years, the use of nanocarriers for improving the transport of chemotherapeutics has been one of the more important points of research. Among the assortment of structures used as drug delivery systems, the use of ultrasmall iron oxide nanoparticles reports as a good carrier thanks to their properties such as its biocompatibility, their good incorporation into the cells or their facility to get conjugated to metallodrugs. One of the most commonly use drug in clinical environments is cisplatin (cis-diamminedichloroplatinum (II)). As this drug has a lot of limitations, such as its high toxicity or resistance, the emergence of cisplatin (IV) prodrugs is getting value as they are resistant to ligand substitution reactions, minimizing unwanted side reactions with biomolecules prior to binding its cellular target (DNA) [1].

Although the use of 2D cell models gives us a great point of view on how tumor cells behave to different types of drug testing, its lack of complexity is one of the failures in order to simulate a tumoral environment that could give us an idea of a real situation. Therefore, 3D cultures are getting importance as they are defined as micron-sized self-assembled aggregates tumor cells [2]. This type of cultures has all 2D advantages, such as simplicity, but they mimic better the heretogeneity that could be found in tumoral microregions without the use of animal models, which makes them a valuable one.

Herein, we explore the capabilities of the previously synthesized biocompatible ultrasmall iron oxide nanoparticles coated with tartaric and adipic acid, to be directly conjugated to the cisplatin prodrug cis-diamminetetrachloroplatinum (IV). We have studied the comparison between the platination level of the different cell populations depending on their status (viable, apoptotic and necrotic cells) in order to understand the drug damage by combining Single-Cell-ICP-MS advantages with cell sorting. Furthermore, the use of SC-ICP-MS for addressing the efficiency in the nanodelivery of Pt (IV) prodrugs in 3D cellular models like spheroids and organoids will be also illustrated aiming to have a more complete picture on the behavior of the nanosystem than the previously reported.

nanodelivery, iron nanoparticles, cisplatin, Single-Cell analysis, ICP-MS, complex models

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Evaluation of Matrix EffectsUsing Different Plasma Views

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Matrix effects play important role in ICP-OES analysis, causing bias and inacurate analytical results. With changing plasma load or with increased electron density the influence can be strong.

The effects of several matrices on the plasma excitation conditions and the line intensities were studied using different plasma views. It is known that the effects are more severe when using axial configuration of the plasma torch compared to the radial view. Recently the dual side on view is becoming more important due to benefits in terms of stability, robustness, and sensitivity. The effects of the plasma load and temperature are not yet completely investigated for the dual side-on technology, this topic will be discussed in the present study.

Several atomic and ionic analytical lines of different elements and having different excitation and ionization energies were investigated as it is known that atomic and ionic lines are affected different by the matrix effects.

matrix effect, plasma view

Low-temperature (flame) plasma as a thermochemical reactor for generation of monofluorides for fluorine determination using high-resolution molecular absorption spectrometry

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Fluorine is an element with extreme properties, which makes it difficult/impossible to determine it using most spectral techniques. Recently, intermediate spectral methods for determining fluorine using various measurement techniques have been investigated, including inductively coupled plasma mass spectrometry or laser-induced breakdown spectrometry. In particular, high-resolution continuum source molecular absorption spectrometry with graphite furnace has found many applications. This presentation deals with the much less common high-resolution continuum source flame molecular absorption spectrometry (HR-CS FMAS), which has been used to determine fluorine in gasoline components dissolved in xylene [1-3]. The aim of the presentation will be consideration of physicochemical factors determining the signal size of several monofluorides (GaF, CaF and SrF), generated in acetylene-air and acetylene-nitrous oxide flames. The formation and magnitude of the molecular absorption signal depend primarily on: - the breakdown of initial fluorine-containing compounds, - binding energy of the target measuring molecule (it is assumed that it should be higher than 500 kJ/mol), - formation and persistence of other fluorine molecules than the target one, - formation and stability of other molecules of the complementary element (e.g. Ga, Ca, Sr). These processes can be significantly affected by flame conditions (flow rate of oxidizer and acetylene) and the observation point. The situation is complicated by the nature of the tested samples, which stand additional fuel for flame and can radically change the properties of flame. The question arises of how to design and control the above-mentioned processes to achieve the best possible accuracy, sensitivity and detectability. The answer will be shown in the presentation. The technique of high-resolution continuum source flame molecular absorption spectrometry turned out to be [1-3] a useful tool for determining a difficult analyte, fluorine, in difficult and diverse samples, gasoline components, which provides a good prospect for other applications.

fluorine, flame, molecular absorption spectrometry, HR-CS, MAS, hydrocarbon, xylene, gasoline

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Comparison of Rh determination by stripping voltammetry and ICP-MS - source of new information

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Due to its unique chemical and physical properties, rhodium is applied in many industries, including automotive, jewelry, medicine and electronics. Car catalysts are the main source of this element's emission to the atmosphere. Despite its negligible chemical activity, rhodium can be transformed from the insoluble metallic form into some soluble ones. The environmental factors influencing this process are soil pH and redox potential, pH of water, salinity and the presence of inorganic (mainly chlorides) and organic ligands (humic acids). Rh(III) forms complexes with soft ligands such as chlorides, sulfides, polysulfides, cyanides, and natural organic acids.

One of the tasks of the undertaken studies was to propose procedures giving the possibility of selective leaching of ionic and metallic forms of rhodium from plant and soil samples.Application of two analytical techniques - Mass spectrometry with inductively coupled plasma (ICP-MS) and Adsorptive stripping voltammetry (AdSV) for rhodium determination in solutions obtained after extraction/digestion of environmental samples made it possible to distinguish between labile (ionic) and non-labile (metallic) Rh forms. In Adsorptive stripping voltammetry NPs are electrochemically inactive- independent of their size.

The proposed two-step digestion procedure (conc. H_2SO_4 and conc. HNO_3 in sequence) ensures efficient Rh NPs dissolution and allows to determine the total content of Rh (both ionic and metallic forms) in environmental samples by ICP-MS. Based on single extractions with selected extractants, it was found that independently of its chemical form Rh is substantially immobilized in soil. The mobility of Rh(III) and Rh NPs was below 38% and 0.02%, and the accumulation factor in leaves of Sinapis alba. equaled 0.2 and 4.4, respectively.

Transmission Electron Microscopy (TEM) supported the investigation of Rh NPs decomposition and proved the presence of uptaken nano forms in plant tissues.

The poster summarized part of study presented in Science of the Total Environment 806 (2022) 151272.

Rhodium nanoparticles bioavailability andmobility Ultrasound extraction, Selective digestion, comparison of voltametry and ICP-MS

Rolling over interferences: How triple quadrupole ICP-MS facilitates the analysis of challenging samples for electric vehicles

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The continuous development of lithium-ion battery technology is a key step to move away from the combustion of fossil fuels at point of use. Lithium based batteries are most promising, as they combine high capacity, good cycle stability, and moderate cost. To achieve the intended performance, it is of high importance to assure consistent quality and especially purity of the raw materials used. This includes specifically the cathode material (like binary or ternary alloys containing lithium, cobalt, manganese and nickel) and the electrolyte (lithium hexafluorophosphate and organic compounds), but also other components of the battery.

To analyze trace elements at the required levels, techniques based on inductively coupled plasmas are the ideal choice, in many cases combined with optical spectroscopy (ICP-OES), but also increasingly in combination with mass spectrometry (ICP-MS). This is especially important when impurities need to be determined at trace and ultra-trace levels, or, when specific analytes suffer from severe interferences caused by the sample matrix. Whereas ICP-OES is a workhorse that can be easily used for most challenging sample matrices, such as saturated brine solutions or metal alloy digests, it cannot always afford the required detection limits. Here, ICP-MS is the method of choice, specifically when using a triple quadrupole based ICP-MS system.

This presentation will give an overview how triple quadrupole ICP-MS is able resolve analytical challenges found when analyzing samples in the automotive industry driving the electrification of vehicles at a large scale. The presentation will include examples from different components of a battery, including raw materials, electrolytes and cathode materials.

Lithium Batteries, ICP-MS, Electrolyte, Battery Materials, Recycling, Interference Removal

Aligning salt crystals along the pre-defined laser-ablation pathway to increase laser-ablation sampling efficiency for laser-induced breakdown spectroscopy analysis of edible salts

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Edible salts, produced from seawater or excarvated in underground mines, are mixtrures of various ionic compounds with a common NaCl matrix. Other than the matrix elements, Na and Cl, they contains Mg, Ca, K, S, O, H, etc. Generally, the salts with rich mineral elements are known to be benefical to human health. The elemental composition of salts depends on production methods and geographical origins. Thus, the price of salts shows very large variation. Often, illegal circulation of salt products with fake origin labels is motivated by the large price differences. Under this circumstance, rapid and reliable elemental analysis techniques would be useful for quality control and screening salt products with fake origin labels.

Laser-induced breakdown spectroscopy (LIBS), based on optical emission spectroscopy, rapidly performs elemental analysis in open air. Moreover, LIBS has proved its strength in analysis of alkali and alkaline earth metal elements. This encourages us to develop LIBS-based methodologies for analysis of edible salt products [1-3]. In this work, we devised a new solid substrate on which salt crystals are well aligned along the pre-defined laser-ablation path. One the silicon substrate, a set of parallel 1-cm long trench lines was produced in 1 cm X 1 cm area by laser patterning. Then, along the four sides of the area, scotch tapes were attached enclosing the laser-patterned area. Salt samples were prepared in forms of aqueous solutions, and a drop of each solution was dropped on the area. The droplet formed a thin square film well fit to the square area. After water was evaporated by placing the substrate with a thin aqueous solution film in the oven, salt crystals were observed to lie along the laser-produced trenches. This could be ideal sample for laser-ablation-based elemental analysis. For LIBS analysis, nanosecond laser pulses were launched along the pre-produced trench lines on which salt crystals had been located. This increased signal-to-noise ratio of Mg, Ca, and K emission lines and provided remarkably improved performances for the analysis of these elements in edible salt products.

LIBS, Edible salts, Elemental analysis, Laser ablation, Sampling efficiency

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Identification of trace elements and biomolecules in extracellular vesicles secreted by human RPE cells by ICP-MS

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Age-related macular degeneration (AMD) is one of the leading causes of irreversible blindness, affecting almost 200 million people worldwide. Previous studies of AMD have revealed that progressive degeneration of the retinal pigment epithelial (RPE) cells play an important role in the development of AMD. Human RPE cells secrete extracellular vesicles (EVs), whose cell-to-cell signalling function may be crucial during early stages of AMD (1). Therefore, the study of the possible implication of EVs in dyshomeostasis and RPE cell degeneration during AMD is of great research interest.EVs are nano-sized vesicles containing nucleic acid and protein cargo that are released from a multitude of cell types and have gained significant interest as potential diagnostic biomarkers. Biological fluids (including cell culture media, urine, plasma and serum) are rich sources of readily accessible EVs. However, the isolation of EVs from proteins and non-EV lipid particles represents a considerable challenge nowadays.In this work we present the development of protocols for the purification of EVs from cell culture media of in vitro models of human RPE cells (hRPE), subjected to a pro-oxidative stress treatment and control, for the determination of trace metals and proteins in EVs. Two isolation strategies were evaluated by differential centrifugation and precipitation. The characterization of purified EVs was further performed by dynamic light scattering, nanoparticle tracking analysis, and transmission electron microscopy. Concerning metals determination, and taking into account the limited sample volume (less than 100 µL), different sample introduction systems were evaluated to obtain Fe, Cu and Zn concentration in EVs by ICP-MS. Metal nanoclusters (MNCs) were employed as the elemental label for CD81 and TSG101 proteins detection by ICP-MS.EVs analysed by conventional nebulization ICP-MS provides information of the whole population as an average. However, it is well-known that cells in all biological systems have a heterogeneous nature and, therefore, EVs can also exhibit a non-homogeneous behaviour. The combination of single cell (sc) ICP-MS with an immunocytochemistry step using MNCs has been explored to identify EVs purified from control and treated individual hRPE cells.

Human retinal pigment epithelial cell, Extracellular Vesicle, Single cell ICP-MS

Flores-Bellver et al. J. Extracel. Vesicles 2021, 10(13), e12165

Authenticating Geographical Origin of Tea from the North-East Region of India Using ICP-MS and Agilent Mass Profiler Professional Chemometrics Software

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India is the world's second largest producer of tea (after China), with most Indian tea being produced in the north-eastern states of Assam, West Bengal, and Tripura. Tea producers blend different varieties to create consistent products with a well-balanced flavor. Blending helps to take the pressure off high-demand tea varieties such as Darjeeling that is only grown in West Bengal. However, if a consumer buys a packet of tea labelled as Darjeeling, it is difficult for them to be certain of the quality – and origin – of the tea, based solely on the labeling. Foodstuffs with a high market value – including high-value tea varieties – are increasingly a target for food fraudsters, who routinely substitute, adulterate, or mislabel food items for financial gain. Tea varieties with a value that depends on their region of origin are more vulnerable to adulteration, especially when demand for the product is higher than the amount produced. To protect consumers and producers from food fraud, analytical methods need to be employed to distinguish the geographical origin of tea and verify its authenticity. Recent studies have shown that the multielement technique of ICP-MS can provide an "elemental fingerprint" for each sample that is indicative of the sample's geographic origin (1). Modern ICP-MS instruments have enhanced this type of analysis by providing higher sensitivity and better control of spectral overlaps. These performance improvements have increased the number of trace elements available for comparison, as well as improving the reliability of data by controlling matrix-based interferences. Elemental data obtained using an Agilent 7850 ICP-MS was processed using Agilent Mass Profiler Professional (MPP) chemometrics software. Principal Component Analysis (PCA) showed that the geographical origin of tea could be differentiated based on the concentrations of 18 of the 68 elements measured. Two MPP approaches (SVM and LDA) that are often applied to food-authentication studies were used to build class prediction models based on the 18 elements. Both of the prediction models were able to correctly identify the geographical origin of 24 'unknown' tea samples, including high-value Darjeeling. The ICP-MS elemental fingerprint method has the potential to characterize the geographical origin of a wide range of foodstuffs (2). The results can be used to authenticate the origin of genuine products or identify products that have been adulterated or mislabeled.

Food authentication, food fraud, geographical origin, elemental fingerprint, Indian Tea, ICP-MS, multielement analysis, chemometrics

Kanrar et.al., Food Chemistry Advance 1, 2022

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Laser induced breakdown spectroscopy (LIBS) - inductively coupled plasma - mass spectrometry (ICP-MS) for the investigation of tattoo pigments in ink and skin samples

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The prevalence of tattoos has increased immensely in recent years, leading to approximately 12% of all Europeans having at least one tattoo. Still, adverse skin reactions to the tattoo ink constituents can occur, even several years after the injection. The triggers of these reaction events remain mostly unknown and are suspected to be linked to the ink ingredients, impurities, or to metabolic and degradative processes in the skin. While the used inks are consisting of a variety of ingredients, such as preservatives and binders, the major compounds are the color giving pigments. Those pigments can be either inorganic substances, such as iron oxides or titanium dioxide or organic substances, such as phthalocyanines or azo compounds. However, the pigments are often technical products, originating from the paint or plastics industry, resulting in an estimated purity of 80-90%. Additionally, for the structures to last in the skin, they must be insoluble in water and multiple solvents, which further adds to the complexity.

In this work, two laser-based analytical techniques were used to specify contained pigments and to monitor potential impurities in tattoo ink samples and tattooed skin. Laser induced breakdown spectroscopy (LIBS) was used to detect major elements of inorganic pigments, heteroatoms of organic pigments, alkali metals such as Na and K, and non-metals such as H, O, C and N. Laser ablation-inductively coupled plasma–mass spectrometry (LA-ICP-MS) was employed to detect commonly occurring impurities such as Zr or Ni. The use of both techniques allows simple and easy analysis of tattoo pigments in ink and skin samples with little need for sample preparation steps. Especially Ti, Fe, Cl, Cu, and Br were detected by LIBS as major pigment related elements in the inks. For the human skin samples, the simultaneous imaging approach allowed the quadrupole ICP-MS to be dedicated to the trace level contaminants, while LIBS provided the major elemental information.

tattoo pigments, laser induced breakdown spectroscopy, laser ablation-inductively coupled plasma-mass spectrometry, tattooed skin reactions

Alkali activation of local slag by using various alternative activators: an environmental assessment of leachates

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Alkali-activated materials (AAMs) are ceramic or concrete-like products and may partly replace Portland cement products in the future, 1) because of the lower carbon footprint and 2) because AAMs are durable and can achieve similar or better mechanical properties than concrete. However, alkali activators are needed for alkali activation (chemical reaction), and usually sodium-Na/potassium-K silicate is used. Unfortunately, Na- or K-silicate contribute the most to the carbon footprint of AAMs, as both activators require a high energy input for their production.

In the present study, alternative alkali activators (AAAs) were prepared using waste materials such as mineral wool (glass and stone wool) and waste glass (cathode ray tube glass-CRTG and bottle glass- BG) and 10 M KOH/NaOH. The glass wastes were boiled at 120 °C for 4 or 24 hours and the prepared AAAs were then alkali-activated with stainless steel slag (electric arc furnace slag - EAFS). The quality of the prepared AAAs and the amount of dissolved Si and Al depend on the waste material, boiling time and the alkali (KOH or NaOH) used. We quantified the amount of Si and Al dissolved in the AAAs using ICP-OES. The AAAs were then used to prepare AAMs. The mechanical properties and porosities of the fabricated AAMs were compared with KOH/NaOH or K-silicate/Na-silicate. The compressive strength of alkali-activated slag prepared with NaOH-based AAAs with the highest concentration of dissolved Si (21 g/L) was 3.47 MPa, while the compressive strength of AAM, activated with 10 M NaOH, had the lowest value (2.01 MPa) and the highest value with Na-silicate activators (34.3 MPa) (1). Similarly, AAM prepared with K-silicate gave the highest compressive strength (27.7 MPa), AAM from CRTG waste had 9.47 MPa, while the lowest compressive strengths were obtained with the KOH-activated slag (1.97 MPa) (2).

Since EAFS contains Cr, As, Ba and other toxic elements, leaching tests were performed to evaluate the immobilization potential of the toxic elements in the prepared alkali-activated slag. The results of the leaching tests show that the concentrations of As, Cr, Mo, and Sb in the leachates of AAMs are increased compared to the regulatory requirements (3). Modification of mix design is needed to decrease the exceeded values.

alkali-activation, alternative alkali activators, slag, leaching, toxic elements

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Comparison of Detection Limits and Purity Analysis of Lithium Carbonate Powders Between ICP-OES, ICP-MS and ICP-MSMS Analysis Techniques.

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Lithium plays an important role in everyday life and can be found around us in nearly every aspect of modern living. One of the most common uses of lithium is lithium batteries. Lithium batteries can be found in cell phones, computers, electric vehicles and every portable electronic device. For decades consumers have been valuing longer battery lives and faster charging capabilities and the advancements in Lithium Battery technology is a reflection of that. Global trends in electrification, renewable energy and the adoption of electric vehicles is creating a demand for more lithium-based materials with higher quality control requirements.

With the demand for higher capacity batteries, current battery production technology must improve, which requires better control of the raw materials used and their physical properties. Lithium salts are commonly refined from brine a highly concentrated solution of NaCl. During the extraction process, sodium has to be removed from the final product since excess sodium can also lead to overheating in the final battery products. Therefore, the capability to identify the presence of impurities in lithium battery materials is critical for manufacturers and suppliers to provide quality assurance that the final battery performance is not compromised. Here we will compare the results from the Avio ICP-OES, NexION 2000 ICP-MS and NexION 5000 ICP-MSMS for the analysis oflithium carbonate powders.

Batteries, Lithium,

What Levels of Ultra-trace Elemental Detection Can Be Achieved Today?

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[1]PerkinElmer Inc., Shelton, United States

For many decades, the semiconductor industry has been designing new devices that are smaller, faster and consume less power than their predecessors. To maintain this trend, the critical features of these devices must become smaller and have fewer defects. Smaller diameters of chip's features require that all liquid chemicals and solid materials used in semi processes should have less and less contaminants.

Inductively coupled plasma mass spectrometry (ICP-MS) traditionally has been an indispensable analytical tool for quality control because of its ability to rapidly determine high number of analytes at the ultra-trace (ng/L or lower) levels in various process materials and chemicals. Traditionally, analyses are performed using conventional, hot plasma conditions in the Standard and DRC (Dynamic Reaction Cell) modes. However, a few elements with a low ionization potential measured in cold plasma mode yield lower background due to more efficient removal of spectral interferences.

A multi-quad quad technology and the Triple Cone Interface incorporated in the NexION 5000 are also components instrumental in further lowering BECs (Background equivalent Concentrations) and improving DLs (Detection Limits).

In this poster the hardware innovations will be discussed and their influence on DLs and BECs needed today by semi-industry will be shown. Examples of analysis of various chemicals would be demonstrated.

ICP-MS, Semiconductors, Detection Limits, BECs

The Use of LA-ICP-MS and Related Techniques for the Analysis of Essential Elements in Plant Tissue

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Metals are essential for normal plant development and are involved in growth, regulation, and metabolism. Maintaining the nutritional metal content in plants is crucial. The work aimed to use LA-ICP-MS bioimaging alongside complementary techniques to determine the effect of the inclusion of adjuvants in a zinc-containing seed film coating, on the uptake of Zn into wheat crops. The work also investigated the effect of the source of Zn on uptake and the effect of adjuvant inclusion with a range of Zn sources.

Laser Ablation was performed using an Elemental Scientific Lasers imageBIO266 Laser Ablation System, coupled to a Perkin Elmer NexION 350X ICP-MS.

Analyses were carried out on treated seeds over 12 months to investigate the impact of the inclusion of adjuvant on the stability of the seed film coating after storage, and to investigate the mechanisms by which seed-applied zinc is uptaken by wheat seeds with and without the presence of adjuvant in the film coating formulation. Imaging studies carried out at 12 months post-treatment suggest that the inclusion of adjuvant may increase the uptake of Zn during the imbibition process of wheat seeds. This is supported by bulk analysis data, along with imaging studies carried out using micro-computed tomography (micro-CT). The studies on the effect of the source of Zn show significant differences between the uptake of Zn from different Zn sources. They also show significant benefits of the inclusion of adjuvant on the uptake of ZnO.

Laser Ablation, ICP-MS, Agriculture, Seed Treatment, Zinc, imageBIO266, microCT, Bioimaging

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Design and Performance Review of Innovative Microwave Inductively Coupled Atmospheric Plasma – Optical Emission Spectroscopy (MICAP™-OES 1000) Utilized in Mining and Mineral Exploration

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Design and Performance Review of Innovative Microwave Inductively Coupled Atmospheric Plasma – Optical Emission Spectroscopy (MICAP™-OES 1000) Utilized in Mining and Mineral Exploration

Eric Moen, Lead Application Chemist, Jake Biesterveld, ICP-OES Chemist, Dylan Rehbein, ICP-OES Chemist

Author/Presenter: Christine Rivera, Director of Product Management Spectroscopy/Chemist

Due to the power, exhaust, weight and gas supply constraints, traditional high performance atomic spectroscopy instruments are designed for laboratory use.While custom adaptations can be made to equip a mobile unit for spectroscopy, the normal use is the laboratory.

MICAP-OES 1000 operates on industrial grade (99.998%) nitrogen and 1000 W power.The technology to create the stable plasma is called Cerawave™ which replaces the traditional electric water-cooled coil.The design of a microwave plasma with an echelle-based spectrometer provides flexibility in instrument installation location from mine exploration sites to real-time manufacturing floor monitoring.The design innovations and expected performance of the MICAP-OES 1000 will be presented with respect to mining and mineral exploration.The performance test results will include stability, limit of detection (LOD), accuracy and precision of several OREAS CRMs.

Smallest ICP, Cerawave, MICAP-OES 1000

Determination of Elemental Nutrients and Micronutrients in Functional Food by ICP-OES

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[1]Agilent France, [2]Agilent Australia

The functional food and beverage industry has experienced rapid growth over the last decade, furthered by consumer response to the COVID-19 pandemic (1,3). Some of these products are marketed to boost immune functionality that extends beyond basic nutritional value, claiming prevention and treatment of disease (2,4). These therapeutic claims are frequently related to the elemental content of the product.

ICP-OES is an ideal tool for verifying the concentration of elements listed on the labels of functional foods and beverages. This study investigated the efficacy, speed and simplicity of this technique for the determination of calcium, magnesium, potassium, sodium, phosphorous, iron, copper, manganese and zinc in foods.

This study utilized the US FDA Elemental Analysis Manual (EAM) method 4.4 for food and related products on ICP-OES. Three elderberry-based functional food samples (2) were analyzed using an Agilent 5900 ICP-OES.

The use of Agilent's IntelliQuant software feature streamlined method development and simplified wavelength selection by allowing the prescreening of samples for possible interferences. The IntelliQuant function was also able to recommend a suitable calibration range. The SVDV mode (Synchronous Vertical Dual View) of the Agilent 5900 ICP-OES was then used to analyze the samples. The advantages of this mode include removing the need to individually select radial or axial viewing modes depending on the sensitivity of each element. This capability delivered excellent detection limits for all elements in a single analytical run.

The accuracy of the method was confirmed by the analysis of a certified reference material and a spike recovery test for all 8 elements. All recoveries were excellent, detection limits were all within the nominal FDA method requirements and the instrument displayed exceptional stability over time. This study demonstrates the suitability of this instrument and method for confirming the elemental aspects of nutritional labelling.

ICP-OES, functional food

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Direct process accompanying analysis of biomass for critical elements in combusting processes with ETV-ICP-OES

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[1]TU Bergakademie Freiberg, Institute of Analytical Chemistry, Freiberg, Germany, [2]TU Bergakademie Freiberg, Institute of Energy Process Engineering, Freiberg, Germany

Biomass samples often include environmentally harmful elements. For example, wood from construction sites is usually coated or painted or might be infested with vermin. Other materials, such as sewage sludge, contain next to hazardous components, elements like phosphorus that must be recovered.

Those waste products are usually used as energy resources and therefore lead to combustion in coal-fired power plants or other incinerators. For phosphorus recovery, to meet emission limits and to achieve a high combustion temperature without slagging and fouling, the chemical composition of the materials has to be known.

To analyze the composition, a fast and direct method for the analysis of solids is required. As a robust solid sampling method, the electrothermal vaporization (ETV) as a sample introduction system for inductively coupled plasma optical emission spectrometry (ICP OES) was found to be qualified. To be able to analyze different samples, the parameters of the method need to be optimized. This process includes the selection of a suitable reaction gas, plasma parameters, temperature program and emission lines. Due to the restriction of chlorofluorocarbons like CCl2F2, which are usually used as reaction gases for ETV-ICP-OES, alternative modifiers were evaluated. Furthermore, customized temperature programs allow speciation analysis of several elements.

For this purpose, a method for calibrating the systems had to be found in order to be able to analyze as many different sample types as possible with the same calibration, both quantitatively as well as qualitatively. By optimizing the various parameters, a simultaneous determination of all relevant elements from main constituents to trace elements can be achieved with one measurement.

ETV ICP OES trace elements combustion process

Potential of ICP-MS/MS to study the impact of trace metals released from offshore wind farm corrosion protection on marine biota.

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The demand for renewable and independent energy sources in Europe has gained significant attention during the last months. Within this context, offshore wind farms are a key technology towards a sustainable future and a decreased use of fossil fuels. The harsh conditions to which offshore wind farms are exposed require the use of corrosion protection systems, such as coatings and/or galvanic anodes. Sacrificial anodes made of AlZnIn alloys can contain additional elements as supplement or contamination (e.g. Ga, Cd, Pb), whose possible release and impact on the marine environment is not yet assessable.

To investigate the impact of these potential pollutants on marine biota, mussels (Mytilus edulis) were harvested from steel foundations of different wind farms. For each mussel, the condition index was calculated and the age was estimated based on annual growth rings. The mussel tissue was frozen, dried and homogenized for each individual, from which triplicates were subjected to microwave-assisted acid digestion.

To identify the potential accumulation of pollutants, digests were measured via ICP-MS/MS using different reaction/collision cell modes (no gas, He, N_2O, H_2, H_2 HMI). This variety allows the routine measurement of a total of 68 analytes (e.g. traditional pollutants (Pb, Cd, Zn), geogenic tracers (rare earth elements) and technology-critical elements (In, Ga)). Method validation was carried out with three matrix-matched certified reference materials (CRMs) (NIST-2976, BCR-668 and NCS ZC73034).

The study provides the first data set for the North Sea with regard to the distribution of trace metal pollutants in marine biota from offshore windfarms, in order to assesses potential accumulation of elements released from corrosion protection systems. In addition, the study provides first information values on the mass fraction of a number ofnon certified emerging metal contaminants in mussel CRMs. The data presented here allows a better understanding of the unintended side effects of offshore wind farms on the marine environment. In addition, data for non-traditional tracers (Al, In, Ga) in marine organisms is provided to contribute to future applicable assessment criteria of new possible pollutants.

Multi-elemental analysis, emerging contaminants, Mytilus edulis, marine biota, technology-critical elements

Quantification of Trace Metals in Drinking Water – Effect of Acid Digestion

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Groundwater is a vital source of drinking water for many rural residents. The concentration of metals is an important indicator of groundwater quality. Therefore, it is critical to monitor the concentration of metals in water in order to ensure the water quality and safety. The US EPA Method 200.8 is typically utilized by laboratories and drinking water utilities to quantify trace metals in drinking water using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). In this method, it is required to perform a hot acid digestion procedure for samples with turbidity of 1 NTU or greater. We conducted a study to assess the effects of digestion on the quantification of trace metals, particularly the parameters that are health concerns and have established maximum acceptable concentrations (MAC) in drinking water as defined by Health Canada (e.g. Al, Sb, As, Ba, B, Cd, Cr, Cu, Pb, Mn, Se, Sr and U) [1].

In this study, 15,687 untreated well water samples were tested for turbidity, and 2,511 samples (16% of total) had turbidity of ≥1 NTU. Acid digestion was performed for turbid samples by the addition of HNO_3 (2%) and HCl (0.5%) and heating samples on a hot block at 95 °C for three hours. The concentration of dissolved metals was measured before and after digestion using ICP-MS.

Comparison of the concentrations of metals between digested and undigested samples showed a significant difference for Al where a concentration increase of >10% was observed for more than 75% of samples after digestion. Al was above MAC value in 0.48% of samples before digestion while it increased to 2.55% of samples after digestion. MAC exceedances between pre- and post-digestion were not significantly different for Mn (17.72 vs 18.20%), Pb (15.17 vs 15.77%), As (5.50 vs 5.97%), U (1.75 vs 1.91%), Cu (0.24 vs 0.56%), Sb (0.44 vs 0.44%), Ba (0.40 vs 0.44%), Cd (0.12 vs 0.12%), Sr (0.12 vs 0.12%), Cr (0.20 vs 0.28%), Se (0.04 vs 0.04%) and B (0.04 vs 0.04%).

Considering the adverse health effects of trace metals exposure (e.g. lead exposure being associated with IQ deficits and behavioral changes in children), accurate quantification of the metals concentration in water is important to assess the potential human exposure to trace metals through drinking water.

Drinking Water, Trace Metals Analysis

Guidelines for Canadian Drinking Water Quality, Health Canada, Ottawa, Ontario (2020).

History and Outlook of (metal) pollutant measurements at the atmospheric background stations of the German Environment Agency Air Monitoring Network

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Within the framework of multiple international conventions, Germany like other states is committed to monitor the air quality in the atmospheric background. Therefore, atmospheric measurements are realized by the German Environment Agency (Umweltbundesamt (UBA)) with its network of 7 remote measurement stations throughout the rural background of Germany. These stations are operated by personnel and contribute data on pollutant deposition and transboundary long-range transport to the following monitoring programs: Global Atmosphere Watch (GAW), European Monitoring and Evaluation Program (EMEP), Helsinki convention (HELCOM), OSPAR Convention and as well as to the EU commission within the directive on ambient air quality and cleaner air for Europe (2008/50/EC).

Some pollutants are measured continuously since the late 1960s, while other pollutants especially metals and semi-metals (e.g., Pb, Hg, Cd, Ni, As) are monitored since the early 1990s, first by atomic absorption spectroscopy (AAS) later on by inductive coupled plasma mass spectrometry (ICP-MS). With the general improvements in air quality enforced by stronger regulations most pollutant concentrations and depositions decreased over time and reached a low plateau in the atmospheric background. Nevertheless, the continuous improvement of measurement techniques and the observation of new potentially problematic pollutants is one major goals of the UBA air monitoring network. Persistent organic pollutants (POP) addressed by the Gothenburg protocol as well as fluorinated chemicals (PFAS) are of high interest together with the integration of novel techniques such as single particle measurements. Therefore, the UBA air monitoring network presents itself open for collaborations and testing of new measurement techniques for environmental matrices at its facilities.

Air Monitoring, Pollutants, Metal Deposition

Measuring fluorine in biological systems: from total content to fluoro-proteomics

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In recent years, more and more attention has been paid to the study of the effect of fluorine and its compounds on the human body. This includes both products that contain fluorine, e.g. toothpaste, plastics or drugs, as well as various tissues of living organisms in which fluoride (e.g. in the form of microplastics) or its compounds (e.g. biologically active substances) can accumulate. The determination of traces of fluorine in a biological systems is not straightforward, mainly because fluorine is not an analytically easy element. Therefore, a great deal of effort is devoted to developing effective measurement procedures that will ensure the obtaining of valid results.

The conducted works concern, among other issues, the possibility of determining the total content of fluoride in order to understand its transportation and accumulation in the body. Another important aspect of research is to understand the transportation of low-molecular, biologically active compounds containing fluorine. This mainly applies to drugs stabilized with fluoride. Another research challenge is to understand the metabolism of such substances and the potential influence of fluoride on protein expression.

Several new developments in the area of the determination of fluorine will be discussed, from the novel procedure enabling the determination of traces of fluorine in complex biological objects to fluoro-proteomics research, enabling the evaluation of the potential risk of fluorine introduced in a form of fluorine-containing pharmaceutical compounds.

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fluorine, fluoro-proteomics

Prof. Katarzyna Wróbel

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Hg speciation in Tuna fish flesh by HPLC-ICP-MS

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The toxicity of mercury (Hg) is strongly dependent of its chemical form, for instance, organic Hg compounds are generally more toxic than inorganic ones. Moreover, inorganic Hg (Ino-Hg) can be converted into organic forms, such as methyl Hg (MeHg) and ethyl Hg (EtHg), thus, heightening the concerns regarding Hg species biomagnification throughout food chain. Therefore, in addition to assess the total Hg content the need to separate and quantify Hg species in the environment and biological matrices has significantly grown. In this context, a method for Hg speciation is proposed by means of species separation and quantification by HPLC-ICP-MS. For this task, Hg compounds separation was performed through reverse-phase chromatography by using a Phenomenex Synergi Hydro-RP C18 column (150 x 4.6 mm, 4 µm), and an aqueous 0.1% (w/v) L-cysteine and 0.1% (w/v) L-cysteine-HCl-H2O at pH 2.3 as mobile phase in isocratic mode. Hg species in Tuna fish samples were extracted with a 1% (w/v) L-cysteine-HCl-H2O aqueous solution during 120 min at 60 oC. Three Hg species, namely, Ino-Hg, MeHg and EtHg were accordingly separated and measured in Tuna fish samples. Spiked samples were also considered to assess the feasibility and accuracy of the proposed HPLC-ICP-MS method for Hg speciation in biological samples.

Hg, Mercury, speciation, Tuna, HPLC-ICP-MS, ICP-MS, food toxicity

Critical comparison of experimental and computational fluid dynamic results for a sample introduction system in plasma spectrometry

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Sample introduction has a substantial influence on the performance of spectroscopic methods. A nebulizer and a suitable spray chamber is the most common sample introduction system in ICP-MS. The main task of the spray chamber is to appropriately modify the aerosol emitted by the nebulizer in terms of particle size, particle velocity and aerosol concentration in order to subsequently make it spectroscopically useful. In addition, the turbulence in the chamber caused by the atomization process must be damped. An optimal sample introduction system should transport only droplets with a diameter < 10 µm into the plasma and efficiently separate all droplets > 10 µm. In practice, significant fractions of useful smaller droplets are lost due to wall contact.

To understand the modification processes of the aerosol in the spray chamber (i.e., impacts, droplet breakup and coalescence, evaporation, decay of turbulence etc.), knowledge of the flow behavior is required that is experimentally nearly inaccessible. In this work, the aerosol flow in a Scott-type spray chamber equipped with a micro-uptake glass concentric nebulizer is studied using a computational fluid dynamics (CFD) approach. Nebulizer characteristics, such as the aerosol size distribution generated by the nebulizer itself (primary aerosols), the aerosol size distribution at the outlet of the Scott spray chamber (tertiary aerosols), and velocity distributions are obtained experimentally by phase Doppler anemometry (PDA), laser diffraction and particle image velocimetry (PIV) measurements.

Using these experimental data as input parameters, the results of the numerical calculations provide an approximation of the transport phenomena occurring inside the chamber and confirm the tendency that only a small amount of droplets is able to reach the plasma in relation to the injected liquid. Considering different conditions in the spray chamber, it is also found numerically that cooling the chamber leads to a better performance of the sample introduction system by reducing the solvent plasma load. Measurements of the analyte transport show that as the temperature of the spray chamber increases, the mass of solvent transported increases and thus also the solvent plasma load, but not necessarily the mass of the analyte to the same extent. Hence, the analyte transport efficiency remains almost unchanged in the temperature range (2 to 20ºC) studied.

computational fluid dynamics, sample introduction

Coupling of a flow cytometer to the prototype ICP-TOFMS for single-cell analysis

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Even though the use of ICP-TOFMS for single-cell analysis offers outstanding advantages such as high sensitivity, low limit of detection (LOD) and simultaneous detection of elements/tags, there are still limitations preventing high sample throughput. For example, the nebulizer and spray chamber systems commonly used result in low sample transfer efficiency. Additionally, information of cell morphology such as size and internal complexity remain unknown due to the absence of optical elements. However, some methods such as membrane staining assay such as wheat germ agglutinin (WGA) or osmium tetraoxide (OsO4) can be applied to gather information about the cell size [1].

Some of the existing challenges can be avoided by using a prototype of a vertical downward-pointing ICP. Such a vertical configuration of the plasma torch enables 100% sample transfer efficiency independent of sample mass, size and shape due to the gravitational force [2]. Additionally, the prototype ICP-TOFMS can be operated up to 1000 Hz dispensing rate while keeping the oxide ratio below 3% using an autodrop pipette or a microdroplet generator (MDG) to introduce single-particles or single-cells [3].

We try to eliminate the some of the above-mentioned challenges by coupling the prototype ICP-TOFMS with a fluorescence-activated cell sorting (FACS) flow cytometer. The optics of the flow cytometer provide the capability to analyze the cell morphology and furthermore a gating strategy for the sorting can be designed to prevent double events and recognize dead cells. However, the flow cytometer generates larger droplets than the autodrop pipette and MDG used in our previous studies. Therefore, desolvation devices are needed to prevent drastic plasma cooling and high oxide formation. The prototype ICP-TOFMS is currently operated by using a falling tube device filled with helium gas and a gas exchange device (GED) for droplet drying and solvent vapor removal. The presentation will show the current status of the coupling of the two devices for fast and high throughput single-cell analysis.

prototype ICP-TOFMS, coupling, FACS, flow cytometer, single-cell analysis

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Potential of Mesenchymal Stem Cell Secretome of Human Uterine Cervix in Breast Cancer Therapy

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Mesenchymal stem cells (MSCs) are multipotent stem cells that can differentiate into other types of cells. In humans, MSCs can be isolated from a variety of tissues, such as bone marrow, adipose tissue, umbilical cord tissue or amniotic fluid. Recently, the Research Unit of Jove´s Hospital (Asturias) has isolated, identified and characterized a new type of MSCs from human uterine cervix (hUCESCs) that are highly proliferative [1]. Despite being a powerful tool for clinical applications, MSCs present limitations in terms of delivery, safety, and variability of therapeutic response.

Interestingly, the MSCs secrete a variety of biologically active substances to the conditioned medium (CM) used for growing them.Secretome is composed by cytokines, chemokines, growth factors, proteins, and extracellular vesicles. Secretome-based treatments using CM may present considerable potential advantages over living cells in terms of manufacturing, storage, handling, product shelf life and their potential as biological therapeutic agent and could represent a valid alternative. Among MSCs, human uterine cervical stem cells (hUCESCs) may be a good candidate for obtaining secretome-derived products. In fact,CM derived from hUCESCs (CM-hUCESCs)have potent antitumoral, anti-inflammatory, antibiotic, antimycotic and re-epitheliasation-enhancing properties [2].For clinical translation of secretome-based treatment, characterization of the secretome composition is needed to better understand the induced biological processes.

In the present work, we studied the in vivo antitumor effects of CM-hUCESCs after intraperitoneal administration in mouse breast cancer model. Finally, identification/determination of functional protein components in three different CM-hUCESCs has performed by HPLC-ESI-MS/MS. The identification of the secreted protein components with therapeutic effects is expected to be useful for future breast cancer therapy.

mesenchymal stem cells, secretome, breast cancer, protein identification, mass spectrometry

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Fundamental studies to explore the potential of isotope dilution for LA-ICPMS imaging

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Isotope dilution analysis (IDA) offers highly accurate and precise quantification of elements or elemental species in complex matrices. To use this approach for LA-ICPMS imaging, a homogeneous and accurate distribution of the spike solution is required. Compared to external quantification, IDA provides poor precision of isotope ratios at low count rates, when the evaluation is performed on a single pixel base.

In this work, a quantification method based on isotope dilution by LA-ICP-TOFMS was developed by precise dispensing of isotopically-enriched gelatin micro-droplets using a micro-spotter. For IDA, a 196Pt enriched spike was used. Through initial preliminary tests with gelatin standards from a natural platinum solution and a 196Pt spike solution, the data interpretation was optimized by a pixel-based evaluation.

For a proof-of-concept, the methodology was tested to quantify platinum in biological relevant samples after platinum-based metallodrug treatment. With this, work we explore the limits of isotope dilution mass spectrometry for imaging with LA-ICPMS.

quantification, isotope dilution mass spectrometry, LA-ICPMS imaging

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Microwave-sustained inductively coupled atmospheric-pressure plasma for elemental analysis of environmental samples: Citius, Altius, Fortius

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Inductively coupled plasma optical emission spectrometry (ICP-OES) is the workhorse technique for trace elemental analysis in environmental samples due to its outstanding multi-elemental detection capabilities and limits of detection at µg L-1 levels. Main technique drawback is the high analytical cost derived by the Ar consumption and the r.f. generator required to sustain the plasma. Microwave induced plasma optical emission spectrometry (MIP-OES) has gained widespread attention in the last few years as alternative to ICP-OES due to the use of nitrogen as the plasma gas and a simpler hardware setup. Among the new generation of MIPs, it is worth to mention the microwave-sustained inductively coupled atmospheric-pressure plasma (MICAP) which allow sustaining an annular plasma as with ICPs using a dielectric resonator ring and a 2.45 GHz microwave field. Previous works have shown that MICAP-OES detection capabilities are on a par with those afforded by ICP-OES. Nevertheless, this instrument has not yet applied to real sample analysis. Therefore, the goal of this work is to evaluate MICAP-OES performance (e.g., analytical figures of merit, matrix effects, etc.) for elemental analysis of different environmental samples (e.g., water, sediments, etc.). Experimental data shows that this instrument is highly robust operating matrices with high-solid contents. Unlike previous MIP instruments, MICAP spectrometer design allows real-time simultaneous analysis of different elements as well as internal standardization to minimize non-spectral interferences. Finally, MICAP-OES can be successfully applied to the elemental analysis of different environmental samples according to current international policies.

microwave plasma, optical emission spectrometry, metals, environmental analysis

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Excitation of elements from water solutions in the free discharge tip and in the discharge tube of the plasma pencil

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An alternative approach of elements determination in water solutions is presented. A plasma pencil excitation source was used. It is a radiofrequency two-electrodes 13.5 MHz discharge (120-170 W rf power) in a quartz tube (o.d. 4 mm, i.d. 2 mm) operated in argon (2-6 l min-1) at the atmospheric pressure. The tube is an asymmetrical T-piece with a shorter branch for the sample aerosol intake. The sample introduction system consists of a Scott spray chamber with a concentric nebulizer and a peristaltic pump. The system is adopted from an ICP spectrometer. However, the carrier gas and the sample flow rate are lowered down to 0.25 l min-1 and 0.7 ml min-1 respectively.

The plasma pencil is originally designed for the treatment of solid surfaces, mainly objects of cultural heritage, and the production of advanced hydrophobic or hydrophilic surfaces. However, it is also capable of excitation of some elements coming from water solution. The excitable elements are alkali metals, alkali earths and some transition and other metals (e.g. Mn, Fe, Cr, Ni, Co, Cu, Zn, Ag, Cd, Hg, In, Tl, Ga). The point of the spectra acquisition can be set arbitrarily along the discharge tube and also from the free discharge tip without the participation of the tube wall. However, best lines intensities are measured close to the ground electrode. Here the sensitivities of the elements lines are compared as a function of the acquisition point position. The free discharge tip may bring higher intensities but more intensive OH bands and nitrogen bands which can interfere with some analytical lines. The concentrations can be measured from about 0.1 mg l-1. The observed changes of the intensities are accompanied with optical emission diagnostics including electron number density from the Stark effect on the H-beta line, excitation temperature from Ar lines and neutral gas temperature from rotational OH lines.

Acknowledgment: AH, KN and VK acknowledge the project MUNI/A/1412/2021 PS acknowledges the project LM2018097 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

plasma pencil, emission spectrometry, elements, analysis, excitation, discharge, radiofrequency

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The sweetest time capsules - The MP-AES analysis coupled with AMS age determination Hungarian acacia samples

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Honeys are excellent indicators of the environment, several studies show that the elemental content of honey entirely depends on the botanical and geographical origin, but the information is incomplete regarding time-dependent composition changes. Twenty-six acacia and four honey samples with unknown botanical origin were collected between 1958-2018 and analysed for elemental composition by microwave plasma optical emission spectrometry (MP-AES). The elemental analysis was coupled with independent dating method by accelerator mass spectrometry (AMS) to determine the real age of the honey samples and test the possibility of radiocarbon based dating of bee products, which has not been applied before.

According to the analytical measurements and statistical analysis, we can conclude that the elemental composition shows change with time in the acacia honey during the last five decades. We have proven that honey preserves information of previous times and thus can be applied as an environmental indicator in reconstruction studies by analysing the non-degradable mineral content. Our results further show that acacia honey is a suitable material for radiocarbon dating, proved by the results compared to the atmospheric radiocarbon bomb-peak. The presented new approach for investigations of honey by radiocarbon-based age determination coupled with elemental analysis can be used in biological, dietary, archaeological or other multidisciplinary studies as well. Some samples show slightly depleted radiocarbon content, based on these results, honey could be used for atmospheric monitoring.

environmental indicators, honey, MP-AES, AMS, radiocarbon, analytical spectrometry

The sweetest time capsules - The MP-AES analysis coupled with AMS age determination of Hungarian multifloral honey samples

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Our former study highlights that acacia honey can be successfully applied for long-term environmental assessment as old samples keep inorganic compounds preserved as well as they serve as a proper material for radiocarbon dating. Good agreement was observed between the radiocarbon activity of the acaica honeys and the atmospheric bomb-peak that was used for calibration. In present study the time-dependent elemental composition and AMS dating results of 36 rape, sunflower and multifloral honey samples are presented, collected between 1985 and 2018 in geographically close locations. Elemental concentration data were gained by MP-AES method. Based on the elemental analysis we concluded that bee products regardless the type provide useful environmental information of the previous decades, such as the decreasing trend of airborne Pb emission can be traced. However, radiocarbon results agree less with the atmospheric bomb peak. Random offsets were observed in the specific radiocarbon activity of the honey samples. FTIR-ATR analysis was used to gain a deeper knowledge regarding the organic material composition of the honey samples. Results indicate that neither the inorganic composition nor the organic constituents show corresponding pattern to the AMS deviation. Even the 5-(Hydroxymethyl)furfural content following the expected age trend in acacia honeys has no such pattern in present sample series. This work indicates that rape and sunflower honey samples are not as reliable materials for radiocarbon dating as acacia honeys. Thus, the complex application of honey samples for environmental reconstruction requires the species-separated investigation of bee products to reveal their adaptability for assessment approaches. The research was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2-15-2016-00009 'ICER'. E. Baranyai and Z. Sajtos are grateful for the financial support of the János Bolyai Research Scholarship of the Hungarian Academy of Sciences and for the support of the ÚNKP-20-5 (Bolyai+) and ÚNKP 22-4-1 New National Excellence Program of the Ministry of Innovation and Technology from the source of the National Research, Development and Innovation Fund of Hungary.

MP-AES, AMS, honey, elemental analysis, bomb peak, radiocarbon, HMF-content, environmental indicators

Hola, Kanicky, Spectrochimica Acta Part B 17, (2022) 4-9.

Fostering inclusive access to analytical instrumentation

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For inclusion and diversity in science, chemists with disabilities need accessibility and operability of analytical instrumentation, such as mass spectrometers. With current laboratory infrastructure and instrumental setup, ranging from simple benchtop devices to more sophisticated analytical equipment, these aspects are often not considered. As a result, competent individuals are excluded from using these tools, or their operability is made cumbersome: access to critical parts of instrumentation can be difficult or impossible to reach, software is not adaptable for possible disabilities, and warnings are mostly visual and involve colors that cannot be differentiated by visually impaired people. When looking in close details, truly operator-friendly instruments are rare when considering people who have disabilities.

Within this project, we aim to evaluate support strategies for promoting barrier-free access for disabled scientists to analytical instrumentation. The primary objective of the project is to improve accessibility and operability to analytical instruments with regards to software and hardware. The outcome and success of the project will be directly evaluated by the actual stakeholders with disabilities as the immediate target group.

In the course of the project, a questionnaire was developed to investigate the situation of people with conscious and unconscious disabilities in the laboratory, specifically regarding analytical instruments. The questionnaire is open for every interested person and supports the contribution of staff experience and opinion concerning disabilities in the laboratory. Hereby, the questionnaire is fully anonymous and no personal data is provided to the authors. The results of this survey should benefit scientists with disabilities to create a more inclusive and consequently more diverse workplace in chemistry laboratories. In the end, the results will be presented to laboratory suppliers and instrument manufactures for future consideration.

Please support the project by taking the survey: https://icpms-leoben2022.at/inclusion-in-lab

inclusion, diversity, disability, laboratory infrastructure, questionnaire

Poster - We 34 Imaging

Potential of quantitative LA-ICP-ToF-MS imaging to improve understanding of Wilson’s disease therapeutics

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Deficiency or excess of essential metals in the body is associated with metal metabolism disorders including Wilson’s disease. Reliable methodology for bio-distribution markers is essential to underpin biochemical tests for disease diagnostics and guiding therapeutics. In this study, methodology for quantitative LA-ICP-ToF-MS tissue imaging was developed to obtain complementary information to that of histopathological measurements that aimed to monitor the loading of a copper chelating drug, Bis-choline tetrathiomolybdate, in key organs of rats as part of a toxicology study. This drug is currently under testing to treat Wilson’s disease. Taking advantage of the improved sensitivity and throughput achieved using low dispersion LA combined with multi-elemental detection by ICP-ToF-MS, it was possible to demonstrate dose dependent Mo accumulation by monitoring Mo to Cu ratios and other key endogenous elements in rat organs; including brain (1). This highlighted the limitations of conventional histopathology techniques which only provided indication of drug loading but neither confirmed the presence of Mo nor determined its concentration.

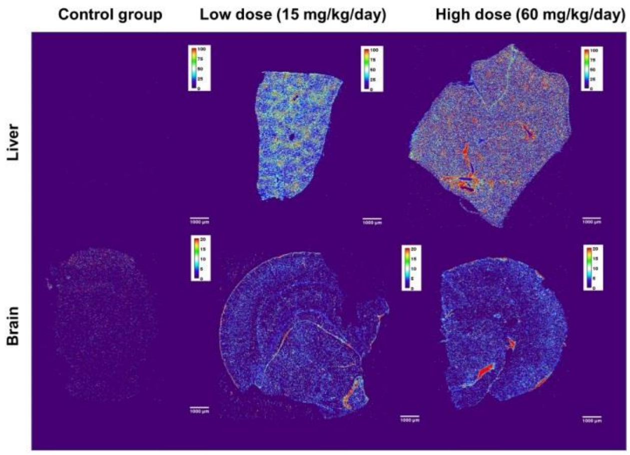

Figure 1: LA-ICP-ToF-MS images showing Mo in liver and brain tissue sections from control (vehicle only), low (15mg/kg/day oral drug administration) and high dosage groups (60/mg/kg/day). Colour scale indicates Mo concentration in fg/pixel, scale bar = 1mm.

LA-ICP-TOF-MS imaging, metal accumulation, tissue imaging, quantification, Wilson’s disease therapeutics

Foster et.al., J Appl Toxicol., 2022, doi: 10.1002/jat.4358

LIBS imaging for support diagnostic of pulmonary idiopathic disease

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Diffuse interstitial lung diseases (DILD) cover a wide range of pulmonary diseases in which the lung elasticity slowly decays. Unfortunately, there is actually no treatment for such pathologies, and in many cases, medical doctors tend to have difficulties in finding the origin of the lungs deterioration. Even if in rare cases theses “idiopathic” diseases may come from a genetic dysfunction, often the pathology is caused by external contamination, which comes from the exposition from the environment or from work. Medical doctors have limited flexibility in terms of providing elemental information on biopsies, so no clear connections can be highlighted between the exposition the patient has experienced during his life and the lungs contamination. In this frame, LIBS imaging developed at the Institut Lumière Matière [1] is used as a support analysis for pulmonary biopsies from patients suffering of DILD. The technique was already used for the analysis of skin cancer recently [2]. In addition to the histology routine analysis, LIBS imaging can provide useful information on the lung elemental composition. Elemental traces in patients’ lungs are then compared with a bio-bank of references lungs biopsies. Thus, the medical doctor has all the keys for trying to connect the amount of trace elements found in the biopsies and the patient’s history, for a better support of the patient. In this work, the lastest improvement in the methodology of lung biopsies analysis by LIBS imaging is described, and relevant cases studies of patients suffering from pathologies are proposed.

LIBS, lung diseases, medical application

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LA-ICP-MS analysis of teeth: A comparison of discrete spot analysis using Q-ICP-MS and imaging analysis by ICPTOF

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Deciduous teeth begin growing in utero before the 2nd trimester and are shed starting from age 6.Various elements, both essential and toxic that are present in blood during tooth growth co-precipitate in the hydroxyapatite matrix. Stable temporal signals can be measured in dentine, which contains collagen and where mineralization is immediate. Spatially resolved elemental analysis of teeth can reveal changes in nutritional status or exposure to trace elements during sensitive windows of fetal development, which have health consequences later in life. There are very few, if any, comparable biomarkers that provide time-resolved elemental status during this stage of gestation, and none that are collected non-invasively. Teeth are accretionary biominerals; elemental concentrations can be 'dated' relative to the date of birth using a visible stress line in the tooth cross section that is formed at birth called the neonatal line.The conventional method involves (1) 50 μm spot ablation of teeth from cusp to root following the enamel-dentine junction (EDJ) using an NWR 213 laser coupled to an Agilent 7900 ICP-MS, (2) calibration using a pressed pellet of a bonemeal standard (NIST 1486) and (3) offline ablation point dating calculated from the distance between the EDJ the neonatal line along the prism path.An alternative approach, made tractable by fast laser-ICPTOF is to image the whole labial side of a sectioned tooth, encompassing both enamel and dentine.This allows for analysis of all elements in an equivalent time, and potentially allows higher temporal resolution.Furthermore, our preliminary data suggest strontium may have potential use in showing stress lines such as the neonatal line, obviating the need for a time-consuming microscopy stage. The drawback of the ICPTOF approach may be a lack of sensitivity for some trace elements, such as Hg and Sn. We will present data collected from teeth sections from three distinct cohorts; an historic US cohort (1958-1970), a contemporary rural US cohort (2009-) and a contemporary African cohort and evaluate the relative merits of spot analysis compared to the imaging approach.

LA-ICP-MS ICPTOF teeth imaging environmental exposure

Quantitative multiplexed imaging of breast cancer biomarkers by immunohistochemistry-assisted LA-ICP-MS

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Breast cancer is the most frequently diagnosed cancer in the vast majority of countries and is one of the leading causes of cancer death worldwide. As such, significant research work is undertaken to provide clinical methods for producing valuable diagnostic and prognostic information. MMP-11 and CD45 are tumour-associated antigens and potentially valuable biomarkers for grading aggressiveness and metastatic probability. The assessment of these biomolecules may provide complementary information to the current slate of histological parameters, increasing the information available for treatment decisions.

Combining the sensitive elemental analysis of ICP-MS and the imaging capability of laser ablation (LA), the emerging techniques of elemental bio-imaging (EBI) and immuno-mass spectrometry imaging (iMSI) are well-positioned for studies of potentially valuable biomarkers in a large variety of diseases. In this work we demonstrate a method for the quantitative multiplexed analysis of MMP-11 and CD45 in breast cancer. (Ref 1) These biomolecules, usually not detectable by LA-ICP-MS due to their lack of hetero-atoms, are probed by multiplexed immunohistochemical staining with lanthanide-tagged antibodies. The respective lanthanide tag is then imaged by LA-ICP-MS and quantified as a proxy for the biomolecule of interest. In order to directly relate the concentration proxy tag to the target antigen, characterisation of the tagged antibody was performed with a size-exclusion chromatography (SEC) - ICP-MS hyphenated technique. (Ref 2) This allowed for determination of the average number of tags per antibody, effectively an amplification factor. After this factor correction was applied, the generated quantified images of MMP-11 and CD45 distribution in non-metastatic, metastatic breast cancer, and normal breast tissue were statistically analysed to identify trends in overall concentration of both biomolecules of interest. This study demonstrates the utility of IHC-assisted LA–ICP–MS and dedicated characterisation steps to accomplish quantitative imaging of bio-indicative proteins.

biomarker quantification, cancer, elemental bioimaging, hyphenated techniques, SEC-ICP-MS

Johnson et.al., Metallomics 2022, 14 (8)

Clases et.al., Anal Bioanal Chem 2019, 411 (16), 3553–3560

Bioimaging of Pt in mice tumours treated with cisplatin using LA-ICP-MS

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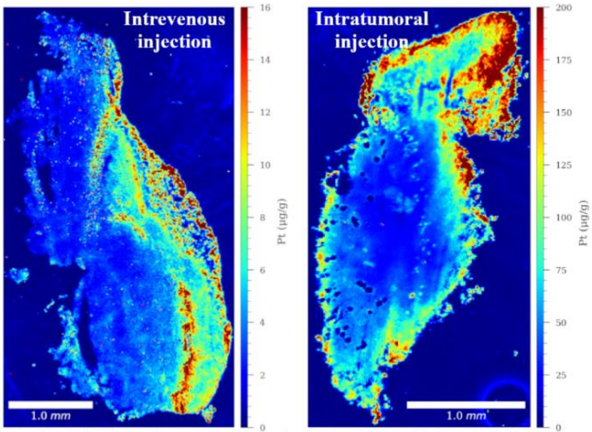
In order to study the cisplatin uptake and distribution in mice tumours, intratumoral and intravenous drug application methods with different exposure times were tested at the same cisplatin dosage and characterised using LA-ICP-MS. Pt spiked gelatine standards were selected as the quantification method most suited for this application. Their wide concentration range and stability made them an ideal solution for long measuring times and wide cisplatin concentration range expected in the samples. The LOD and LOQ of the LA-ICP-MS measurements expressed on a dry mass basis (of gelatine) were found to be 0.078 and 0.260 µg g-1 of Pt, respectively. The results show that intratumoral application oversaturates the tumour tissue, releasing cisplatin with time. However, the intratumoraly injected cisplatin concentrations in tumour tissue were significantly higher than in intravenous injection. When injected intravenously, cisplatin binds unspecifically to DNA and proteins throughout the whole organism. Consequently, a lower cisplatin concentration is delivered to the targeted tumorous tissue. Therefore, to achieve the same drug concentration in the tumour, a smaller dosage is needed with intratumoral administration. This allows for a more targeted approach, with reduced side effects from the treatment.



Quantitative Pt distribution in B16F10 mice tumours, 10 min after treatment with 4 µg of cisplatin per g of body mass.

tumours, cisplatin

Marković et.al., Analytica Chimica Acta, 2021, 1162, 338424-1-338424-12

Statistical analysis of the distribution of the cell cycle phases of different cell cultures via LA-ICP-TOFMS

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In this work we have developed an analytical method for the determination of the four different cell cycle phases of different cell cultures in form of cytospins. The cell cycle progression plays a major role in tissue homeostasis and an imbalance in the cell cycle phases is part of disease's mechanisms such as cancer, arteriosclerosis, or inflammations.[1] Up to now, the cell cycle phases are routinely analyzed by flow cytometry. Another possibility is mass cytometry by using metal-labeled antibodies[2] which implicates the potential to develop a method for imaging mass cytometry by using laser ablation in combination with inductively coupled plasma time of flight mass spectrometry (LA ICP TOFMS). The developed method will thus enable the investigation of the role of the cell cycle in metal-based drug mode of action via imaging mass cytometry which will narrow the knowledge gap regarding the effects of different treatments on the distribution of the four cell cycle phases. For method development, different cell cultures were treated under several conditions (control, cisplatin, taxol and with serum free medium) to arrest the cells in different cell cycle phases followed by an optimization of the laser ablation parameters to achieve a subcellular resolution enabling a statistical analysis at the single cell level. Besides using metal labeled antibodies for the tracking of the phases (G1, G2 and M), IdU (S), a thymidine substitute, is used as well as a DNA intercalator (DNA or nucleus). Four single cell segmentation methods were tested, and pipelines were set up for optimal segmentation of the cytospin. This data and method allow for fast and straightforward statistical evaluation of a defined cell population based on their cell cycle and provides the possibility to screen metal based candidate drugs for their accumulation in specific cell cycle phases in organs, tissue and tumors.

LA-ICP-TOFMS; single-cell-analysis, cell cycle phases, laser ablation

Zhivotovsky, S. Orrenius, Journal of Internal Medicine 2010, 268, 395-409.

Behbehani et.al., Cytometry Part A 2012, 81A, 552-566

Recent improvements in Mpx/hr LA-ICP-TOFMS mapping

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[1]TOFWERK AG, Thun, Switzerland, [2]Elemental Scientific Lasers LLC, Huntington, UK

Laser ablation ICPMS mapping is continuously striving for ever faster speeds and ever higher spatial resolution. The main physical limitations in this endeavour are 1) the wash-out time and dispersion of laser-produced aerosol being transported into the ICPMS, 2) the repetition rate at which the laser can fire, 3) the spatial precision at which individual laser shots can be placed at very high speeds and repetition rates, 4) the optical quality of the laser ablation system, and ultimately for smaller and smaller laser spot sizes, 5) the detection sensitivity of the ICPMS.

While point 2) could advance much beyond current state-of-art, 1) poses a physical limit on maximum repetition rates achievable. Both are fields of intensive technological development in the past decade. Points 3) and 4) are well understood technical challenges, and while ultimately the interplay of stage precision and laser spot size will also put a physical limit on feasibility, technological improvements can still be expected.

Here, we present current developments on the LA-ICPMS mapping capabilities of the icpTOF (TOFWERK AG, Switzerland) coupled to an imageGEO (ESL, USA). We demonstrate excellent spatial precision and reproducibility of the ablation at high repetition rates by encoder triggering on the laser system, as well as improved sensitivity under dry-plasma conditions and improved data acquisition speed on the ICP-TOFMS. In combination, this allows for routine sample mapping in the Mpx/hr range without compromising data quality or sensitivity.

laser ablation imaging mapping ICP-TOFMS LA-ICPMS time-of-flight TOF

Fast and high-resolution LA-ICP-MS imaging for improved characterization of speleothems as paleoclimate archives

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Speleothems are important environmental archives due to their potential of recording variations in temperature, rainfall regimes, soil/vegetation dynamics and many other processes through changes in growth speed, isotopic signature and trace elements concentration. From the geochemical point of view, the vast majority of approaches rely on the analysis of replicate transects along speleothems' main growth axis, where lateral variability is averaged out as a disturbing feature. However, lateral variability is an important component of individual growth conditions which are fundamental for any environmental interpretation. Extracting such information requires an extra-investment in developing integrated analytical approaches (multi-technique and multi-disciplinary) specifically optimized to elucidate the relationship between chemistry and microstructure in two dimensions at least. We propose a novel LA-ICP-MS method for fast high-resolution elemental imaging specifically adapted and assessed for the analysis of speleothems, derived from a method we recently developed for ice cores [1]. Instrumental settings were optimized to achieve artifact-free mapping at 20 µm lateral resolution of 5-7 masses per run at the speed of about one square mm per minute. Quantitative analysis is achieved by combining internal normalization, external calibration with multilevel pellets of aragonite obtained from KNI-51 stalagmites (Kimberley, Australia), and validated by standard liquid ICP-MS analysis. The method was applied to the pilot elemental mapping of slow growing (1 mm/ka) subaqueous calcite deposits from Devils Hole (Nevada, USA), previously used to date groundwater oscillations at orbital and multi-millennial timescales [2]. Preliminary results show dramatic differences in the 2D spatial distribution amongst Mg, Sr, Ba and U; particularly associated to the microstructural features of dense mammillary calcite (formed under water) and porous folia (formed at the water surface), including structurally complex mineralogical boundaries, and transition zones undetected by microscopy alone. Integrating longitudinal and lateral variability in the microstructural investigation of speleothems opens the way to elucidate how reconstructing minerogenic processes can bring to light the effects of past climate changes on delicate cave environments. Additionally, more accurate linear (temporal) records can be extracted as reductions of high-resolution maps being able to visualize, characterize and eventually avoid irregularities post-acquisition.

Elemental imaging; LA-ICP-MS; speleothems; paleoenvironment; Devils Hole; KNI-51

Bohleber et al Journal of Analytical Atomic Spectrometry, 2020, 35(10):2204.
Moseley et al. Science, 2016, 351(6269):165

LA-ICP-TOFMS as a tool for exploring the mechanisms of chemoresistance in oxaliplatin-treated HCT116 tumors

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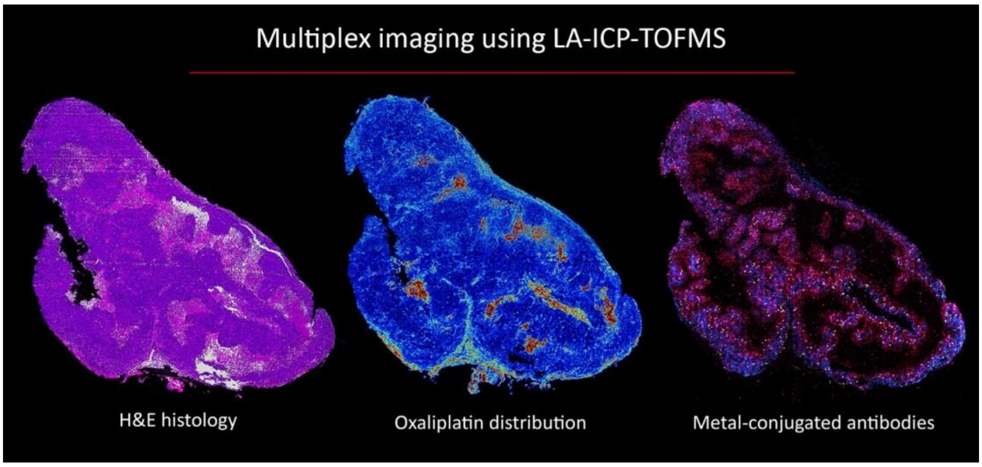
Studies on the interactions of metal-based anticancer drugs (e.g., cisplatin, oxaliplatin) with the tumor microenvironment are still fragmentary to this date (1). State-of-the-art analytical methods are required to answer complex questions like chemoresistance of certain tumor types. Immuno-mass spectrometry imaging (iMSI) using metal-conjugated antibodies in combination with LA-ICP-TOFMS detection has great potential to set a new standard for cancer research (2,3). In addition to the distribution and quantification of the metallodrug at the single-cell level, it is possible to visualize structural features and immune cells via antibodies as well as endogenous elements, leading to a multiplex imaging approach. In this work, this technique is applied in a comparative study of sensitive and resistant HCT116 tumors treated with oxaliplatin, in order to explore potential mechanisms of chemoresistance.



ICP-TOFMS, laser ablation, imaging, immunostaining, tumor, metallodrug, oxaliplatin, chemoresistance

A. Bergamo et al., Coord. Chem. Rev., 2018, 360, 17-33

D.P. Bishop et al., Sci Rep, 2021, 11, 1128

H.R. Ali et al., Nat Cancer, 2020, 1, 163-175

A 3D approach to visualize ion diffusion in polymers using LA-ICP-MS and LIBS

Birgit Achleitner[1], Lars Varain[1], Michael Nelhiebel[2], Günther Fafilek[1], Silvia Larisegger[2], Andreas Limbeck[1]

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Increasing industrial demands for more capacity and faster processing speeds lead to miniaturization and weight reduction in the product development of microelectronic devices. High performance polymers like polyimides play an important role in this process due to their high thermal stability, high chemical resistance and high mechanical toughness. Therefore, they function as an insulating film, passivation layer or mechanical stress buffer in a variety of different applications. To improve the durability and reliability of electronic devices, the uptake and diffusion of corrosive species within those polymers is of utmost importance. In general, LA-ICP-MS and LIBS are powerful techniques to uncover the migration pattern of ionic species within a polymer.

In this work, we use LA-ICP-MS and LIBS to enable rapid mapping of commercial polyimide films which were exposed to various aqueous solutions containing potassium chloride and copper(II) chloride. In order to measure these three analytes, both techniques as well as a tandem approach are executed to map the exposed area. A comparison between the measurement methods is done to achieve optimum conditions for all analytes. Both, lateral mapping and depth profiling is applied to gain insight into the diffusion behaviour and obtain 3 D information.

LA-ICP-MS, LIBS, diffusion, polymers

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Nanoparticle-enhanced discrimination analysis of polymers and microplastics by laser induced breakdown and Raman spectroscopy

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A relatively novel development in LIBS is the use of metal nanoparticle (NP) deposition on the sample surface, which can improve the sensitivity with one or two orders of magnitude via a plasmonic effect. This approach, called nanoparticle enhanced-LIBS (NELIBS), is nowadays a popular way to improve the performance of localized quantitative LIBS analysis of a variety of samples [1-3]. In our present work, we made efforts to extend the application of the approach to two new fields. One of them is qualitative discrimination analysis, where NELIBS can potentially increase the discrimination accuracy by boosting the signal to noise ratio of the spectra. The other application field is chemical mapping, which could also benefit from a signal enhancement, thereby potentially allowing for a higher spatial resolution analysis or better discrimination. Both of these efforts have substantial experimental and computational challenges. In addition to the above efforts, we also tested the possibility to improve the performance of qualitative discrimination by data fusion from LIBS and Raman spectroscopies, with or without nanoparticles.

Several nanoparticle generation and deposition techniques were tested and optimized during this research, including droplet deposition, spray coating, sputtering, electrical discharge generation, laser ablation and chemical synthesis. The laser fluence and spectral data acquisition parameters were also optimized. Various polymers and industrial plastic samples, including microplastics, were used as test objects. Striped and patterned polymer and plastic samples were used to test the performance in chemical mapping. The performance of multiple machine learning approaches including PCA, LDA, CT and RF, with and without data fusion between LIBS and Raman spectroscopies were also assessed. Our presentation will provide an overview of the present status of our research.

LIBS, Raman, nanoparticle, chemical imaging, signal enhancement, qualitative discrimination

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Liquid standard addition calibration for laser ablation inductively coupled plasma optical emission spectrometry

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The analysis of stochiometric ratios in solid-state samples is crucial in various fields when materials with a defined structure are employed for different applications. The stochiometric composition impacts the material's properties, such as reactivity and stability. Especially in applications in electrochemistry, like high-performance ceramics used in cathode materials of solid oxide fuel cells, the stochiometric composition is vital to meet the high demands imposed on the material.

Conventional methods for the determination of the elemental composition of solid samples include the dissolution and subsequent analysis with ICP-MS or ICP-OES. Problems can occur with samples that cannot be dissolved in sufficient quantity. Solid sampling with LA is desirable, but due to occurring matrix effects, reliable quantification is often impaired. Hence matrix-matched standards are necessary, which are not available for most samples. The preparation and characterization of in-house matrix-matched solid standards have the drawback of being challenging and time-consuming.

Thompson et al. [1] developed a method for element concentration analysis with LA-ICP-OES using an aqueous solution as an external standard, applying a dual gas flow inlet system. Further developments allowed mixed-sample introduction [2] and were applied for on-line additions calibrations [3]. In this work, a multiple standard addition approach using liquid standards to create a matrix-matched LA-ICP-OES calibration was employed and applied for inert metal oxides. While absolute quantification of elements requires knowledge about ablation rate and transport efficiency, this is negligible in the case of stoichiometry determination if no fractionation occurs. For the analysis, the solid sample was ablated with a 213 nm laser and the resulting sample aerosol was mixed with aerosol carrying the aqueous calibration standards from a nebulizer before entering the ICP-OES. This simultaneous introduction results in the aqueous standards being analyzed within the sample matrix. The concentration of the standard solution was stepwise increased, creating a matrix-matched standard addition calibration which allows the signal quantification and thus stochiometric determination of electrochemical cathode materials for solid oxide fuel cells.

Laser ablation, Standard addition calibration, Matrix-matched standards, Sample stochiometry

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Semi-quantitative LIBS analysis of austenitic steel using the intensity ratio of spectral lines

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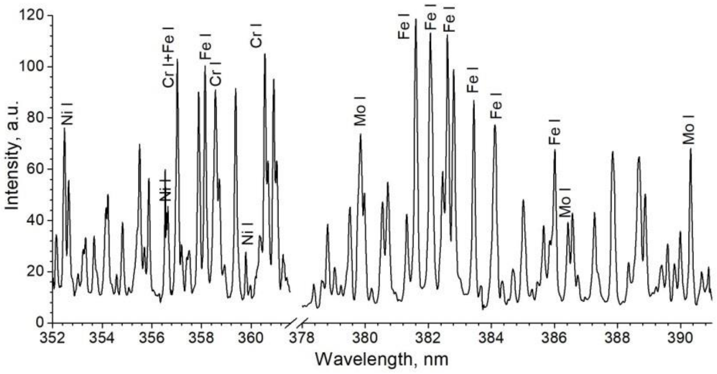
Austenitic steels are relevant materials for plasma-facing components (PFC) of fusion reactors. Elemental analysis of these materials is essential for the safe operation of fusion devices, and Laser Induced Breakdown Spectroscopy (LIBS) is a very suitable technique for analyzing metal samples. The two most often used analytical approaches are the calibration curve and the calibration-free (CF) method (1). The intensity ratio of the spectral lines of two elements depends on the excitation temperature, electron number density, and analyte concentration (2). If the plasma parameters are known, analyte concentration can be determined using a know concentration of one matrix element. This approach was applied for LIBS semi-quantitative analysis of steel, and it could provide more accurate results for trace elements than the CF method. The excitation temperature was determined from the Boltzmann plot of atomic iron lines, and the electron number density was determined from the Stark profiles. Using the Fe lines for comparison, the preliminary results showed a good agreement between the known and measured concentrations of Cr, Mo, and Ni.



LIBS, semi-quantitative analysis, austenitic steel, intensity ratio

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Time-resolved investigation of copper scaling at different temperatures by in-situ LIBS measurements

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Operating conditions of technologically relevant materials often require elevated temperatures in oxidizing or corrosive environments. This can cause diffusion inside the material or a change of stoichiometry, like oxidation. Both mechanisms impair the function of the material and can lead to the device's failure. Therefore monitoring material behavior in environments that simulate the operating conditions is a crucial task to avoid an early malfunction. However, estimating the impact of the operating conditions on the material properties and their lifespan can be challenging and time-consuming. Considering that most of the time the ageing and the subsequent measurements are separated, additional changes of the sample induced by cooling to room temperature can’t be controlled. To overcome this potential drawback in-situ measurements during operating conditions are recommended.

Therefore an in-house built heating stage, which can be placed inside the ablation chamber of a commercial LIBS system, is utilized. This stage allows heating up the sample to 1100°C in different atmospheres while offering the possibility to make in-situ LIBS measurements. In this way, time-resolved analysis of the impact of elevated temperatures in oxidizing environments on technologically relevant materials can be conducted. The applicability of the proposed in-situ LIBS measurement is demonstrated by the oxidation behavior of copper at different temperatures.

in-situ LIBS, oxidation, diffusion, heated sample stage

High-Speed Imaging with LIBS-ICPMS

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The TwoVol3 (TV3) was recently introduced as Elemental Scientific Lasers newest ablation cell which is ideal for high-resolution, high-speed LA-ICP-MS elemental imaging. The TwoVol3 is a redesigned two volume sample chamber that offers two different operation modes, imaging or analytical. Laser induced breakdown spectroscopy (LIBS) is the newest capability that is now possible with the TV3. LIBS offers the added advantage of measuring elements that can be difficult or impossible to detect by ICP-MS, such as H, O, and F. In addition, when performing imaging experiments, the ICP-MS (quadrupole based) can be dedicated to the ≤ 5 elements of interest, while LIBS can collect information about everything else (e.g., major elements such as Ca, Na, Mg, K, etc.).

Here we will push the limits of what has been considered high-speed simultaneous LIBS and LA-ICP-MS imaging. A set of unique samples (geological, biological, and industrial) will be analyzed at laser repetition rates up to 1000 Hz utilizing 3 simultaneous detectors (multi-channel LIBS, ICCD LIBS, and ICP-MS). Data quality and performance will be evaluated within iolite laser reduction software which includes new data processing features for LIBS data.

LIBS, LA-ICP-MS, high-speed imaging

Tandem LIBS/LA-ICP-MS: an alternative tool for dried blood spots devices analysis

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Dried blood spots (DBSs) are devices used to collect blood. They can store and stabilize the blood sample after drying. Using DBSs is an alternative method for blood sampling compared to venipuncture, which is invasive (syringe with a needle), generally performed in a clinical facility, and the whole blood is stored in its liquid state. Therefore, if one needs the sample for a long-term analysis, it should be frozen. The DBSs devices circumvent this issue, because several analytes can be stabilized in the sorbent material (usually paper filter). Moreover, there are commercial devices that aim self-collection: the patients would handle the device by themselves, collect their own blood, let it dry (according to the manufacturer's instructions), and finally pack and send it by mail to the clinical laboratory for further analysis.

At first, the DBSs were used for biological compounds (such as proteins, carbohydrates, etc.) analysis, however there are studies that developed analytical methods for elemental analysis. Moreover, several analytical techniques require the sample to be liquid, i.e., after receiving/obtaining the DBS, a sample pretreatment is needed before analysis. There are studies that analyze DBS directly, making use of techniques such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [1].

Laser-induced breakdown spectroscopy (LIBS) is a powerful tool to elemental analysis which was not yet used for such samples. Its throughput compared to other laser-based techniques and the information acquired from its plasma emission can be useful for the determination of different elements simultaneously. Moreover, the J200 (Applied Spectra, USA) equipment can be coupled to an ICP-MS, converting it to a tandem LIBS and LA-ICP-MS. Therefore, it is a powerful tool to use both techniques simultaneously to achieve the sensitivity for different analytes, depending on their concentration. Using elements present in the sorbent matrix, such as C, H and O, can be useful as internal standards to normalize the analytical signal of the analytes in order to correct fluctuations from the plasma generated by the laser shot and/or irregularities over the DBS surface.

Tandem LIBS and LA-ICP-MS is the aim of this study for direct and multi-element analysis of DBSs.

DBS, blood analysis, tandem LIBS LA-ICP-MS

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Laser-induced breakdown spectroscopy as an universal platform for investigating proton conducting oxides

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Proton conducting oxides (PCOs) offer a promising class of electrode materials, which permit proton-mediated electrochemical reactions at intermediate temperatures. Their applications span from classical solid oxide fuel and electrolyzer cells (SOFCs/SOECs) to the electrochemical synthesis of compounds such as ammonia and hydrocarbons from excess electricity. Therefore, they are a crucial component in the shift to renewable and sustainable energy utilization for reducing the ongoing energy and climate crisis. (1) To understand their properties, knowledge of the amount and distribution of the incorporated hydrogen (typically in the form of OH-groups) is of vital interest to obtain thermodynamical data and diffusion properties. However, the limited number of methods for detecting hydrogen, especially in the lab, complicates this task. Thermogravimetry (TGA) is currently the primary method to monitor the hydrogen content indirectly by measuring the water uptake of the material. (2) However, this approach lacks elemental specificity and the ability to perform spatially resolved analysis. A method that can potentially overcome these limitations is Laser Induced Breakdown Spectroscopy (LIBS), as it provides the ability to perform spatially and depth-resolved analysis of all elements in the periodic system under any atmosphere. However, the main drawback of LIBS is that quantification of the signals remains challenging due to heavy matrix effects and thus requires matrix-matched standards. (3) In this work, we present a workflow to quantify hydrogen in PCOs by loading standards with defined amounts of hydrogen in TGA. For comparison, conventional pressed powder reference materials are prepared. Two LIBS systems with different laser wavelengths and optics were used, and their performance was evaluated. With this method, it is possible to measure hydrogen diffusion profiles and gain, in combination with a throughout electrochemical characterization, insights into the hydrogen/water uptake mechanisms and optimize the materials' composition and production process.

The possibility to perform in-situ LIBS measurements is exploited using a new in-house developed sample chamber. This avoids any adverse effect of contamination with water or loss of hydrogen during the sample transfer. Further, electrochemical polarization is possible during the hydrogen/water uptake, which allows spatially resolved hydrogen detection while tailoring the defect chemistry of the sample.

LIBS, quantification, Proton conducting oxides, diffusion, hydrogen, electrochemistry

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Investigation of metal diffusion into polymer films by measurement of quantitative LA-ICP-MS depth profiles

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Polymers are nowadays part of uncountable aspects of our daily lives, reaching from relatively trivial applications, e.g., packing materials, to highly demanding technological applications. An application where the polymer properties have to meet specific requirements is the use for electrical insulation and corrosion prevention in electronic devices. The electric fields, the increased temperature, and ambient humidity during operation can cause degradation of the polymer but also induce the diffusion of the conducting materials into the polymer. The introduction of metals into the polymer layer is of particular interest since it leads to an increased conductivity and thereby an increased risk of component failure.

To investigate the diffusion of metals into polymers, suitable testing equipment, as well as analytical techniques, are required. Conventional methods for elemental analysis of polymers, i.e., sample combustion or digestion followed by liquid ICP-MS/OES analysis, are not appropriate since they do not allow a differentiation between the metal on the surface and the metal ions that have diffused into the polymer. Moreover, these approaches require work-intensive sample preparation and provide only bulk information. To overcome these limitations, LA-ICP-MS is a very attractive method for direct solid sampling, offering high sensitivity and the possibility of spatially resolved analysis.

This work investigates the diffusion of aluminum and copper into polyimide. Polymer films with a thickness of 6 µm and attached metal electrodes were weathered within a climate chamber, exposing them to increased temperature, humidity, and an electrical bias. Additionally, samples were treated on a heating stage with temperatures from 100 to 300 °C for different time intervals. Subsequently, quantitative determination of Al and Cu depth profiles in the aged samples was performed via LA-ICP-MS. The measurements were performed with a 193 nm Excimer laser, offering a sufficiently high depth resolution in the order of 100 nm. Derived findings give insight into the metal diffusion into the polymer and the influence of temperature, humidity, bias, and time.

LA-ICP-MS, metal diffusion, polymer analysis

Investigation of degradation of the aluminum current collector in lithium-ion batteries by glow-discharge optical emission spectroscopy

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Lithium-ion batteries (LIBs) are one technology to overcome the challenges of climate and energy crisis. They are widely used in electric vehicles, consumer electronics, or as storage for renewable energy sources. However, despite innovations in batteries' components like cathode and anode materials, separators, and electrolytes, the aging mechanism related to metallic aluminum current collector degradation causes a significant drop in their performance and prevents the durable use of LIBs.[1] Glow-discharge optical emission spectroscopy (GD-OES) is a powerful method for depth profiling of batteries' electrode materials.[2,3] This work investigates aging-induced aluminum deposition on commercial lithium cobalt oxide (LCO) batteries' cathodes. The results illustrate the depth-resolved elemental distribution from the cathode surface to the current collector. An accumulation of aluminum is found on the cathode surface by GD-OES, consistent with results from energy-dispersive X-ray spectroscopy (EDX) combined with focused ion beam (FIB) cutting. In comparison to FIB-EDX, GD-OES allows a fast and manageable depth profiling. Results from different positions on an aged cathode indicate an inhomogeneous aluminum film growth on the surface. The conclusions from these experiments can lead to a better understanding of the degradation of the aluminum current collector, thus leading to higher lifetimes of LIBs.

lithium-ion battery, aging mechanism, depth profiling, elemental analysis

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Parametric analysis on GDMS measurement: investigation of source conditions and material properties.

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Glow discharge mass spectrometry (GD-MS) allows direct elemental analysis of a solid-state material. Therefore, by using GDMS techniques, we can to avoid numerous potential contaminations that plague other mass spectrometry or spectroscopic techniques relying on sample digestion. However, in glow discharge mass spectrometry, the ionization of sputtered material in the source depends on a large variety of factors including source conditions and sample composition. Therefore, in addition to certified reference material RSF (Relative Sensitivity Factors) calibration issues, a number of issues can affect the final analytical result. In this work, we use the THERMO Element GD plus MS with pulse mode to investigate the key parameters upon which the results could rely. Our preliminary work is based on standard conducting materials (e.g. aluminium; steel; nickel; copper) and we focus on quantifying the effects of contamination (from the resurfacing processes and acid etching), surface roughness, source geometry and interferences. Ultimately, this work attempts to explain or hypothesise on several major differences in composition obtained by GDMS relative to other plasma techniques.

GDMS, matrix effect, source condition, plasma

Understanding the synergic bactericidal activity of silver-based nanomaterials/antibiotics by using Single Cell-ICP-MS

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Antimicrobial resistance is one of the greatest public health challenges worldwide, because it is a growing threat that affects the efficacy of antibiotics. One strategy to reduce antibiotic consumption and fight this antimicrobial resistance is the use of silver-based nanomaterials. Silver compounds are used for their bactericidal effect, and their use in the particulate form may present additional advantages. The aim of this work is the study of the bactericidal effect of silver-based nanomaterials and the synergistic effects that can arise from the use of these nanomaterials in combination with conventional antibiotics. The analytical aim is based on the development and application of different methods to identify and quantify the different silver species present in individual bacteria previously incubated with silver nanomaterials and antibiotics.The technique single cell inductively coupled plasma mass spectrometry (SC-ICP-MS) allowed the quantification of total silver that had been internalized or adsorbed by the bacteria during microbiological cultures. The synergistic effects of silver-based nanomaterials/antibiotics were studied by combining of silver-based nanomaterials with different concentrations of an antibiotic. The obtained results showed differences in total silver depending on the antibiotic concentration. To determine the biodistribution of the silver (intracellular or cell wall-adsorbed silver), an enzymatic digestion was performed. The intracellular silver was quantified by SC-ICP-MS. Results about intracellular and cell wall-adsorbed silver will be presented. As a general conclusion, single cell-ICP-MS allows detecting and quantifying internalized or adsorbed silver by bacteria. Complemented with other digestion methods that remove the cell wall, SC-ICP-MS allows the discrimination of the intracellular and the cell wall-adsorbed silver species, helping to explain the bactericidal activity of silver nanomaterials and their action mechanisms.

Acknowledgements

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single cell-ICP-MS, silver nanoparticles, bactericides

Development of a novel method based on single particle ICP-MS/MS a high sensitivity sample introduction (apex) system for the characterization of titanium dioxyde nanoparticles in food simulants

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Titanium dioxide (TiO2) is a white powder of nanoparticles (NPs) used as a pigment for its whitening, opacity and ultraviolet light absorption properties in many industries including food & food packaging industry. TiO2 food additive (E171, anatase form) was banned (2022) from the European Union foodstuffs after EFSA assessed (2021) that it could no longer be considered as safe due to its potential genotoxicity by ingestion. TiO2 is also present in various food packaging, hence it is important to evaluate TiO2 NPs (or another Ti-containing pigment) release from food packaging into food upon its storage and consequently the risk for human health. « Single particle » Inductively coupled plasma-mass spectrometry (Sp-ICP-MS) has become a key approach for the characterization of TiO2 NPs as it provides particle number concentration even in very diluted environments, which may occur in food packaging release. Few studies investigated the transfer of TiO2 NPs from food contact materials into the foodstuffs and the majority measured only total Ti level (by ICP-MS) in the food simulant. Addo Ntim et al. 2018 employed Sp-ICP-MS to assess the release of TiO2 NPs from cookware as food contact material, but in their study the cookware was kept in contact with food much less time than in case of food packaging. Kocic et al. 2022 proposed micro-droplet injection ICP-MS as tool for TiO2 NPs analysis in solvents, but their method was not specifically developed for food simulants or transfer studies. This study reports the development of a novel approach based on Sp-ICP-MS/MS (using O2/H2 reaction mode) coupled to a desolvating system (APEX device) for the characterization of TiO2 NPs in food simulants recommended by the European Commission. This experimental setup allows the analysis of TiO2 NPs in various food simulants without isobaric interferences on Ti isotopes (due to the use of the MS/MS mode) but also to obtain a lower limit of detection (in size) compared to the conventional sample introduction systems due the use of the APEX device. The APEX Ω proved to be an excellent approach to avoid the matrix effects caused by the organic nature of food simulants.This accurate and robust Sp-ICP-MS method will be applied to the assessment of the transfer of TiO2 NPs from food packaging and for their characterisation in various food simulants.

Nanoparticles, Single Particle ICP-MS, TiO2, Food simulants, APEX, E171, Solvents.

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Kocic et al. - 2022 - Direct analysis of nanoparticles in organic solvents by ICPMS with microdroplet injection

Probing mercury detoxification potential of biogenic selenium nanoparticles using spectrometric techniques

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Selenium is a trace nutrient essential for human and animal health and well-being. In order to prevent pathologies resulting from Se deficiency, a variety of nutritional supplements are used. Selenium nanoparticles (SeNPs) have been recently proposed as a new innovative Se source due to their unique biological, chemical and physical attributes. In our recent study,highly stable SeNPs issued from a novel microwave-assisted green synthesis using yeast extract as a source of non-toxic reducing and capping agents, were investigated. They proved to be highly stable andtheir behavior under gastrointestinal conditions has been evaluated confirming their usefulness as a novel Se source [1]. Among many features of the Se, its role in the detoxification of mercury and its compounds is noteworthy. Mercury is one of the most common environmental pollutants and toxic elements [2]; it is listed among the top 10 most dangerous chemicals threatening public health. SeNPs may be considered as an alternative to the commonly used selenium compounds in Hg detoxification process, however, their potential needs to be verified by appropriate analytical tools. The aim of this work was to characterize SeNPs extracted from the yeast biomass exposed to mercury species. The SeNPs and SeNPs-Hg conjugates were mechanically extracted from the biomass using glass beads and analyzed by single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). In the independent time scans, both Se and Hg signals were recorded in selenized yeast cells after their incubation with inorganic Hg and ethylmercury (EtHg). The signals intensities recorded for inorganic Hg were higher than that for EtHg, indicating that more mercury atoms interact with individual SeNPs. The influence of mercury on the size distribution of SeNPs was also verified. For the culture exposed to inorganic Hg, the increase of the number of smaller nanoparticles was observed. In turn, the correlation of the signals recorded for Se and Hg by microwave-induced plasma optical emission spectrometry operating in a single particle mode (SP-MWP-OES) confirmed the presence of both elements in the analyzed particles. The above findings support the hyphothesis of the mercury binding by SeNPs and thus their potential Hg detoxification.

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selenium nanoparticles, mercury, yeast, single particle analysis

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Application of single particle and single cell ICP-MS for the characterisation of microplastics and unicellular algae via carbon analysis

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The discharge of plastic waste and subsequent formation and global distribution of microplastics (MPs) has caused great concern and highlighted the need for dedicated methods to characterise MPs in complex environmental matrices like seawater. Single particle inductively coupled plasma mass spectrometry (SP ICP-MS) is an elegant method for the rapid analysis of nano- and microparticles and to characterise number concentrations, mass, and size distributions. However, the analysis of carbon (C)-based microstructures such as MPs by SP ICP-MS is at an early stage [1,2].

In this work, the application of ICP-MS and ICP-MS/MS was investigated for the characterisation of MPs in ultra-pure water and seawater. Different acquisition modes (mass shifting and on-mass analysis) were evaluated using different cell gases. SP/SC ICP-MS for the analysis of MPs and cells in seawater was assessed using a high matrix introduction (HMI) system. The concept was applied for the analysis of C in individual algae in seawater and polystyrene-based MPs were used for instant mass and size calibration. In a proof of principle, five different unicellular Symbiodiniaceae species were analysed for C content and results were validated using complementary methods (coulter counting, microscopy, TOC) [3].

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imaging, quanitfication strategies, isotope dilution analysis, gelatine standards, size exclusion, immunohistochemistry

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Taylor dispersion analysis and ICP-MS hyphenation for size determination of ultrasmall metal-containing nanoparticles in biological media

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In recent years, the use of hybrid nanoparticles (NPs) as platforms for cancer therapy has attracted a growing interest. Ultra-small NPs (size less than 8 nm) in particular, appear to be a promising route because their rapid renal elimination leads to a massive reduction in their toxicity. However, their passage in the clinic is slowed down by the lack of methods allowing the characterization of these nanomedicines. One of the issues is the measurement of the hydrodynamic diameter of these particles in a biological medium, which can be quite different from the diameter measured in an aqueous medium. Many studies have been conducted on the interactions between NPs and proteins and the formation of a protein corona around the NP when the latter comes into contact, which leads to modifications in biodistribution and cellular internalization. For ultrafine NPs (size less than 8 nm), this phenomenon does not seem to always occur. However, in a medium such as blood, where the majority protein (albumin) has a size of the order of 6 to 8 nm, it is difficult to distinguish between ultrafine NPs and proteins without introducing purification steps.

Rapid and specific analytical methods are thus necessary in order to follow the evolution of the size of NPs in a biological medium. The coupling of the ICP-MS, allowing the specific detection of metals, with the analysis by dispersion of Taylor (TDA) can be extremely advantageous because it makes it possible to combine the use of biological buffers (e.g. human serum) and small sample volumes, without additional purification steps or extraction of the analyte of interest. In this context, we will focus on a particular ultrasmall nanoparticle (USNP), AGuIX, composed of a polysiloxane core and grafted with gadolinium complexes. The contribution of TDA-ICP-MS will be illustrated through the determination of the size distribution of this ultrasmall NP but also the study of its degradation process in both serum medium and urine, leading to a better understanding of its behavior in the body.

Ultrasmall nanoparticles, Gadolinium containing drug, Taylor dispersion analysis, Inductively coupled plasma mass spectrometry, Biodegradation

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Asserting the icpTOF's place in the analytical toolbox for nanoparticle analysis through an interlaboratory comparison study

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With its high-speed mass spectral acquisition and simultaneous analysis of all isotopes, the icpTOF is the ideal ICP-MS detector for multi-element single particle (sp) analysis. Indeed, the icpTOF always records complete mass spectra, meaning that All the elements are recorded All the time. Because no analytes are missed, it is consequently possible to differentiate diverse nanoparticle populations based on the detected elemental fingerprints. While multiple applied case studies have already highlighted the benefits of TOFMS for multi-element NP analysis, the processing of the data has always been an important part of the challenge. Thus, in order to support researchers in their sp-ICP-TOFMS work, an automated software was developed to facilitate single-particle experiments. TOFpilot now proposes a fully integrated Particle Workflow, which comprises experiment setup and subsequent data processing[1] and quantification. [2] Additionally, after development of a standard operating procedure (SOP) within the frame of ACENANO, an interlaboratory laboratory comparison was performed to validate the workflow. Two platinum nanoparticle samples were sent to 9 laboratories for characterization using the developed workflow. Results in terms of particle mass, respectively size and particle number concentration as well as isotope ratio will be discussed.

sp-ICPTOFMS, sp-ICPMS, ICP-TOFMS, nanoparticles, SOP, automated workflow, particle processing

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Development of a new Guidance Document on the determination of concentrations of nanoparticles in biological samples for (eco)toxicity studies – A systematic review of single particle ICP-MS

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To support the undertaking of (eco)toxicity studies, carried out in accordance with a number of existing Test Guidelines and Guidance Documents (GD), a new GD is under development on the determination of concentrations of nanoparticles (NPs) in biological samples. This GD aims to provide guidance on; i) the state of the art and available analytical techniques; ii) the selection of the most appropriate analytical approach and treatment of samples; iii) validation approaches and acceptance criteria. Single particle ICP-MS is anticipated to be a key analytical technique for the detection and characterisation of metal-based NPs and as such a systematic literature review was undertaken to assess the current state of the art for this technique from sample collection, storage, preparation and analysis.

The collection and storage of samples is critical, and considerations should be taken to prevent contamination and preserve NPs in samples over an appropriate timescale. Existing studies have largely focused on small number of NP types (e.g., Au, Ag and TiO2), and data is lacking for some key biological matrices such as reproductive organs.A ‘one size fits all’ approach to sample preparation and treatment is not practical, instead the most appropriate approach should be selected based on the known characteristics of the NP and biological matrix with the following considerations; i) the protocol should be appropriate for the breakdown of the biological matrix of interest; ii) the protocol should preserve NPs whilst not promoting the formation of new NPs; iii) The required reagents must be of appropriate purity. Within the literature there is a lack of consistency in how metrics are determined (e.g., size limit of detection) and the terminology used. There is a distinct lack of certified reference materials for NPs in biological matrices; the production of such CRMs is problematic dues to the wide range of NP and matrix combinations and the difficulty in long term storage of these materials. The systematic review identified the most promising sample preparation protocols and aspects of good practice, such as control samples and quality assurance. The next step for the scientific community to arrive at standardised methods for the most promising approaches, and the production of technical guidance documents on how best to select and apply the methods, and to reach agreed nomenclature and technical definitions relating to spICP-MS.

single particle ICP-MS, Guidance Document, Sample Preparation, Review

Clinical diluent effect on gold nanoparticle characterization for Nanotheranostics applications

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Nanotheranostics aims to perform a premature and non-invasive diagnosis combined with therapy focused on the specific place where the disease is by using nanomaterials [1]. To evaluate the ability to penetrate and retain the nanoparticles (NPs) in the cells, analytical techniques such as Single-Particle ICP-MS (SP-ICP-MS) are required to characterize these NPs. SP-ICP-MS not only provides the size distribution and concentration of NPs but also the concentration of the dissolved element [2].

In recent years, direct alkaline dilution of blood, serum, and urine is performed in clinical laboratories for routine analysis [3]. This alkaline diluent is named Clinical Diluent and it is a mixture of ammonia, EDTA, 2-propanol, Triton X100, and purified water, among otherts. Nevertheless, for SP-ICP-MS analysis, the presence of this diluent may affect the behavior and stability of the NPs. For this reason, in this work, AuNPs stability in clinical diluent is studied. Linearity for particle size and particle concentration is evaluated. Moreover, the accuracy of AuNPs characterization in blood and urine samples diluted with clinical diluent is determined by SP-ICP-MS. Furthermore, the detection limit has also been estimated.

Nanotheranostics, nanomaterials, SP-ICP-MS

Combination of proteomics and imaging plasma spectrometry methodologies to elucidate the size dependent toxicological effects of AgNPs in zebrafish larvae

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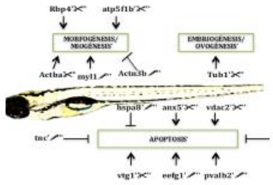
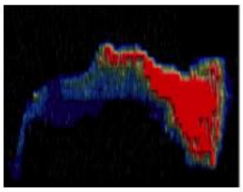
Nowadays, AgNPs, due to their antioxidant power and strong antimicrobial activity, are used in a wide variety of consumer products, as well as in biomedical applications. In the toxicological field, proteomics in combination with mass spectrometry plays a fundamental role since it allows to identify and quantify a high quantity of proteins in complex biological samples. Additionally, the use of imaging techniques may give complementary information about the distribution as well as concentration levels of the AgNPs in biological samples.

Both methodologies have been applied to an in vivo model (zebrafish larvae) that has been exposed to two different sizes AgNPs (10 and 60 nm). The results obtained from the combination of LA ICP/MS and Super-SILAC strategies have demonstrated morphological and histological alterations in both cases but more pronounced alteration when larvae were exposed to the smaller AgNPs. According to these proteomic results, the images obtained by LA-ICP/MS showed a greater accumulation of the smallest AgNPs throughout the entire body of the larvae, while the largest accumulated to a much lesser extent and only in the head area. These informations have confirmed AgNPs size dependent toxicological and distribution patterns.





Silver nanoparticules, zebrafish larvae, toxicology, LA ICP/MS, super-SILAC

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EAF4-ICP-TQ-MS as a potential powerful tool for the study of metallic nanoparticles

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The outburst of Nanoscience and Nanotechnology has involved a huge increase in developments and applications of metallic nanoparticles (NPs) in many fields, such as electronics, environmental remediation, and medicine but the impact on human health and the environment are not fully known. NPs can suffer different transformations in biological systems, such as agglomeration/aggregation, adsorption of proteins or release of metallic ions. Therefore, sound knowledge on the behavior and transformations of NPs in biological systems is required for the assessment of human and environmental risks of these materials. New analytical techniques and developments are required to get this information.

An increasingly used technique is Asymmetrical Flow Field-Flow Fractionation (AF4). The introduction of an electrical channel in these instruments has provided an additional driving force, the electric field, for the fractionation, giving way to the EAF4 mode. This emerging approach is suitable for mono- and polydisperse colloidal suspensions with high-resolution and can be seamlessly coupled to multiple detectors, i.e., ultraviolet-visible (UV-vis) and multi-angle light scattering (MALS). However, it is EAF4 hyphenated to inductively coupled plasma mass spectrometry in triple quadrupole (ICP-TQ-MS) that can give simultaneous information about particle size range, concentration, composition, and surface charge, which are all relevant to study the behavior of NPs in biological systems, thanks to its high sensitivity, selectivity and multielement capability.

The aim of this work is to develop a new analytical strategy via EAF4-ICP-TQ-MS system combined with optical detectors that give complementary information to study different metallic NPs, i.e., AuNPs, AgNPs, and PtNPs, with both citrate and phosphate coatings. NPs have been characterized in terms of size and electrical parameters, such as electrophoretic mobility and zeta potential. NPs showed different retention times and signal intensities under different electrical current (positive and negative) as a function of the coating. The potential of system has been demonstrated for the characterization of NPs and it is expected to be applied for the study of complex biological and environmental matrices in further studies.

Acknowledgments: PID2019-104381GB-I00, EQC2018-004010-P, EQC2019-005508-P, and SBPLY/16/180501/000356.

EAF4, ICP-TQ-MS, metallic nanoparticles

Palladium nanoclusters as label to determine GFAP in biological fluids by bimodal detection: ICP-MS & cyclic voltammetry

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Stroke is one of the leading causes of death worldwide, with more than 15 million cases reported annually. There are two main types of strokes, ischemic and haemorrhagic, and it is necessary to know the type of stroke that is occurring before starting the appropriate treatment. Currently, clinical differentiation is usually carried out by computerized axial tomography, which is unavailable in the pre-hospital setting. It has been found that mortality rates and the occurrence of permanent aftermath are greatly reduced if treatment is started promptly. Thus, there is great interest in the development of fast and sensitive analysis strategies to accurate differentiate between the two types of strokes. GFAP protein has been identified as a biomarker for early stroke differentiation (1). Due to its low concentration in biological fluids is necessary to resort to sensitive analytical techniques for its precise and accurate determination. The use of elemental labels has shown a high potential for sensitive detection of biomolecules by ICP-MS. Within this context, single chelates and commercial polymers containing several lanthanide atoms covalently attached have been investigated as elemental labels. The use of labels with many atoms of a given metal per tag, such as metal nanoclusters (MNCs), will allow high signal amplification, and thus, good sensitivity for detection of the corresponding biomolecule (2). In this work, the synthesis of PdNCs was developed to obtain highly stable, monodisperse and water soluble nanostructures with diameters below 2.5 nm composed of more than five hundred atoms. This small size allows the bioconjugation to specific antibodies with their functionality unaltered, even using high molar ratio (Antibody:PdNCs 1:20). Additionally, it has been observed that PdNCs present catalytic activity on the hydrogen evolution reaction (HER) (3). In our experiments, the synthesised PtNCs were bioconjugated, via carbodiimide, to anti-human GFAP antibody and evaluated for the determination of GFAP in human serum and nasal exudate samples by cyclic voltammetry and ICP-MS. To corroborate the GFAP content obtained with the methodology using PdNCs label, a commercial ELISA kit was employed in those samples with sufficiently high GFAP concentration.Acknowledgements: This work was financially supported through project AYUD/2021/51289 (PCTI Program of the Government of the Principality of Asturias and FEDER Program of the European Union) and PID2019-107838RB-I00/Agencia Estatal de Investigación (AEI)/10.13039/501100011033) in Spain.

Stroke, GFAP protein, Palladium nanocluster, Electrochemistry, Bimodal detection

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Nanoparticle identification using single particle ICP-ToF-MS acquisition coupled to cluster analysis. From engineered to natural nanoparticles

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spICP-MS where a single isotope signal can be acquired continuously at dwell times between 10-100 µs is a particularly helpful technique when investigating the number and size of of individual elemental nanoparticles. The technique is improved upon when using an ICP-Time of Flight -MS as the multi-element compositions of each particle can be determined. The ICP-ToF-MS is further optimized for the single particle technique when able to continuously collect the ion beam at a few tens of µs per spectra with no interruption as it allows

i/ the complete evaluation of each NP signal

ii/ collecting all NP signals without loss

iii/ determining the (multi)-elemental composition of NPs individually

This makes the information on the NP population in the sample more thorough and reliable compare to information provided using a conventional single isotope ICP-MS method. Indeed, single particle composition is given simultaneously, and part of the interest of using a multi-elemental spICP-MS analysis is its potential for the identification / classification of natural or synthetic compounds for the determination of the risk assessment and of the possible health hazard. In this study, the signal of mono-, bi- and tri-metallic synthetic nanoparticles either alone or mixed will be analysed using a novel ICP-ToF-MS with the desired performance characteristics (Nu Instruments Vitesse) and multiple ways to examine the data produced will be explored.

In addition, natural particles including aluminium oxide, montmorillonite and kaolinite which are particles now dispersed in the environment due to the increase of anthropogenic activities (ie. soil erosion in the critical zone), will be investigated.

SP-TOF-ICP-MS, Cluster analysis

Tharaud et al., Journal of Analytical Atomic Spectrometry, 2022

Characterizing and evaluating the antibacterial activity of biogenic SeNPs produced by edible mushrooms

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Selenium (Se) is a chemical element which compounds have been reported as an antimicrobial, antioxidant and anticarcinogenic agent. Its nanoparticulated form (SeNPs) arouses great interest in the field of biomedicine, as its particular physicochemical characteristics confers its lower toxicity as well as greater bioavailability with respect to other selenium species (1). In contrast to the ones produced by means of chemical processes, biogenic SeNPs, which are synthesized by biological systems such as plants, bacteria, or fungi, present a greater biocompatibility and stability. Moreover, their biological origin can confer them special behavior and physiological properties, which grant this type of NPs special relevance from a biomedical point of view (2). In this work, different species of edible fungi, cultivated in a selenite enriched medium, have been studied as potential biogenic nanoparticulated selenium producers. Additionally, after their extraction and characterization, the antibacterial activity of these nanoparticles was also evaluated.

Following an optimized extraction method to isolate the nanoparticles, single particle analysis by ICP-MS (SP-ICP-MS), which has been already reported for the characterization of individual selenium nanostructures in yeast (3), was applied in this work to address the presence, characteristics, and number concentration of SeNPs in the mentioned fungi samples. Regarding the study about their antibacterial activity, several bioassays were carried out employing both gram-positive and gram-negative bacterial species, and the MIC value (minimum inhibitory concentration) was calculated.

Biogenic nanoparticles, ICP-MS, single particle-ICP-MS, antibacterial activity, MIC.

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Investigation on Accumulation Patterns of three Pt-based Drugs in Cisplatin–Sensitive and –Resistant Cell Models using single cell ICP-MS

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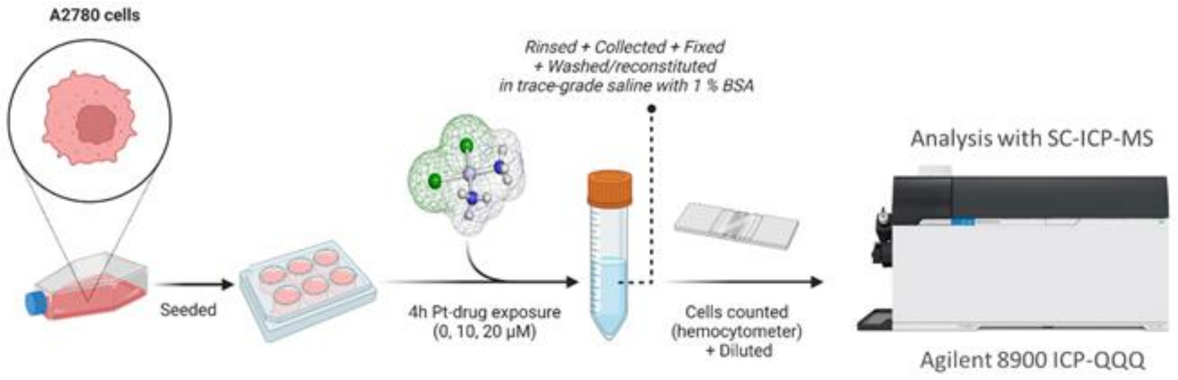
Pt-based drugs are widely used in cancer therapeutics. However, some cancer cells develop chemoresistance against them1 Further studies are important to understand the mechanism of Pt-drugs accumulation in chemoresistant cancer cells. Single Cell Inductively Coupled Plasma Mass Spectrometry (SC-ICP-MS) determines signals derived from single cells2.All the components in single cells are ionized in ICP and yield to ion cluster for each single cell.Since ICP-MS has extremely high sensitivity and fast time-resolution mode, those ion clusters can be quantified as transient signals.SC-ICP-MS technique provides four aspects of data; number of cells which include analyte element(s), mass of element(s) in each single cell, mass of element(s) in cell buffers, and cell population distribution for each analyte. Also, some challenging endogenous elements for ICP-MS such as sulfur and phosphorus can be detected at physiologically relevant concentrations by using ICP-MS/MS3. In this presentation, a comparison across three Pt-drugs (cisplatin, carboplatin, and oxaliplatin) in A2780 (cisplatin-sensitive) and A2780cis (cisplatin-resistant) ovarian cancer cell models is made.The Pt accumulation patterns and mass in single cells of A2780 were contrasted against those of A2780cis by the technique of SC-ICP-MS.



ICP-MS, sNP, Single Cell, platinum, cisplatin, carboplatin, oxaliplatin, cancer, resistant, SC-ICP-MS

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Development of a biomarker of early toxicity from electronic cigarette metal exposure using single-cell ICP-MS

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The use of electronic cigarettes (e-cig) among youth (<18 years old) in the United States is currently at alarming levels with 2.06 million youth reporting use. Increased use at a young age and the high addictiveness of nicotine products is cause for great concern due to potential long-term health effects.However, current knowledge on the long-term health effects of e-cig use is limited, highlighting a critical knowledge gap. Heavy metals such as chromium (Cr), nickel (Ni), lead (Pb), as well as nanoparticles have been found in e-cig aerosols and are a potential source of toxicity. These metals have also been detected in blood and urine samples collected from users at levels that are higher compared to conventional cigarette users. Low levels of Pb in blood have been associated with cognitive impairment, immune dysfunction, and anemia.Additionally, research conducted on Ni and Cr exposure suggests that these metals can suppress the immune system. We hypothesize that inhaled metals and metal nanoparticles in e-cig aerosols are taken up differentially by peripheral blood mononuclear cells (PBMCs).Here we present preliminary data for the development of a method to measure low levels of metals in a subset of PBMCs using Single Cell Inductively Coupled Plasma Mass Spectrometry (SC-ICP-MS) analysis.A subsets of blood mononuclear cells were fixed for SC-ICP-MS analysis and used to optimize the single cell setup, these conditions include the concentration of cells that can be introduced at one time, the sample flow rate, the nebulizer and spray chamber gas. These conditions will play a crucial role in the transport efficiency of the PBMCs. The goal is to maximize the transport efficiency to get better detection of metals in minor lymphocyte subpopulations. Our method will help the understanding of which PBMC subpopulations take up metals and metal nanoparticles, which hopefully will lead to the ability to predict potential long-term immunotoxicity due to e-cig use.

E-cigs, Metals, Single-Cell ICP-MS

Comparison of direct mercury analyzer and ICP-OES for the analysis of mercury in environmental samples

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A comparative study was carried out to determine the total mercury content of environmental samples (soil, plant, sediment, plankton and fish) with a direct mercury analyzer and ICP-OES. The comparative study of methods for determining total mercury content used five certified samples ERM CC135a (contaminated soil), ERM CC580 (sediment), BCR 414 (plankton), ERM BB422 (fish muscle), NIST 1515 (apple leaves), and CTA-VTL-2 (Virginia tobacco leaves). For the first method, samples were analyzed with a direct mercury analyzer MA-3000 System (Nippon Instruments Corporation), with a fully automated system and no pretreatment. In the second method, samples were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-OES) (Prodigy 7, Teledyne Leeman Labs) with sample pretreatment. The Microwave Digestion System MARS 6 was used for sample preparation. The total mercury content of the samples was determined after microwave digestion in closed pressure vessels: soils and sediments according to ISO 12914:2012 (aqua regia), plants, plankton and fish with a mixture of nitric acid and hydrogen peroxide. The comparison of the results obtained for total mercury by the two methods was performed by regression analysis using the Windows SPSS program. Both methods were validated for a limit of detection, linearity, accuracy and precision of results.

The mercury concentrations in the samples detected by the direct mercury analyzer and ICP-OES were comparable. The results obtained for total mercury by both methods agree with the respective certified values. Direct analysis for mercury is preferable when monitoring environmental samples for mercury only, as this method is less labour intensive (no pre-digestion of samples is required), faster, and with a lower detection limit. ICP-OES with optimized conditions (extension of washing time and choice of wavelength - 194 nm) leads to a reliable determination of mercury in environmental samples and is preferable in cases of analysis of a large number of samples and simultaneous determination of several elements.

mercury, inductively coupled plasma atomic emission spectroscopy, direct mercury analyzer, reference samples

Determination of boron in skin cancer cells by ICP-MS technique

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One treatment option for skin cancer is Boron Neutron Capture Therapy (BNCT). During therapy, non-radioactive isotope of boron (^{10}B) in a form of organic compound e.g. boronophenylalanine (L-BPA) is injected into the body, and selectively captured by melanoma cancer cells due to its higher activity compared to less melanotic cells.Then the affectedskin fragmentis irradiated with a thermal neutron beam, what leads to the production of short-lived excited ^{11}B. Finally, the nuclide produced is spited into ^{7}Li and alpha particles, that kill cancer cells.The success of this therapy is possible if there is a higher uptake of boron compound into cancer cells than in normal cells, and to obtain a high concentration of boron . Therefore, the uptake of boron in a form of BPA by melanoma cells was assessed and compared with the uptake by normal skin melanocytes in an 2D in vitro model [1]. Finally boronin cell cultures was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis. In this technique, some difficulties can be highlighted: boron contamination form laboratory glass and chemicals, boron leaching from tubes in spectrometer interface, orpresence of spectral overlap between 12C+ and 11B+ while carbon matrix is analysed. To overcome this effects, highlighted in literature [2], both sample preparation and boron determination steps were optimized. For preparation the cell samplesdifferent protocols were tested: (i) digestion of fresh samples with nitric acid; (ii) microwave digestion of frizz-dry samples; (iii) microwave digestion of fresh samples or (iv) microwave digestion of fresh samples of initially acidified with concentrated nitric acid. Finally samples were digest in high pressured microwave digestion system. From the other hand stability and leaching effect of the boron determinations was evaluated, recovery test and LOQ/LOD was found. Tested procedure was applied for determination of boron uptake in two cancer cell lines WM115 and WM266-4 and melanocytes (HEMa-Lp). The cell washing protocol was evaluated for itseffectiveness.

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boron, cancer, ICP-MS, radiotherapy, sample preparation

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Synthesis and characterization of capillary based-monolithic supports to study interactions of actinides with biological material

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Biodistribution of radioelements is governed by their physicochemical properties and their interactions with biomolecules. Accidental contamination of workers by aged plutonium (Pu), may also lead to americium (Am) contamination as a product of radioactive decay of Pu. Evaluating the differential interactions of Pu and Am with biological components at the molecular level, is thus of major concern to better understand the impact of Pu aging on its biological behavior. Our project is therefore divided into two main stages, the first is to develop an analytical microsystem containing dedicated monolithic supports, allowing the immobilization of different and controlled Pu:Am proportions simulating different degrees of aging of Pu. The second step is to evaluate the interactions of Pu and Am immobilized on the monolithic support with biomolecules. In this work, the synthesis and the characterization of different monolithic supports in capillaries will be presented, as well as their performance to immobilize thorium (Th) and samarium (Sm) as simulants of Pu and Am in order to select the most efficient support. Three monolithic supports (M1, M2, M3) based on different functional monomers [1–3]dedicated to immobilize Th and Sm have been locally synthetized within fused silica capillaries. They have been further characterized in terms of permeability, filling homogeneity within the capillary and morphology. They have a comparable permeability and size of globules around 1µm. The ability of each support to immobilize Th and Sm was determined online by coupling the functionalized capillaries to inductively coupled plasma mass spectrometry (ICP-MS). Approximately the same Th and Sm number of moles was fixed on M1, while more Sm was fixed on M2 and M3 as compared to Th. Work is presently in progress to evaluate the fixation rate of Th:Sm mixtures on M1 and M3, and select the best candidate for the future studies. In the long term, this miniaturized analytical method will be validated with the elution of reference proteins on the selected capillary based-monolithic and applied to Pu and Am. Through this strategy, the influence of Am on Pu-protein interactions will be then evaluated.

monolithic support, Pu, Am, immobilization, ICP-MS coupling

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Laser-induced breakdown spectroscopy for proximal soil sensing in precision agriculture

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Spatial variations of soil properties on agricultural land, especially the different chemical soil parameters, are relevant for the soil's fertility and thus for crop yields. The usually homogenous fertilization of fields can lead to local over- or underdosing. This can be prevented by using precision agriculture. It is based on measuring the spatial variations within a field by, e. g., chemical sensors, which avoids the time-consuming and cost-intense soil sampling and laboratory analyses. However, only a few sensor technologies, such as geoelectrical, potentiometric pH, gamma-ray and spectral-optical sensors, are currently used. The method presented in this work is the laser-induced breakdown spectroscopy (LIBS). It delivers direct and spatially well resolved data on the nutrient content without any sample preparation. It is therefore a suitable tool for the direct on-side analyses needed precision agriculture.

The presented work focuses mainly on the characterization of soil samples of a field near Bölingen (North Rhine-Westphalia, Germany) [1,2]. A set of 68 samples were taken from the entire to ensure representability as well as wide a range of soil properties. These properties, directly quantified using LIBS, were the total amount of metal nutrients (K, Ca, Mg) and non-metal nutrients (N, P, S). Additionally, it was possible to determine soil parameters such as humus content, pH, and silt and clay content (soil texture) by using multivariate methods.

Most of the recently published work, focusing on the agricultural soils application of LIBS, is also based on such multivariate methods due to the strong matrix dependence of the LIBS signals. Multivariate analysis intrinsically takes these matrix effects into account. In the work presented four multivariate regression methods were used to predict the soil parameters. Two linear methods are PLS and Lasso regression, and two non-linear, non-parametric methods are Gaussian process (GP)- and SVM-regression. This, combined with the high sampling frequency of LIBS which results in a high spatial resolution of the soil characterization, provides the basis for the on-side measurements. These can be performed either as single-point measurements using a handheld spectrometer or as a dense mapping of the soil parameters by a sensor platform spectrometer. A comparison between these two, as well as between these two and an additional high-resolution benchtop instrument is described in this work.

LIBS, precision agriculture, nutrients

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Study of the use of a new multi-purpose nebulizer in multiple conditions: from total elemental analysis to single-cell ICP-MS with one nebulizer.

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During the last years, different dedicated sample introduction systems for single-cell ICP-MS analysis have appeared in the market, including spray chambers and nebulizers. The optimal working parameters of these systems are usually determined by their design and going beyond the specifications usually results in a decreased performance in terms of sensitivity, signal stability and/or transport efficiency due to the worsening in the aerosol quality. This is especially critical for single-particle and single-cell analysis applications, where transport efficiency becomes crucial for the measurements. However, a good quality of an aerosol formed by small and monodisperse droplets affects to the sensitivity of the measurements of the total elemental content as well, since a higher transport efficiency usually implies a bigger fraction of the sample being analyzed and, therefore, increased sensitivity.

In this work the characterization of a new Teflon nebulizer will be presented. This nebulizer has been designed after previous in silico studies on fluid dynamics to optimize the droplet size and dispersity during nebulization. This design produces smaller and more monodisperse droplets, improving the ICP-MS instrument performance. This nebulizer allows a wide range of operating conditions in terms of sample flow (from 10 µL/min up to 0.4 mL/min) and nebulizer gas flow. This versatility allows its use for different applications, from HPLC-ICP-MS to single-particle and single-cell elemental analysis with high transport efficiency. Additionally, this is a robust nebulizer that can not be broken under normal working conditions, with low memory effects and compatible with both conventional and single-cell analysis spray chambers.

The nebulizer’s performance, in terms of sensitivity and transport efficiency, will be compared with these of conventional systems using similar operating conditions. For this aim, the nebulizers will be evaluated for both total elemental analysis and single-cell/particle ICP-MS analysis.

Nebulizer, single-particle ICP-MS, single-cell ICP-MS, solution, transport efficiency

Uptake of selenium species in neuroblastoma cell lines related to Alzheimer´s disease by using single-cell-ICP-MS.

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Alzheimer's disease (AD) is the most prevalent form of dementia. Organic forms of selenium (Se), such as selenomethionine (SeMet), have been reported to have great potential in AD prevention due to their capability to increase neuronal activity and supports synaptic preservation (1). Furthermore, selenium nanoparticles (SeNPs) have also been proposed as promising anti-Ad agents thanks to their excellent anti-amyloidogenic properties (2). Based on that, the present work explores the uptake and accumulation of Se species in neuroblastoma cell lines related to Alzheimer´s disease by using transmission electron microscopy (TEM) and inductively coupled plasma mass spectrometry in single cell mode (SC-ICP-MS) to get deeper insights into the interaction of Se species with neuronal cells which may open new perspectives about the use of these compounds as neuroprotective agents.

For this purpose, two different AD model cell line have been employed: mouse (Neuro-2a) and human (SH-SY5Y) neuroblastomas. Cells were exposed to SeMet, Se-methylselenocysteine (MeSeCys) and SeNPs at 10, 50 and 250 µM during 48h and their ability to accumulate these analytes was quantified at single cell level by SC-ICP-MS.

Optimization of sample introduction was carried out by varying Ar carrier and make up gas flows achieving a nebulization efficiency as high as 60% for AuNPs, 80% for 2.5 µm calibration beads and 97% for Neuro-2a cells. However, for SH-SY5Y cell line only 15% of cells introduced in the system were able to achieve the plasma. Results shown that Se uptake ranged from 19.9-41.4 and 1.2-167.5 fg/cell when Neuro-2a and SH-SY5Y were exposed to 250 µM of SeMet. However, less fg of Se per cell were quantified in MeSeCys experiments for SH-SY5Y, without detecting events for Neuro-2a cells. Otherwise, signal spikes for those incubated with Ch-SeNPs were detected for both neuroblastoma cell lines at all concentrations studied, in which Se ranged among 1.2-89.5 and 1.2-129.8 fg/cell for Neuro-2a and SH-SY5Y cells, respectively. These results may indicate that SeNPs would be more readily accumulated by both cell lines than organic selenium species. Finally, the internalisation process of SeNPs by neuroblastoma cell lines and their effect on cell organelles were evaluated by TEM.

Alzheimer´s disease; Se species; SeNPs; intracellular localisation; single cell-ICP-MS.

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Laser ablation ionization mass spectrometry on the lunar surface

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With NASA's increased focus on exploration of our Moon within the Artemis program, new scientific goals have been formulated to better understand the history of our Solar System, including the evolution of the Earth-Moon system. For building a permanent human presence on the Moon in-situ resource utilization (ISRU) of lunar material is a necessity, which needs methods of in situ analyzing and selecting suitable materials. These tasks require sensitive instrumentation capable of determining the elemental and isotope composition of geological features found on the lunar surface. Furthermore, NASA's Artemis program is also meant as a stepping stone to the future exploration of Mars. This means that instrumentation applied successfully on the Moon might find its application in the future on the Martian surface.

In this contribution, we present our progress in designing, building, and testing a prototype instrument of the miniature laser ablation ionization mass spectrometer (LIMS) for in-situ measurements on the lunar surface. Such an instrument will be deployed on a Commercial Lunar Payload Service (CLPS) mission to be flown late 2026. Defining and determining the necessary technical requirements of such an instrument, building it accordingly, and verifying its performance is key for maximizing the scientific return of this CLPS mission. For this task, appropriate laboratory test setups are necessary. To this end, a Nd:YAG microchip laser system (SB1 series, Bright Microlaser Srl, Italy) operating at 532 nm (max. pulse energy of 40 µJ, pulse repetition rate of 100 Hz), was integrated into our laboratory LIMS setup consisting of a miniature reflectron-type time-of-flight mass analyzer (160 mm x Ø 60 mm) designed for in situ space applications. The laser source and the optics are modelled after the envisioned flight design, and therefore are used to determine the required optical and electronical performance characteristics of the future flight instrument.

The results of laser ablation experiments on lunar regolith simulant aimed at demonstrating the technical feasibility of the setup will be discussed.

LIMS, Space Instrumentation, Moon, TOFMS

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Particle Analysis of Two High Purity Grades of N-Methyl-2-Pyrrolidone (NMP) using a Single Particle (sp)ICP-MS/MS Method

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Contamination control is vital to the quality, reliability, and yield of the final devices manufactured in semiconductor fabrication plants (FABs). But methods of contamination control, including the quality control of process chemicals used during the manufacture of integrated-circuits (ICs), must constantly evolve to keep pace with developments in chip design. The trend towards higher density devices with ever narrower linewidths at the nanometer scale increases the risk of contamination, as more process steps are needed. Given the nanometer scale of device features, some FABs have begun to monitor metallic nanoparticles (NPs) as well as dissolved metals in bulk chemicals, and wafer processing and cleaning baths.

Single particle ICP-MS (spICP-MS) is a powerful technique that can be used to characterize the NP content of semiconductor process chemicals including organic solvents. In this study, 18 elemental NPs were monitored in two high purity grades of N-methyl-2-pyrrolidone (NMP) using an Agilent 8900 Triple Quadrupole ICP-MS (ICP-MS/MS). The 18 elements were selected after a preliminary screening check. The ICP-MS instrument uses a fast time resolved analysis (TRA) acquisition mode and integration time of 0.1 ms to detect and characterize individual NPs and MS/MS technology to control interferences.

Comparative data obtained using the multi-element spICP-MS/MS method for the two grades of NMP will be presented. The method provided information on the identity, size distribution, and concentration of element NPs of interest to semiconductor IC FABs. Differences were found in the presence or absence of particles in the two grades of NMP, as well as in the size distribution and concentration of the particles. Higher concentrations of NPs were determined in the electronics grade product than in the higher purity sample.

The spICP-MS/MS method satisfies the emerging needs of the semiconductor industry to monitor low concentrations of small sized particles in high purity solvents.

Semiconductor, nanoparticle, process chemicals, single particle, spICP-MS, size distribution, particle concentration

On-site separation of arsenic species using a sorbent C18 modified with APDC - ICP-MS determination

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In the water environment, inorganic As compounds are mainly present. The inorganic As(III) forms (more toxic than As(V)) are dominant in the reducing environment, while As(V) acid dominates at very low pH (<2) under oxidative conditions. Both can be converted reversibly into the other, and the process is matrix and concentration dependent. The separation of unchanged As(III) species, just after sampling, is crucial for reliable speciation analysis of that element in water systems. After water sampling, As (III) quickly transforms into As (V).

In the presented work already published data (JAAS 37 (2022) :229-232) describing the simple and quick procedure for As(III) separation from a water matrix on the sampling site, integrated with speciation analysis using ICP-MS are summarized.

For the separation of As(III) anions, a C18 column was saturated with APDC. The acidification of the water sample to pH 2 ensured 100% retention of As(III) inions and effective separation from As(V), MMA and DMA. C18 columns chemically modified with APDC can be prepared and stored in the laboratory for up to 24 hours before use on the sampling site. The influence of Pb, Cd, Tl, and Cr cations can be limited with the addition of EDTA. Anions such as sulfate ions and phosphate ions do not significantly affect the efficiency of As(III) anion retention.The proposed procedure prevents changes between As speciation forms during sample collection (oxidation of As(III)) and pretreatment (reduction of As(V)). Arsenates(III) are separated from other forms within a few minutes during site sampling, which effectively prevents their change into an oxidized form.

As(III) on the sampling site,C18 column was saturated with APDC, speciation analysis using ICP-MS

ELEMENTS AND PROTEINS IMAGING BY LA-ICP-MS: MEDICAL AND PHARMACEUTICAL RESEARCH

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In the last decades, increased interest in imaging of elements/metals/proteins distribution, mainly in pharmaceutical, biomedicine research, or life science with direct application of research to specific problem/disease [1-3]. The main emphasis of this contribution is to demonstrate the unique method of laser ablation with inductively coupled plasma and mass spectrometry (LA-ICP-MS). It is a well-established method for multi-elemental analysis of elements at trace and ultra-trace. Nowadays, it is also starting to be used as a technique for the simultaneous specific determination of the protein of interest, which opens up the possibility of achieving the so-called multiplex analysis. Protein determination, protein imaging, and finally their distribution in clinical samples are presented.

Proteins are imaged using an immunohistochemical method (binding nanoparticle-labeled antibodies to a specific protein) and LA-ICP-MS. The main advantages of utilizing LA-ICP-MS are the acquisition of comprehensive (Metallo)proteomic information about the tissue of a given disease (in this case, cancer or stroke) or low detection limits compared to other conventionally employed protein imaging techniques in combination with multiplex analysis of one sample.

bioimaging, stroke, cancer, simultaneous detection, protein, elements

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Extending the capabilities of single particle ICP-MS for the detection of small microplastics in environmental water samples

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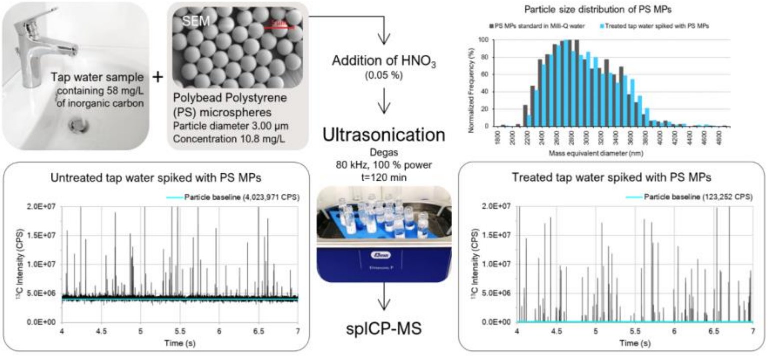
Environmental contamination with microplastics (MPs) has become a major cause of concern due to their potential adverse effects, which are expected to be enhanced for smaller MPs. To study their occurrence in the environment, reliable, selective and sensitive analytical methods are required. Single particle inductively coupled plasma mass spectrometry (spICP-MS) has been proposed for quantification and size characterization of small MPs by monitoring the signal of ^{13}C isotope (1-3). In this study, we investigated the feasibility of the spICP-MS to detect small MPs in environmental water samples. For this purpose, we spiked polystyrene (PS) MPs standards with sizes from 1 to 5 µm to tap and bottled water, surface and wastewater, and developed sample pre-treatment procedures to remove carbon-containing compounds present in the environmental samples that could interfere with the spICP-MS measurement. For tap and bottled water that contained only inorganic carbon, sample acidification followed by bath sonication effectively removed carbon background, without affecting the concentration and size of MPs. The applicability of the spICP-MS method will be extended to MPs analysis in surface and wastewater samples by developing additional pre-treatment procedures for removing organic carbon compounds.



small microplastics, environmental water samples, spICP-MS, quantification, size characterization

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Determination of selected elements in model biological fluids by ICP-MS/MS

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Accurate determination of elements in biological fluids by inductively coupled plasma mass spectrometry (ICP-MS) is often limited by the presence of spectral interferences originate from the rich matrix of such samples. There are several method for elimination of the influence of unfavorable phenomena on analytes signals, of which the use of ICP-MS spectrometers equipped with collision/ reaction cell creates the greatest possibilities [1]. In a triple quadrupole ICP-MS spectrometer, an additional quadrupole was placed before the collision/reaction cell, what allows pre-filtering of the ion beam to selectively transmit only the masses of interest. It limited the production of unwanted interference caused by collisions between other masses in the sample and the cell gas. This pre-filtering capability also allows to conducted selective chemical reactions in the cell in order to enhance polyatomic interference removal.

This work presents the examples of the elimination of spectral interferences during the determination of some elements as: Se, As, Mn, and Ti in model physiological fluids using the 8800 ICP-QQQ mass spectrometer. The effectiveness of removing spectral interferences of selected elements in the presence of interfering components was studied under a variable flow rate of cell gas (He, NH3 and O2). Under optimal measurement conditions, the detection limits of analytes were determined and the accuracy of the proposed methods was confirmed by analysis of reference materials (surface water SRM 1643e) or spiked samples. The developed methods were applied to study migration of Ti from dental implants andpotentially toxic elements from toys.

spectral interference; As, Se, Mn, Ti; saliva; dental implants; toys

Balcaen et.al., Anal. Chim. Acta (2015) 894, 7-19.

Determination of Heavy Metals and Nutrient Elements in Alternative Proteins Using ICP-MS

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Demand for alternative proteins, derived from plants, fungi and other biological sources, is booming and is expected to grow considerably due to consumer interest in health, sustainability, and food ethics (1, 2). The ICP-MS technique is widely used in the food industry for the elemental analysis of trace metals and contaminants in foods to ensure food safety and quality assurance. This study shows the analysis of the heavy metals; arsenic, cadmium, chromium, lead, mercury, and other elements in different protein-based food samples. Heavy metals were measured in the ppb levels and the nutrient elements at the ppm levels. All the metals were measured at the same time.

Agilent ICP-MS with ultra high matrix technology (UHMI) was used for this study due to the high matrices typical of these samples type. These advantages of this technology include lowering the risk of contamination introduced by sample dilution and not having to use matrix-matched calibration standards. Using the collision cell of the ICP-MS in helium mode, combined with double-charged ion correction remove polyatomic and double-charged ion interferences, simplified the analysis.

The study used 4.7 in the US FDA Elemental Analysis Manual (EAM) for food and related products. The accuracy of the method was evaluated by analyzing two food-based standard reference materials and conducting a spike recovery test for all elements in the four protein-based food samples. Excellent recoveries were achieved in all cases. The instrument also exceeded the nominal detection limit requirements specified in the EAM method and showed excellent stability over time. The study demonstrated that the instrument and method are suitable for the routine, multi-element screening of trace level elements in alternative protein foods, making them ideal for food safety programs.

ICP-MS, alternative protein, food safety

Tso et.al., Foods, 2021, 10(1), 2

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Characterization of technologically produced carbon applied in agriculture

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The application of biochar and graphite in agriculture has proven to improve soil characteristics. This study aims to analyse different chemical and physical properties of a novel material, technological carbon (TC) in comparison to graphite and biochar, in order to investigate its potential for application in agriculture.

The thermal decomposition of methane (methane pyrolysis or thermal cracking) is a process of splitting of CH_4 into its components (gaseous hydrogen H_2 and solid carbon C). The process was primarily developed for the production of hydrogen. The use of hydrogen in industry, mobility and heat generation has a great potential to contribute to a climate-neutral energy transformation. However, when producing hydrogen from methane, large amounts of carbon are produced as additional raw material. One of the most important climate-neutral areas of application is agriculture.

In a pilot study, the effect of TC soil amendment on soil plant growth characteristics as well nutrient uptake was studied and compared to graphite and biochar amendments, using maize as model plant. For the elemental analysis of graphite, biochar and TC, a combined combustion and microwave digestion approach was used for sample preparation prior to ICP-MS analysis. The effect on chemical soil characteristics was assessed by analysing extractable nutrients from soils as well as macro- and micronutrients (especially Ca, K, P, Fe, Zn, Cu, Mn, Ni) in the maize shoot biomass by inductively coupled plasma mass spectrometry (ICP-MS) applying collision and reaction cell technology.

The analyses clearly showed that TC has no negative effects on the investigated soil characteristics but provides similar effects compared to other carbon sources.

trace elements; carbon; agruculture

TotalQuant Technique - More than Semi-Quantitative Analysis

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TotalQuant (TQ) is a software feature unique to the NexION ICP-MS platform for quantifying 80 elements in a sample, in a single run, by heuristic interpretation of the complete mass spectrum. Measuring the full mass range requires only a couple of minutes and the spectral calculations itself takes just a few seconds. During the TotalQuant analysis, each element is assigned a response value (cps/ppm) which is updated when a calibration is performed.

Even though TotalQuant is an ideal tool for semiquantitative analysis during the method development, it can also be used for a final material characterization. Additionally, TotalQuant could be used as a tool for fingerprinting and a fast survey scan of unknown samples before quantitative analysis.

This poster will show variable applications of this versatile technique, called – TotalQuant.

ICP-MS, Software, Semi-Quant

Elemental analysis of brine samples used for lithium extraction

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Rapid expansion of the electric vehicle market is supercharging demand for lithium. Supply of lithium for lithium batteries can come from several different sources:

- Mining solid lithium minerals from the ground in the form of spodumene, lepidolite and petalite
- Pumping lithium-rich brine from underground aquifers
- Extracting lithium from seawater brines

The raw source of lithium needs to be purified through processing and refining as lithium batteries require high purity metals to maximize performance and lifetime. The refining and processing costs of lithium vary, depending on the level of contamination by the other elements. Elemental analysis is used to determine the contamination levels. This study used ICP-OES analysis to determine the elemental content of lithium-containing brines.

Elemental analysis of lithium brines can be challenging when using the ICP-OES technique, due to the level of Total Dissolved Solids (TDS), particulates and even algae that are sometimes present in samples. Appropriate selection of sample introduction system components, along with innovative automation accessories greatly assist with sample throughput, reduced routine maintenance, and longevity of instrument parts and consumables. Lithium brines have complex matrices and an unknown elemental profile. This sample complexity causes instrument calibration to be time consuming and there are often spectral interferences that need to be considered. In this study, a screening tool called IntelliQuant was used to gather insight into which elements were present, what spectral interferences there might be, and what the approximate concentrations of each element were. In the absence of a certified reference material for this matrix type, the accuracy of the method was confirmed by a spike recovery test. All recoveries were excellent, and the instrument displayed considerable measurement stability over time. This study demonstrates the suitability of this instrument and method for determining the elemental analysis of brine samples.

ICP-OES, lithium purity analysis, Lithium Battery, Spectral Interference

Agilent Technologies Inc., Application Note Mining, Energy and Chemicals. Elemental analysis of brine samples used of lithium extraction. Marc-Andre Gagnon. 5994-5149EN
What Are The Sources For Lithium? (ibatterymetals.com)

Assessing the purity grade of lithium carbonate and lithium hydroxide using ICP-OES and ICP-MS

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The global demand for lithium salts has dramatically increased in recent years due to the fast-developing market for lithium-ion batteries (LIB), specifically for the automotive industry. The two most important compounds in which lithium is traded are lithium carbonate (Li2CO3) and lithium hydroxide (LiOH).

ICP-OES is considered a key technology for analytical testing of battery materials as it can perform full multi-elemental analysis in a short time and is able to handle a wide variety of potential sample types.

ICP-OES enables the detection and quantification of impurities in concentration ranges between sub µg/L and % levels. Since batteries with better performance and longer life are required in the future, higher purity raw materials will be needed. In just a few years, many manufacturer's lithium salt purity requirements are likely to increase to 99.99% (or even higher), and this trend will probably continue for some time. This level of purity will challenge the current methods used for analysis, so that other analytical techniques, such as ICP-MS, will be required.

This poster will highlight how both techniques can be employed to determine impurities in both Li_2CO_3 as well as LiOH. In order to keep sample preparation at a minimum, a method was developed that allows the analysis of both compounds directly after dissolution in aqueous phase to a level of 0.5% (m/m). The method developed includes common impurities, such as alkali and alkaline earth elements, transition elements, heavy metals, and the lanthanide series elements. In total, 45 elements were analyzed using ICP-OES, whereas more than 60 analytes are included in the purity assessment using ICP-MS.

Lithium-ion batteries, LIB, ICP-OES, ICP-MS, purity assessment

Trace analysis of light naphtha samples using HR-array ICP-OES

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[1]Analytik Jena GmbH+Co. KG, Jena, Germany

Trace metal contaminants such as arsenic, mercury or silicon are known to seriously affect the performance and significantly reduce the lifetime of hydrotreatment catalysts. For example, different silicon species adsorb at the surface of the catalytic system causing its inactivation and its replacement representing a great economic loss. Therefore, monitoring potentially trace element impurities in incoming goods, process intermediates and final products down to the low µg/kg range is of great importance to refineries. The total content of these elements can be measured directly by inductively coupled plasma optical emission spectroscopy (ICP-OES).

The direct analysis of organic matrices is still challenging for ICP techniques. The high load and carbon content of organic mixtures require a robust sample introduction and plasma system, which reliably excites the samples within the ICP and does not suffer from carbon build-up at the torch system.

Here we present the application advantages for trace analysis in light naphtha samples originating from an ICP-OES instrument with high-resolution (HR) optics (2 pm @ 200 nm), intelligent torch design and high plasma robustness. Additionally, the benefits of the implementation of powerful software tools (ABC, CSI) for background correction and correction of spectral interferences are demonstrated.

HR ICP-OES, light naphtha, silicon, arsenic, mercury

LIBS-ICP-MS: An emerging technique for geologic imaging of traditionally challenging elements

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Over the last few years, collecting element maps to identify zoning or concentrations of fluid mobile elements in geologic samples via laser ablation ICP-MS has become increasingly popular due to new technologies that allow higher image resolution and faster analysis speeds (1). Understanding how elements are incorporated into mineral structures and the surrounding rock can provide information on a mineral's geologic history (2). Difficult to monitor elements like fluorine, which can show this zoning, are not able to be analyzed by ICP-MS. With the use of simultaneous laser induced breakdown spectroscopy (LIBS) and inductively coupled plasma mass spectrometry (ICP-MS), elements such as fluorine can now be analyzed providing important information related to elemental zoning while trace element data can be collected by LA-ICP-MS. When these two techniques are combined, the new method is referred to as LIBS-ICP-MS.

Here we observe the ability and benefits of simultaneous LIBS-ICP-MS to detect, identify, and map zoning and fluid mobile elements in geologic samples. These experiments were conducted with the imageGEOLIBS coupled with an Agilent 8900 ICP-MS. Simultaneous LIBS-ICP-MS collection allows the analysis of major elements (high ppm to wt.%) by LIBS that would normally be beyond the upper range of the ICP-MS detector. Further, by monitoring some elements by LIBS, the overall duty cycle of the ICP-MS is shortened, facilitating higher image resolution and faster analysis speed.

LA-ICP-MS, LIBS-ICP-MS

Van Malderen et al., J. Anal. At. Spectrom., 2016, 31, p. 423-439

H. Keppler, Am. Min., 2017, 102, p. 5-20

Determination of SARS-CoV-2 proteins by means bioassays based on ICP-MS detection

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The COVID-19 pandemic caused by the SARS-CoV-2 has infected more than 590 million people and caused nearly 6.5 million deaths worldwide (1). This health crisis has highlighted the need of novel methodologies for detecting and monitoring virus infections. The determination of SARS-CoV-2 is mainly based on RNA viral load by means real time polymerase chain reaction (RT-PCR), but it suffers from low sample throughput (2,3). Alternatively, virus detection could be achieved through the molecules present in viral envelope, such as the Spike or the Nucleocapsid proteins, via bioassays (either immunoassays or aptamer assays). Even though these methodologies are simpler and faster than RT-PCR, they suffer from poor sensitivity and high limits of detection (LoD). Over recent years, a significant number of works have shown the benefits of using inductively coupled plasma mass spectrometry (ICP-MS) as a highly sensitive detector for ultra-trace determination of molecules. Therefore, this work explores the use of ICP-MS for Spike and Nucleocapsid determination in bioassays. To this end, different sandwich-based bioassays have been developed using 40 nm streptavidin-modified gold nanoparticles (SA-AuNPs) as the element tag. The influence of the ICP-MS detection mode (conventional ion detection vs single particle mode) on the analytical figures of merit has been evaluated.

SARS-CoV-2, bioassay, nanoparticles, single particle, inductively coupled plasma mass spectrometry

WHO COVID-19 Dashboard. Geneva: World Health Organization, 2020. https://covid19.who.int/ (08/26/2022)

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Closed-vessel thermally convective wet digestion: a reliable sample preparation approach for trace analysis

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This work presents a new digestion system for sample preparation of organic matrices aiming at ICP OES and ICP-MS analysis. It is versatile and combines the simplicity of the heating block with the key advantages inherent to closed vessels1, wherein 24 samples can be simultaneously digested using 45 mL quartz tubes sealed with PTFE lids, equipped with breakable disks (> 20 bar), in a resistively-heated aluminum block. Pressure and temperature of liquid phase were measured during the digestion process. Digestion procedure was optimized for 250 mg of coffee powder by varying the volumes of concentrated HNO3 (1 to 2.5 mL) and 30 % v/v H2O2 (0.5 to 1.5 mL), and temperature (220 to 240 °C). Heating rate was 10 °C min-1 and dwell time was 20 min. After digestion, quartz tubes were automatically removed from the block and cooled to 60 °C in 10 min. Lowest residual carbon content (600 mg L-1) and pressure < 15 bar was achieved when 2.0 mL HNO3 and 1.5 mL H2O2 were used, at 240 °C. The temperature of the liquid phase (190 °C) was lower than the temperature of the aluminum block (240 °C) due to dynamic condensation of the gaseous phase during digestion. The optimized procedure was applied for the digestion of certified reference materials (CRMs) of plants (SRM 1570a, 1547, 1573a and 1575a), animal tissues (SRM 8414, 1577b and BCR 186) and milk (SRM 8435 and 1549). The concentrations of Al, B, C, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn were determined by ICP OES (Thermo iCap-7000), and the concentrations of As, Cd, Cr, Mo, Pb and Se were determined by ICP-MS (Agilent-8800). In general, all CRMs presented no significant differences between the determined and the certified analytes concentrations, at 95% confidence level. Recoveries varied from 75 and 108%, and coefficients of variation of measurements (n = 3) were < 3 % for Al, B, C, Ca, Cu, Fe, K, Mg, Mn, P, S, and Zn, and < 6 % for As, Cd, Cr, Mo, Pb and Se. The proposed digestion system based on thermally convective wet digestion in closed-vessels is a reliable alternative for sample preparation of organic samples for ICP OES and ICP-MS analysis, being able to simultaneously digest 24 samples in only 50 min.

Sample preparation, acid digestion, closed vessels, organic samples, ICP OES, ICP-MS

Miranda et al. J. Anal. At. Spectrom.,2014, 29, 825.

Active and passive tracing of non-metallic inclusions in steel using rare earth elements

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Non-metallic inclusions can have considerable negative effects on both the physical properties and corrosion resistance of steels. In addition, the build-up of clogging, i.e. the aggregation of non-metallic particles especially at the nozzle, can further reduce steel quality or even interrupt the steel casting process. In order to improve steel cleanness, a better understanding on the formation of non-metallic inclusions during steel casting is required. Within the present study, two approaches for tracing the formation of non-metallic inclusions and clogging in titanium alloyed ultra-low carbon (Ti-ULC) steel based on rare earth elements (REE) are followed:

In the passive tracing approach, variations in the distribution patterns of REE of the samples are used as chemical fingerprints. REE fingerprints are determined by means of ICP-MS and laser ablation ICP-MS. REE patterns in samples of clogging material are compared to those of reference samples of alloying elements, auxiliary materials and refractory lining used in the casting process. As a consequence, materials likely contributing to the formation of the clogging material can be identified.

For active tracing, individual REE, namely La or Ce, are added to the steel melt on an industrial scale. Because of their high oxygen affinity, these elements tend to react with oxides present in the steel, which subsequently form inclusions or clogging, or migrate into the slag layer on top of the steel melt. Samples of steel and slag are taken at different stages of the casting process and analysed using ICP-MS and XRF, respectively. By means of SEM/EDS, La and Ce can also be detected in the clogging layer deposited at the nozzle, as well as in individual inclusions in the steel samples. Therefore, the spatial and temporal distribution behaviour of REE in the steel-slag-inclusion system can be tracked.

The results gained using both approaches consistently link the clogging material formed in the nozzle to aluminium oxide particles formed during the deoxidation step, when the steel melt is treated with aluminium metal. They indicate that agglomeration of these particles is the main reason for clogging during the Ti-ULC steel casting process.

steel, inclusions, clogging, rare earth elements, Sr isotopes, laser ablation ICP-MS

In situ U-Pb carbonate dating by fs-LA-ICP-MS imaging combined with a virtual spot approach data treatment.

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[1]UPPA - E2SUPPA - UPPATech, Pau, France, [2]UPPA - E2S UPPA - CNRS - Total - LFCR, Pau, France, [3]UPPA - E2S UPPA - CNRS - IPREM, Pau, France

Although U-Pb dating by LA-ICP-MS begun in the early 2010's, the use of imaging to date calcite samples has only appeared in 2018 with the paper from Drost et al. (Geochemistry, Geophysics, Geosystems, 2018, 19, 4631–4648 https://doi.org/10.1029/2018GC007850). This approach allows identifying areas of interest (rich in U) as well as impurities that has to be discarded. The dating is then based on extracting the age from LA-ICP-MS mapping using different pixel selection or subsets.

Here, we present a simple approach for the U-Pb dating of carbonate minerals from isotopic maps, benefiting from the use of a high repetition rate femtosecond laser ablation system (Lambda3, NEXEYA, Bordeaux, France) coupled to a sector field inductively coupled plasma mass spectrometer (SF-ICP-MS) Element XR (Thermo Fisher Scientific, Bremen, Germany) fitted with the Jet Interface. The isotopic ratio maps are built from linear scans, which ablation depth are of ~20 µm, therefore suitable for the analysis of thin sections. 238U, 232Th, 208Pb, 207Pb and 206Pb are recorded on the sample, NIST614 and WC-1 by LA-ICP-MS mapping. Normalization is made by sample standard bracketing using NIST614 for 207Pb/206Pb ratio and WC-1 calcite for correction of 238U/206Pb ratios, using the Iolite 4 software. The isotopic maps are then discretized into squares using a python script. The squares correspond to virtual spots ("virtual spots") of chosen side length, for which the mean and its uncertainty are determined, allowing to calculate ages with commonly used concordia diagrams. The major interest of this approach is that the size, and thus the number of virtual spots can be easily adapted after the analysis. A low size will result in higher uncertainty of individual spots, but their higher number and potentially larger spread along the isochron can result in a more precise age. We will present examples of the approach, for which in the most favorable cases (U > 1 ppm, 238U/206Pb >> 1, and highly variable U/Pb ratios) a reliable age may be obtained from images as small as 100 µm x 100 µm.

dating - LA-ICPMS - imaging - geochemistry - calcite

A novel combination of ICP-TOF-MS beam attenuation and encoder laser triggering to map elements between 100% and sub-ppm levels at high repetition rates

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In situ techniques based on Laser Ablation and Inductive Coupled Plasma Mass Spectrometry (LA-ICP-MS) have been rapidly evolved into well-established, powerful tools for direct analysis of solid samples.

Recent advances in laser ablation have allowed for particulate plumes from each laser shot to be efficiently transported to the detection system with minimal diffusion, enabling a clear differentiation of each shot at very high ablation rates. Furthermore, integration of advance stage technology that facilitates the referencing of the position of each spot is now sufficiently accurate that individual shots from multiple ablation passes will occur in the exact same location, even at kHz ablation rates.

Fully leveraging these advances requires a new type of detector. Sequential scanning mass spectrometers are unable to scan more than one or two ions during such rapid events, and efforts to do so result in aliasing effects and pixel lag that cannot be resolved through data reduction. A fast-scanning TOF detector solves these issues by detecting the entire mass spectrum quasi-simultaneously at spectral accumulation times in the sub-millisecond range. Data will be shown which demonstrate high speed LA-ICP-TOF-MS at high lateral resolution with full elemental coverage.

We also demonstrate that the potential issue of limited dynamic range of a TOF-ICP-MS can be resolved using beam attenuation and encoder triggering of stage movements to enable a novel technique which can create maps showing elements between 100% and sub-ppm levels in a single image.

ICP-TOF-MS, Laser Ablation, Imaging, High-Speed

Proving the capabilities of Laser Ablation ICP-TOF-MS data at speeds up to 1kHz

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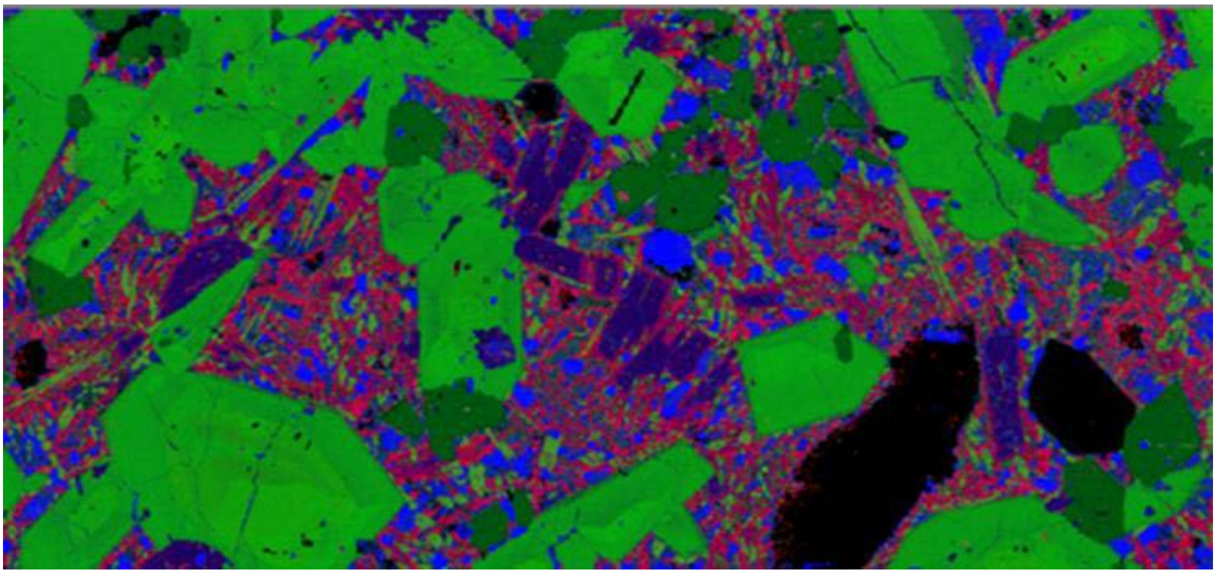
In recent years, commercially available Excimer laser ablation systems (193nm) have evolved into robust high repetition rate systems able to fully transport sample aerosol from point of ablation in the sample chamber to analytical detection in the ICP in times as short as a single millisecond [1]. A recent sample chamber design has now been proven to operate at high duty cycles with laser repetition rates of between 1 Hz and 1000 Hz without compromising data quality in any way [2]. Unfortunately, such high speeds are outside of the typical operating regime demanded by the traditional quadrupole based ICP-MS systems, where the Single Pulse Response (SPR) may dictate the acquisition of a sole isotope unless a multiple-dosage approach is used [3]. To fully evaluate the analytical capabilities of systems operating up to 1kHz a pseudo-simultaneous ICP-TOF-MS setup is required. This work presents preliminary data generated using a 1kHz Teledyne Photon Machines Iridia laser ablation system coupled to a Nu Instruments Vitesse ICP-TOF-MS and demonstrates the performance advantages such technology can provide.



Laser Ablation, Time-of-Flight, 1kHz

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Van Acker et al 2021, J. Anal. At. Spectrom. DOI: 10.1039/D1JA00110H

Šala et al. 2021. J. Anal. At. Spectrom. https://doi.org/10.1039/d0ja00381f

LA-ICP-TOFMS imaging reveals spatial distribution of platinum compounds in mouse organs and tumor tissue at the single cell level

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Laser ablation (LA) in combination with ICP-TOFMShas become a powerful imaging tool to detect endogenous elements as well as metal-based anticancer drugs (Pt, Ru…) or elements (rare earth elements) from metal-labeled antibodies. Therefore, the technique provides promising applications in cancer research, proteomics, metallomics and in the medical sector.

LA-ICP-TOFMS with a resolution down to 1 µm was used to image tumor tissue and organs of colon cancer bearing mice treated with oxaliplatin or a novel analogous platinum(IV) compound. The platinum distribution in the tissue sections was quantified at the single-cell level using gelatin-based micro-droplet standards spiked with elemental standard solutions [1]. The quantitative platinum uptake was compared between the different treatments and mouse tissue samples.

Furthermore, metal-labeled antibodies were used to stain the tissue sections with functional and structural markers, including markers for DNA damage, proliferation, collagen and alpha smooth muscle actin. The use of metal-conjugated antibodies allowed characterizing the tumor microenvironment and visualization of the platinum uptake in different cell types and regions of interest within the tumor tissue and organ samples.

2D imaging, Laser ablation, ICP-TOFMS, metallomics

Schweikert et.al., Anal. Bioanal. Chem., 2022, 414, 485-495.

Multimodal mass spectrometry imaging of key biomarkers to study age-related macular degeneration

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Essential and non-essential trace metals alongside proteins associated with the innate immune system are associated with age-related macular degeneration (AMD). Determining the distribution of metals within the ocular tissue, and mapping metal accumulation in the elderly is important to understand the association between dysregulation and AMD onset. Additionally, determining the location of innate immune receptors thought to be involved in disease pathogenesis is important when assessing how best to target these receptors. Here characterisation of metal species in mouse retinal degeneration models was conducted using an ImageBio266 (Elemental Scientific Lasers, Bozeman, CA, USA) operating at 10µm spatial resolution, coupled to a NexION 350x ICP-MS (Perkin Elmer, Manchester UK). Proteomic data was acquired using a SELECT SERIES MRT MALDI-MS (Waters Corporation, Manchester, UK) at a mass resolution of 200,000 FWHM. LA-ICP-MS has been used to characterize accumulation of both essential and non-essential metals within mouse ocular tissues, both in WT mice and retinal degeneration models utilizing high resolution mass spectrometry to determine spatial distribution of key trace metals within the mouse chorio-retinal microanatomy. Additionally, MALDI-MS has exhibited the distribution of NLRP3 and associated innate immune proteins in mouse and humanretinal tissue. This study exhibits the capabilities of multimodal MSI, and how ICP-MSI and MALDI-MSI have potential to inform on unknown biological mechanisms of retinal degeneration.

LA-ICP-MS, Mulimodal, Imaging, Age-related Macular Degeneration

Ozaki et.al., Life science alliance, 2020, 3

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The Age-Related Eye Disease Study Research Group, The Journal of nutrition, 2002, 132,

LA-ICP-MS as a new tool for neuroscience research

Olga Minaeva[1,2,3], Ning Hua[1,2], Nicola Lupoli[2], Madeline Uretsky[2], Victor E. Alvarez[2,4], Juliet A. Moncaster[1,2,3], Lee E. Goldstein[1,2,3,5]

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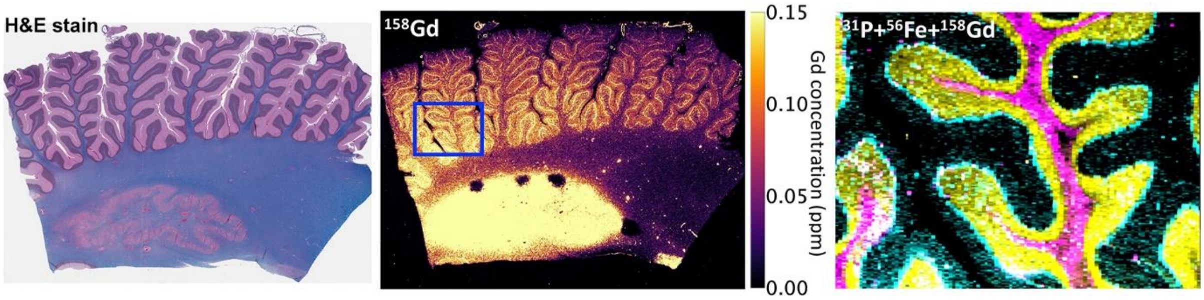
LA-ICP-MS imaging enables precise anatomical localization and ultra-trace elemental quantitation in brains from humans and laboratory animals. We studied regional distribution and retention of gadolinium in rat and human brains after exposure to intravenous gadolinium-based contrast agents (GBCAs). Despite a series of recent studies [1-3], little is known regarding the mechanism of gadolinium deposition in the brain. Here we used the laser ablation system (LSX-213, Teledyne CETAC Technologies) coupled to a quadrupole inductively-coupled plasma mass spectrometer (iCAP-Q, Thermo Fisher Scientific). The samples were scanned line by line with the following scan parameters: spot size – 50 µm, line gap – 0 µm, scan speed – 100 µm/s. Calibrations were performed with 10% gelatin standards. Iron, phosphorus, zinc and other relevant maps were generated in the same scan. Hematoxylin and eosin (H&E) staining was performed on adjacent slides for both human and rat brains [3]. We observed prolonged gadolinium retention in human brains that lasts years after GBCA injection. We showed that Gd retention colocalized with iron enrichment in some brain regions. These results provide new information regarding likely mechanisms by which Gd is transported, distributed, and retained in the brain.



laser ablation, bioimaging, brain, gadolinium

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Fast, high-resolution full elemental laser ablation imaging using time-of-flight ICP-MS for endogenous metal analysis and label identification in biological samples

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Assessing the elemental composition of biological samples is valuable for aiding interpretation and diagnostics in human health. With increasing analytical capabilities elemental bioimaging of prepared thin sections is becoming more routine. Using the newest laser ablation techniques single bursts of data can be generated in a matter of a few milliseconds. This progression in laser technology requires fast detection systems capable of acquiring data on multiple elements. Since several endogenous isotopes and exposures to exogenous materials have been shown to be important in health, analysis of many elements is often required. Therefore, a TOF-ICP-MS becomes an important part of a modern LA-ICP-MS system for elemental bioimaging.

The ability of the Nu Vitesse to record transient full mass spectra in sub-millisecond dwell times enables the full potential of the Teledyne Iridia laser ablation system to create large images at high resolutions at unprecedented rates. Furthermore, the full elemental detection and interference removal capabilities enable the analysis of endogenous elements as well as higher mass isotopes often used as markers to further understand the interactions between metals and biological processes.

Data will be presented showing the latest images of a variety of biological materials highlighting the speed, resolution and sensitivity for many elements. Data reduction can be achieved during acquisition for the live viewing of images using python scripts in the NuQuant software. More detailed analysis in other third-party software packages such as HDIP is also possible though flexible live export formats which will presented. Spot sizes down to single figure micron were achieved while ablating areas of multiple square millimetres due to kilohertz ablation rates and sub-millisecond data acquisition times. This allows an in-depth examination of endogenous elements for detailed analysis of the metabolome of biological samples on a cellular level. In addition, data will be presented showing the feasibility of using antibody conjugated lanthanides to identify a range of biological epitopes showing the versatility of the instrument.

LA-ICP-MS, High repetition rate, TOF-ICP-MS, Bioimaging

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

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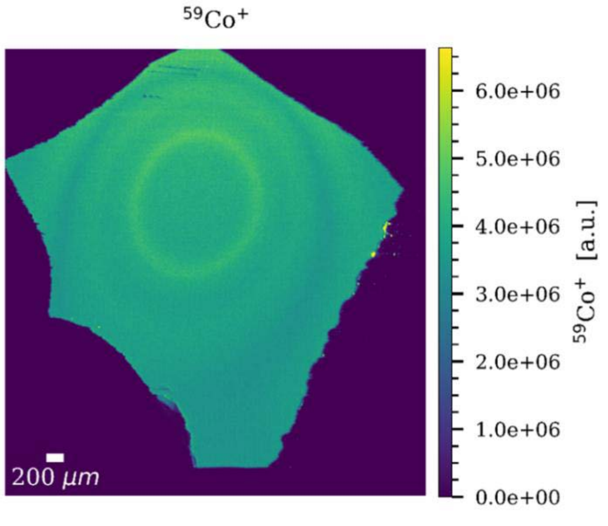
[1]Teledyne Photon Machines, Bozeman, United States, [2]Museum of Dacian & Roman Civilisation, Deva, Romania, [3]Quantel Lumibird, Bozeman, United States, [4]Terra Analytic SRL, Alba Iulia, Romania

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, mostauthors viewed glass vessels as imported luxury goods originating from the Mediterranean Basin from between the 2nd century BC and 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; the area of manufacture; and details regarding the production technique of the vessels. We use LA ICP MS elemental imaging to document chemical heterogeneities in the samples which we believe are closely linked to the manufacturing techniques. We also asses the usefulness of single spot bulk analysis how representative this approach is regarding the chemical composition of the glass.



archaeological glass, laser ablation ICP-MS, imaging

Single particle inductively coupled plasma mass spectrometry imaging of immunochemically labeled spheroid sections

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Spheroids are one of the 3D biological models whose arrangement of proliferating and necrotic cells resembles the tumor microenvironment. One of the markers of proliferation is Ki-67 protein, which is expressed by cells in the active phase of the cell cycle. Immunohistochemical labeling with a primary antibody and a fluorophore-labeled secondary antibody followed by fluorescence microscopy analysis is commonly used for two- and three-dimensional imaging of the target protein in spheroid sections.

We have successfully switched from fluorophore labeling of KI-67 to nanoparticle labeling combined with

LA ICP MS. Recently, gold nanoparticles were used as very sensitive immunochemical tags in conventional UV laser ablation ICP MSI.1 In our approach 20-nm gold nanoparticles tags were desorbed from the spheroid section with 2940 nm laser ablation system. In comparison to UV, IR laser allows tissue ablation and desorption of intact nanoparticle tags, allowing their precise counting leading to high sensitivity. Finally, our technique is compared to mainstream imaging techniques such as confocal fluorescence microscopy or UV LA ICP MS.

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imaging, nanoparticle, single particle, SP ICP MS, LA ICP MS, laser ablation

Tvrdonova et.al., Anal Bioanal Chem 411, 559–564 (2019).

Advances in batch image calibration and phase segmentation

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Software tools in the field of elemental mapping via LA-ICP-MS have greatly improved in the last decade with regards to their data reduction, image reconstruction and image analysis toolkits. Technical advances, such as low-dispersion aerosol transport systems have dramatically increased mapping throughput, allowing multiple megapixel maps to be recorded during a single measurement session, or dozens of smaller maps[1]. Premium data reduction solutions, such as HDIP (v1.7.4+, Teledyne Photon Machines, Bozeman, MT, USA)[2], have improved to allow parallel batch processing of hundreds of samples and maps. Also, the process of calibration has been significantly refined, and approaches such as drift correction, multiple reference materials, matrix-specific calibration and sum normalization are applied by default. Applying these calibration approaches for a batch of maps requires a high level of automation, especially when the mapped areas contain multiple matrix types, which are dispersed within. Each of these matrix types is characterized by a different ablation rate and fractionation behavior; this is often the case for polyphase mineral aggregates or biological specimen.[3]

In this presentation, software tools within HDIP are presented to tackle this challenge, including, but not limited to a json template system to automatically segment images based on a set of rules, segmentation via multi-modal techniques such as optical microscopy linked to the elemental map via image registration, and a calibration tool to perform sum normalization for multiple segments of multiple images, supported by a system to automatically assign matrix compositions to each segment. Furthermore, image feature recognition will be discussed, focused on single cell and zircon grain identification and localization, which is linked to the segmentation approaches mentioned above.

Imaging, Calibration, Image processing, HDIP, software, LA, Laser ablation

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Recognition of proteins using metal-based nanoparticles

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Immunochemical methods are widely used in biochemical research and clinical diagnostics. Commonly used methods are often limited to the analysis of no more than three antigens.Nanotechnologies, more specifically nanoparticles, represent a modern solution. Thanks to their excellently diverse, physico-chemical properties, nanoparticles are used in tumour diagnostics, in the detection and manipulation of biological structures, but also in improving the distribution of biomolecules and drugs in vivo. Therefore, combining the properties of selected nanoparticles with the specificity of antibodies to recognize antigen represents a promising diagnostic and imaging tool.

The work aimed to create conjugates of antibodies with gold and silver nanoparticles with a size of 10 and 60-nanometer and apply them in multiplex analysis to detect model antigene standards. The functionality of the conjugates was verified by dot-blot. Visualization was performed using laser ablation line scans with ICP-MS.

The experimental part shows that the binding, between the antibody and the metal nanoparticle, conjugate, does not impair its ability to recognize and bind antigen. A direct relationship between the size of the nanoparticle used and the intensity of the measured signal was also found. Also, 10-nanometer nanoparticles appeared to function more reliably than 60-nanometer nanoparticles. The data confirm the assumptions for the future use of 10-nanometer nanoparticles in clinical imaging.

gold nanoparticle, silver nanoparticle, protein recognition

Vlcnovska et.al., Molecules 2021, 26 (3), 11

Influence of laser fluence and beam size on aerosol formation and effect on precision in LA-ICP-MS analysis

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In the last few years, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has undergone some major developments, leading to higher resolution, improved sensitivity, and reduction of analysis time. Despite the recent advances, LA-ICP-MS's quantitative capabilities and accurate analysis still continue to present a challenge. Thus, acceptable elemental quantification is constrained to matrix-matched matrices and appropriate internal standards.[1] Additionally, uncertainties related to laser fluence and beam size via various ablation cells and interfaces also affect the precision of the LA-ICP-MS work, and therefore make quantification even more demanding.[2] This work focuses on investigating the influence of fluence, beam size and aerosol transport set up on signal pulse behavior, noise characteristics and laser ablation spot volumes, for a series of elements (Gd, As, La, Ni, Te and Zn), concentrations (between 10 and 1000 μg g−1), and matrices (NIST SRM 612 and in-house prepared gelatin standards). Furthermore, the phenomena of double peaks was observed and further studied with in line filters and cryotrapping. The findings showcase that a selection of appropriate operational conditions depend on the interface between LA and ICP-MS. As such, a laser fluence just above the ablation threshold of the material under study is crucial to prevent excessive Flicker and Poisson noise, and for achieving reliable quantification, maximum sensitivity, as well as to avoid formation of double peaks in single pulses.[3]

laser ablation, mass spectrometry, fluence, beam size, SPR

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Hexagonal sampling – a free upgrade in LA-ICP-MS imaging resolution?

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We present a theoretical exploration of the application of hexagonal sampling to Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) imaging. Hexagonal sampling is a technique that has been widely used in fields such as geology, mineral exploration, agriculture, and meteorology to improve the spatial resolution and sampling efficiency[1–3].

We suggests that hexagonal sampling could be a powerful tool for improving the spatial resolution of LA-ICP-MS imaging, by taking advantage of the higher packing density of hexagonal grids, which allows for a greater number of sampling points in a given area. Additionally, hexagonal sampling can better mimic the natural distribution of many physical systems, reduce the occurrence of "holes" in the sampling pattern, and reduce the problem of anisotropy (directional bias) that is present in rectangular sampling, as the hexagonal grid is rotationally symmetric. The results of simulations comparing the resolution of rectangular and hexagonal sampling are presented in images below. We believe that the implementation of hexagonal sampling in LA-ICP-MS imaging represents a free upgrade in resolution, which can be easily achieved with minimal changes to existing experimental setups

hexagonal sampling, laser ablation, simulation, spatial resolution

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High-precision Selenium isotopic analysis: a novel approach for diagnosing/prognosing neurological disorders?

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Neurological disorders (NDs) have become increasingly widespread and are expected to further rise as the population ages. They are associated with increased oxidative stress linked to the production of reactive oxygen species (ROS), which alter the cell functions. Investigation of biomarkers of NDs at an early stage and not requiring invasive sampling is becoming crucial. In this context, Selenium (Se) is an element of interest as it is a constituent of biomolecules and participates in many biochemical functions, mainly the antioxidant defense of the body[1].

The aim of this work is to develop an analytical method for high-precision isotopic analysis of Se in biofluids, including cerebrospinal fluid (CSF), in order to determine its potential in the diagnosis/prognosis of NDs. Multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) is used as it allows the measurement of very small deviations in the Se isotopic composition with high precision. However, ICP-MS Se measurement is challenging as this element suffers from several spectral and non-spectral (matrix-induced) interferences. Therefore, the primary step consists of the isolation of the target element prior to its isotopic analysis using MC-ICP-MS. Few purification methods have been described in the literature, the main ones involve the isolation of Se from matrix elements for geological samples using a combination of anion and cation exchange chromatography[2] or using in-house prepared or commercially available thiol cellulose powder (TCP)[3]. However, none of the published studies describe the purification of Se from matrix element in biological samples prior to isotopic analysis in the context of our study.

In this work, several chromatographic isolation methods were tested and compared for purification of Se from biological matrixes. Furthermore, Se speciation was controlled using HPLC-ICP-MS/MS prior to the chromatographic isolation to avoid any potential isotopic fractionation. The following step will focus on the set-up of MC-ICP-MS sample introduction using hydride generation, which helps in the elimination of residual matrix elements and improves the precision of the Se isotope ratio data.

Selenium, isotopic analysis, neurological disorders, multi-collector ICP-MS

Loef et.al., J. Alzheimer's Dis. 26 (2011), 81-104

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Study of the protective role of Zn in an in vitro cell culture subjected to pro-inflammatory conditions

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Retina and retinal pigment epithelium (RPE) aging lead to uncontrolled inflammation processes, resulting in cell damage and the onset of ocular disorders, such as Age-related macular degeneration (AMD) [1,2]. These processes may be accompanied by elemental and/or isotopic homeostatic alterations of metals involved in retinal functions, such as Zn, which plays a pivotal role in phototransduction and neurotrasmission processes. In this context, the study of isotope fractionation in in vitro cell culture models has provided valuable information for unraveling biochemical processes. On the other hand, these Zn fluctuations are mediated by metallothioneins and Zn transporters, both expressed by RPE cells, suggesting that an insight in transcriptomics would help to understand the biochemical processes involved in the development of neurodegenerative diseases.

In this context, we aim at investigating the response to an inflammatory process in an in vitro human retinal pigment epithelial cell culture. For that purpose, RPE cells were subjected to pro-inflammatory conditions by means of Interleukin-1alpha supplementation. The effects of such exposure were tackled by transcriptomics and isotopic analysis, and compared to cells also supplemented with Zn. The results showed that these processes responded to inflammation at both RNA and isotopic levels, by inducing immune and cytokine responses and leading to a lighter Zn isotopic composition. Interestingly, this inflammation was partially attenuated by short-term Zn supplementation.

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Transcriptomics, Isotopic analysis, Cell culture, Inflammation processes

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Kauppinen et. al., Cell. Mol. Life Sci., 2016, 73(9), 1765-1786

Expanding the capabilities of a single-quadrupole ICP-MS for lead and strontium isotopic analysis of polar samples

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In many environmental studies, the determination of trace elements and their isotopic composition can provide valuable information on the geographical sources of both natural and anthropogenic inputs, the relative contributions of these sources over time and the corresponding transport routes. In fact, Pb shows pronounced variation in its isotopic composition because three out of its four isotopes, ^{206}Pb, ^{207}Pb and ^{208}Pb, are the stable end products of the decay chains of ^{238}U, ^{235}U and ^{232}Th, respectively. Therefore, there are relatively large differences in the isotopic ratios for crustal and ore Pb deriving from various locations. Contrary to Pb, Sr is typically of natural origin; however, since ^{87}Sr is produced via the β-decay of ^{87}Rb, natural variations of ^{87}Sr/^{86}Sr in rocks occur, and the determination of this isotope ratio can be used for tracing the geographical sources of mineral dust. In addition, the elemental profile of a sample can help distinguish the various sources, mainly when data are processed by multivariate analysis techniques.

The elemental and isotopic analysis of environmental samples collected from polar regions is, however, quite challenging, due to the low analytical concentration, matrix effects, risk of contamination and the limited sample size.

Accurate and precise determination of Pb and Sr isotope ratios in environmental samples coming from polar regions has been obtained by inductively coupled plasma mass spectrometry (ICP-MS). The following relevant parameters have been taken into account: quadrupole and cell rod offsets, cell path voltage, sample uptake rate and spray chamber temperature, along with acquisition parameters such as dwell time and number of sweeps. The optimizations have been performed in a multivariate way, by applying different suitable experimental designs.

The obtained methods have been characterized in terms of working range, precision, accuracy, and robustness, proving to be adequate to the analytical tasks. It was also possible to perform a satisfactory determination of ^{204}Pb, generally not achieved by ICP-QMS for these purposes. Finally, they have been successfully applied to the analysis of real polar samples in the context of the Italian Arctic Research Program and National Research Program in Antarctica.

isotopic analysis, lead, strontium, ICP-MS, Arctic, Antarctica

Development of a new analytical strategy to determine the Hg isotopic composition in gold materials

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Mercury (Hg) is still widely used for gold extraction in artisanal and small-scale gold mines: to extract it from a lode ore or a gold-bearing sand, miners often resort to amalgamation, which consists of adding Hg. However, Hg can also be present in gold naturally (up to 800 ppm in gold-silver deposits[1]), and therefore linked to the gold deposit and its geological origin.

Hg isotopes are usually used to discriminate the origin of Hg and allows a better understanding of its biogeochemical cycle in the environment. Many factors control Hg isotopes fractionation in the environment such as biological, photoreduction processes… leading to a specific isotopic composition in the final product. This fingerprint could be used to track Hg naturally present in gold deposit from Hg used during gold extraction/amalgamation.

The aim of this work was to develop a reliable sample preparation methodology to separate quantitively Hg from Au prior to isotopic analysis. Hg isotopic composition can be determined by cold vapor generation (CVG) hyphenated to a multi-collector plasma induced mass spectrometer (MC-ICP-MS). The measure consists in a redox reaction between Hg and tin (Sn) to produce gaseous Hg which allows to reduce the matrix effects during the analysis. Direct measurements of Hg standard (NIST 3133) by CVG/MC-ICP-MS in the presence of gold (Au) leaded to signal suppression and Hg isotopic fractionation correlated to Au concentration due to its high reactivity with Hg. Thus, several strategies to separate Au from Hg were explored.After acid digestion of the gold material with aqua regia ($2HCl:1HNO_3$), the Hg extraction from the matrix is divided into two steps. The first one is a redox reaction between Au and Sn to form a precipitate of gold nano-particles (Purple of Cassius). This critical step depends on the Au/Hg ratio. Excess of Sn can generate gaseous Hg leading to Hg isotopic fractionation. The second step is the volatilization of Hg from the matrix by purge and trap method adapted from Zheng et al., 2009[2]. Recoveries obtained on Hg standards and gold samples with different Au/Hg ratios are close to 100%, suggesting that Hg is quantitatively recovered. Accurate Hg isotopes measurements in gold samples have been achieved with a precision down to 0.15‰ (as 2SD) for δ^{202}Hg.

Gold mining, Hg isotopes, MC-ICP-MS

Nikolaeva et al., 2013, Geology of Ore Deposits, 2013, 55(3), 176–184

Zheng et al., Journal of Analytical Atomic Spectrometry, 2007, 22(9), 1097-1104

Mercury isotope measurement method in samples with low mercury concentration using MC-ICP-MS

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Currently, the majority of the Hg isotope measurement methods on Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) require at least 0.5 ng/mL of Hg in the solution. This can be problematic to achieve in samples with low Hg concentrations. Therefore, a preconcentration of the sample with a lower concentration of Hg to a solution of lower volume is needed.

The method tested in involved the digestion of samples in a microwave digestion system followed by transfer of the digestate to a bubbler containing 10 ml of 10 % (w/v) SnCl2. The bubbler was then purged for 30 min into a trapping solution of 2.25 ml of HNO_3/HCl (3/1 v/v) acid mixture. The trapping solution was subsequently diluted to 15 ml making the acid concentration around 10 % which was optimal for the subsequent measurement on MC-ICP-MS. The mass balance was tested using ^{197}Hg radiotracer with both pure reagents and spiked tree leaf matrix. The average recovery in pure reagent solution having 10 % (w/v) $SnCl_2$ and 10 % (v/v) HNO3 (suprapur) was 98.9 % (± 1.8 % 2SD) whereas, recoveries were 100.8 % (± 4.0 % 2SD) for the spiked tree leaf matrix. The tests on MC-ICP-MS showed a relatively low fractionation of 0.08 ‰ (± 0.07 ‰ 2SD) for ^{202}Hg with no significant mass-independent fractionation.

The method proposed here is a relatively simple and robust way to prepare Hg samples for subsequent MC-ICP-MS analysis which has been shown to work even for complex biological matrices.

Multi-Collector-ICP-MS, Preconcentrating, Mercury, Digestion, Isotopes, Biological matrices

High precison measurements of lead isotope ratio

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The phenomenon of isotope fractionation consists of the relative division of different isotopes of a given element between two coexisting phases. As the consequence, the diversification of the isotopic composition of objects occurs. The performance of high-resolution mass spectrometry, e.g. multi-collector ICP-MS made it possible to quantify these subtle differences, thus characterizing various processes taking place in nature.

In general, isotopic measurements by MC-ICP-MS requires perfect sample purification. The used protocols are usually time-consuming, and due to the risk of contamination, require clean lab conditions. Bypassing the purification steps, accompanied by the well-fitted calibration strategy is currently one of the most important directions in the development of isotope research.

In the presented work, we compared the Optimized Regression Model (ORM) and Internal Standard (IS) methodology, with the use of Tl as an internal standard, for the measuring of isotope ratios of lead in the heavy matrix without sample purification. We have developed measurement approaches designed to the specific type of sample, using model samples with decreasing analyte to matrix elements ratio. We optimized analytical conditions, e.g. background correction method, the analyte to standard ratio, total dissolved salts level, etc. We evaluated the maximum concentrations of chosen interferents at which the calibration methods ceases to be effective to give accurate results.

Finally, we applied the developed measurement protocols to selected samples with the known (literature data) isotope ratio of lead. We have made every effort to ensure that the range of sample diversity is as wide as possible: archaeological objects (bronzes), pieces of works of art (pigments), geological objects (granite G-2), street dust (NIST 1648), and last but not least oceanic water (NASS-4) spiked with Pb. For any of the samples mentioned, neither purification nor isolation of Pb was applied. Finally, we demonstrated the validity of the simplified protocols for the isotopic ratio measurements with expected accuracy and precision.

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isotopic ratio measurements, ORM calibration, Internal Standard, Pb isotopic ratio

Use of lead isotope composition for source tracing of air particulate matter from upper Meža Valley

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Lead (Pb) isotope composition provides valuable insights into the origin of Pb within a sample, typically allowing for reliable fingerprinting of its source. In the present study, Pb concentration and isotope composition in the air particulate matter, collected in the upper Meža Valley, was used for source appointment.

In the upper Meža Valley lies the largest lead (Pb) and zinc (Zn) ore deposit in Slovenia with a long history of mining and processing of ore. As a consequence, the upper Meža Valley is excessively polluted with Pb, Zn and other potentially toxic elements (PTE). In addition to high concentrations of PTE in the soil, residents of the area are also exposed to these elements daily through dust, mainly via inhalation and ingestion of dust particles. As a consequence, elevated levels of PTE, particularly Pb, were observed in children’s blood (1, 2). Analysis of particulate matter (PM10) for their PTE content in the upper Meža Valley has been carried out since 2007, as part of the Ordinance on areas of maximum environmental impact and on the program of measures to improve the quality of the environment. Regular human biomonitoring campaigns have been carried out since 1976, following the concentrations of Pb in the blood of the upper Meža Valley inhabitants.

After the closure of the mine and smelter, and the introduction of remedial measures, the burden on both the environment and people started to decrease. In the last few years, however, Pb levels in the blood, especially that of small children, and concentrations of Pb and other PTE in the dust particles started to stagnate or even grow. As the focus of previous studies in the upper Meža Valley was mostly on the load of the environment with Pb and its distribution in different environmental compartments, in the present study we aimed at Pb source appointment by the use of its isotope composition. The results indicated a possible new source of Pb in the valley.

Pb isotope composition, air PM10 particles, upper Meža Valley

Ivartnik et al., NIJZ OE Ravne, 2019.

Jež & Leštan, Hazard. Mater., 2015, 296, 138-146.

Elemental and isotopic analysis of dust for authentication of historic manuscripts

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Dust is an indicator of the time and place where a certain manuscript was made. A team of the University for Continuing Education Krems and Montanuniversität Leoben received the permission to collect dust from early documents from the Abbies Kremsmünster and Zwettl, both located in Austria. Dust samples were analyzed for their elemental composition as well as strontium isotope ratio signatures as intrinsic indicators to study the authenticity and origin of historical parchment and paper documents dated back to the 12th (Kremsmünster) and 17th (Zwettl) century, respectively. Both authentic samples from documents as well as samples from the abbies in undisturbed locations were taken in order to investigate the potential of pattern comparison between these abbies and between dust deposited in books as compared to the local surroundings inside the abbies. Particular focus was set on tracer elemental ratios such as Sr/Ca and 87Sr/86Sr isotope ratios. Critical aspects to consider included especially blank control during sampling and the low amounts of total Sr (5-15 ng) leached from dust samples taken on 1 cm x 1 cm cleanroom wipe pieces. Leachates were further analysed by ICP-MS and MC-ICP-MS. A clear differentiation between the two locations was possible based on both elemental and isotopic tracers.

dust, provenance, isotope ratios, archaeometry

Development of methodologies for isotopic analysis by (MC)-ICP-MS in ocular low volume samples

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In recent years, alterations of the isotopic composition of biological fluids have shown to provide valuable information of biochemical processes and, also, as potential diagnosis/prognosis markers of diseases. So far, blood was the most common fluid investigated for such purposes. However, measurement of alterations in biological fluids directly related to the diseased organ could provide a more reliable information (1).

In this context, we aim at investigating the potential of isotopic analysis in ophthalmological disorders, in particularly those related to neurodegenerative processes. Aqueous humor is an intraocular fluid, vital in the physiology of the eye. It is sampled by placing a needle in the anterior chamber of the eye, being typically collected volumes between (0.1-0.25) mL. Methods for elemental and isotopic analysis are a great challenge for this type of sample.

As a representative example, focus on calcium isotopic analysis will be shown, as this element plays a key role in retinal and central nervous system physiology (2). Development of analytical protocols, including sample pretreatment and analysis via single collector and multi-collector inductively coupled plasma - mass spectrometry will be addressed. Critical evaluation of pros and cons of measuring isotopic ratios in comparison to elemental concentrations will be discussed.

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Aqueous humor, calcium, Isotopic Analysis, multi-collector ICP-MS

Costas-Rodríguez et. al., Tends in Analyt Chem, 2016, 76, 182-193

Robertson et al., Calcium in human biology, 1988, Chapter 1, 1-26

Boron isotope ratio measurements with a Q-ICP-MS in seawater samples

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A method was developed for Boron isotope ratios measurements in 9 seawater samples from the Atlantic, Indic, and Pacific Oceans by Q-ICP-MS. The method allowed accurate and precise (±0.4‰) determination of the boron isotope ratio by single collector Q-ICP-MS (PlasmaQuant MS Elite S). We applied a mixture of 0.70 mg/g NaF and 1% (v/v) HNO3 as the ICP-MS matrix for rapid washout (120s) of boron and high sensitivity. The long-term instrumental accuracy and precision of δ11B determination of NIST SRM 951 was 1.07 ± 1.59‰ (2σ, n = 30). The average seawater boron isotopic composition (δ11BSW) of 53.46 ± 1.59‰ (2σ, n = 66) determined on 9 seawater samples is analytically distinguishable from published values. Additionally, we report identical 11B/10B NIST SRM 952 values of 0.0508 ± 0.0040 (2σ, n = 20). This method provided a measured boron isotopic ratio precision in Seawater samples of 0.04% RSD and accuracy of 96% for NIST SRM 952.

Seawater, Boron, Isotopic Ratio

Boron Isotope Ratios in Champagne Wine as a Tracer of Authenticity using a Quadrupole ICP-MS

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French agriculture stands out for the great variety of traditional food, which represent regional excellences with unique characteristics. In a global market context, the consumer decision is increasingly influenced by quality, food safety and territoriality and, compliance with what is declared on the food label. Protecting and promoting these productions certainly leads to advantages from an economic point of view, and at the same time represents a political strategy that allows to highlight the national identity and avoid potential frauds. Wine identification is one of the most important aspects in the classification of wines and consumer protection. In particular, assuring wine authenticity is a crucial issue on which researchers are focusing on. This study aims to evaluate the feasibility of boron isotopic compositions of Champagne wine samples to trace their geographic origins and differentiate them from other regions where they could have been counterfeited, using a quadrupole inductively coupled plasma mass spectrometer (ICP/MS).

The obtained results showed that boron isotope ratio measurements led to a satisfactory degree of accuracy and precision (measured value, 10B/11B of NIST SRM 951a equal to 0.2473 ± 0.0003, (u = 2s) with a certified value of 0.2473 ± 0.0002 (u = 2s).

Isotope Ratios, Wine, Traceability, Authenticity, ICP-MS, Boron

Determination of sulfur isotope ratios in biological and geological reference materials

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Sulfur isotope ratios are often used as biogeochemical tracers to gain understanding of abiotic and biological processes involved in the sulfur cycle in both modern and ancient environments, such as biological metabolism, mineral formation, and climate change. There is however lack of matrix-matched well-characterized isotopic reference materials that are essential for controlling the accuracy and precision. This study therefore focused on expanding and complementing the currently available sulfur isotope ratio data by providing the bulk sulfur isotopic composition, as determined using multi-collector inductively coupled plasma-mass spectrometry (MC-ICP-MS) subsequent to chromatographic purification of the target element, for a comprehensive set of commercially and/or readily available biological and geological reference materials. These reference materials included standards from terrestrial animal origin (NIST 1549 Non-fat milk powder, ERM-BD150 Skimmed milk powder, IAEA H-4 Animal muscle, BCR-184 Bovine muscle, BCR-186 Pig kidney, IAEA H-8 Horse kidney, NIST 1577a Bovine liver, NIST 1577c Bovine liver, USGS89 Porcine collagen), aquatic animal origin (DORM-4 Fish protein, BCR-422 Cod muscle, NIST 1566a Oyster tissue, USGS88 Marine collagen), terrestrial plant origin (NIST 1567a Wheat flour, NIST 1568 Rice flour, USGS90 Millet flour, USGS91 Rice flour, NIST 1515 Apple leaves, ERM-CD281 Rye grass), human origin (Seronorm Whole blood, Serum, Urine, Hair NIES no. 5, ERM-DB001 Hair, GSH-1 Hair) and geological origin (GBW07267 Pyrite, GBW07268 Chalcopyrite, GBW07269 Galena, GBW07270 Sphalerite, 782-1 Dolomite, NIST 1d Limestone, GBW 07410 Soil, NBS 2704 River sediment, NIST 679 Brick clay). For comparison purposes, the sample preparation and sulfur isotope ratio measurements were done separately at two different laboratories for selected reference materials, while at one of the laboratories the measurements were performed using two different MC-ICP-MS instruments, thus aiming at enhanced robustness of the data.

Determined δ34SVCDT values compared well between the different laboratories, as well as between the different MC-ICP-MS instruments, and for standards that were previously characterized, our data are similar to literature values. The δ34SVCDT ranges determined for the different categories of the reference standards – terrestrial animal origin: +2 to +9 ‰, aquatic animal origin: +15 to +20 ‰, terrestrial plant origin: -20 to +7 ‰, human origin: +6 to +10 ‰ and geological origin: -12 to +16 ‰ – fit the expected values based on previous studies of similar types of matrices well.

sulfur isotope ratio; multi-collector ICP-mass spectrometry (MC- ICP-MS); biological; geological; reference material

Antimony Isotope Ratio Measurements Using a Desolvating Nebulizer System with Multicollector ICP-MS Detection:A Study with an Atlantic Ocean Mn Nodule

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Hydrogenetic Fe-Mn crusts precipitate directly from seawater and as such have been used as paleoceanographic recorders of changes in seawater chemistry over time.1 The slow growth rates of Fe-Mn crusts (<10 mm Myr-1)1,2 render them ideal archives of long-term variations in marine isotope compositions.3,4,5

Antimony is a redox sensitive element (with two oxidation states under terrestrial conditions Sb3+ and Sb5+), that may be sensitive to past environmental conditions. The long residence time of Sb in the oceans (35 kyrs)6 is long compared to that of ocean overturning times (1.5 kyrs)7,8; therefore, Sb will reflect ocean wide events.Differences in the Sb isotopic composition can reflect numerous changes in the Earth’s past environment such as hydrothermal inputs9, rate of marine organic burial10 and weathering11.

Modern day variations of Sb isotopes on the Earth's surface show ((123Sb/121Sb)samp /(123Sb/121Sb)std)-1) < 0.5‰ variations12, so a high level of measurement precision is needed to investigate these past processes.This requirement is achieved using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) with a specialized desolvating nebulizer accessory. These studies will also help to better explain Sb geochemical cycling, as this information may improve understanding of Sb inputs in oceans.

antimony isotope ratio multicollector icp-ms desolvating nebulizer

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Interlaboratory comparison on conventional ^{87}Sr/^{86}Sr isotope ratio analysis by applying MC-ICP-MS and MC-TIMS

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The variation of isotope ratios is increasingly used to unravel natural and technical questions. With new upcoming techniques and research topics in the last two decades, such as material provenance or food authenticity studies to animal and human migration studies, the number of published isotope data has strongly increased. Here, isotope reference materials are indispensable to enable a reliable method validation or even SI-traceability. The fast development and broad availability of inductively coupled plasma mass spectrometry instrumentation (ICP-MS) also lead to an expansion of the classical research areas and new elements are under investigation. Owing to this large expansion of the field, the production and certification of isotope reference materials for calibration and validation is lagging behind, even for classical applications such as conventional ^{87}Sr/^{86}Sr isotope ratio analysis. To improve this situation, BAM organized an interlaboratory comparison (ILC) comprising of thirteen international laboratories for the characterisation of ^{87}Sr/^{86}Sr isotope ratios in geochemical and industrial reference materials. Six reference materials (four cements and two rocks) were provided as powder requiring extensive sample preparation prior to isotopic measurement. Additional requirements included the use of the conventional method for obtaining ^{87}Sr/^{86}Sr isotope ratios, also known as radiogenic ^{87}Sr/^{86}Sr isotope ratios, and the assessment of measurement uncertainty. The primary goal was to evaluate potential differences in the application of multicollector thermal ionization mas spectrometry (MC-TIMS) and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) for conventional ^{87}Sr/^{86}Sr isotope ratio determination, with a secondary goal to provide reference values for the ^{87}Sr/^{86}Sr isotope ratios in these potential new reference materials. All reported results are accompanied by an uncertainty statement and are traceable to the conventional method, which will be described in detail within this presentation. Current state-of-the-art statistical models were used to ensure the proper evaluation of the reported results and their associated measurement uncertainties within the frame of this ILC. Combined with results from appropriate homogeneity assessment, reference values for ^{87}Sr/^{86}Sr isotope ratios will be assigned.

isotope ratio, uncertainty, interlaboratory comparison, strontium

Highly sensitive ^{238}U–^{234}U–^{232}Th–^{230}Th dating approach using LA-ICPMS

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Here we present high sensitivity, in situ Th and U isotope ratio determinations in carbonates using laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Online addition of a well characterized 229Th-233U-236U spike tracer to the laser generated carbonate aerosol enabled to monitor the mass discrimination and correct for elemental fractionation effects between U and Th. The efficacy of inter-element, mass discrimination, and peak tailing baseline corrections were critically evaluated. The detection efficiency has been improved to a yield of 1-2% by utilizing a “jet” interface ICPMS. Thereby signal intensities of 30-100 cps for the 230Th+ ion beam can for example be generated for 6,000s-yr-old stalagmites with U contents of 8-12 µg/g, yielding 2-sigma precision of U/Th dates better than ±200 years. A flowstone sample in secular equilibrium, collected from Northern Calcareous Alps, was analyzed to verify the approach and activity ratios of 1.011 ± 0.066 (2 S.E.) for 230Th/238U were obtained. This approach allows for the revelation of accurate age profiles in various materials and carbonates in particular, and will be applicable to diverse fields such as paleoclimatology, oceanography, geomagnetics, and archaeology.

U-Th dating, LA-ICPMS, carbonate

Strontium Isotopes Applied as Provenance Proxy for Brazilian Woods

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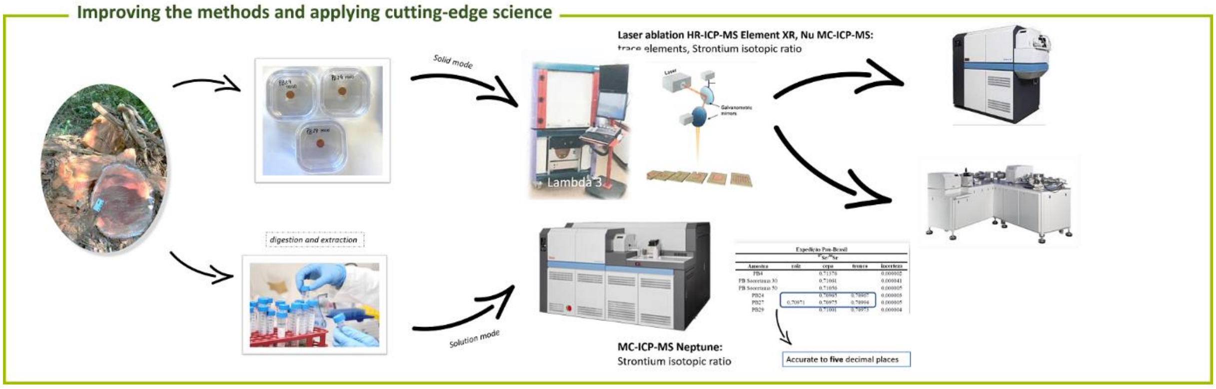
Geochemical proxies have been used to determine the provenance of timbers around the world. The geochemistry of strontium isotopes is relatively well known and 87Sr/86Sr ratios have been used routinely as environmental tracers. In Brazil, it is the first time that this methodology is applied for this type of study.

The objective is to characterize and interpret in an integrated way isotopic data and other wood data (e.g. trace elements) to establish the "Geochemistry of Wood"

First results showed 87Sr/86Sr ratio do not vary within the same individual (roots, trunk and branches), confirming the absence of isotopic fractionation within the body of the tree. the 87Sr/86Sr data obtained grouped the samples by region, being possible to distinguish those from the northern region and even the closest ones (ES and BA). Different values of the 87Sr/86Sr ratio were verified in the rock substrate for each location and these values were indeed reflected in the 87Sr/86Sr ratios from samples analyzed. These findings highlight the sensitivity of Sr isotopes to variations in the lithology on which trees are seated and thus can be used as a provenance tracer for Brazilian woods.



Strontium isotopes, laser ablation, wood

Assessing the level and distribution of trace element distributions in individual cells using single cell ICP-MS analysis

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Trace elements play a key role in many processes involved in living beings. Some elements are found as constituent elements in biopolymers, such as phosphorous as part of the DNA backbone, or sulfur, as part of the key amino acids methionine and cysteine involved in the formation of proteins covering a wide variety of functions. Other elements (in particular the transition elements copper, iron, and zinc) are involved in specific functions, such as acting as co-factors in enzymes. However, the distribution of trace elements cannot be assumed to be homogeneous across a cell cohort, even under ideal conditions. Ultimately, cell-to-cell variability of the metal content may be an important factor in understanding biological diversity. The analysis of specific biomarkers at the single cell level has therefore gained significant interest in recent years.

The analysis of the content of a given metal at the single cell level has remained a challenge. While inductively coupled plasma mass spectrometry (ICP-MS) is well known as a powerful and element-selective detection system, it is only recently that its capacity for analyzing individual cells has been recognized.

This presentation will highlight how ICP-MS can be operated to detect individual cells and establish an understanding about the content of trace elements at the individual cell level. This approach will be applied to detect different elements in selected model species, including selenized yeast (Saccharomyces cerevisiae) as an example.

Single Cell, ICP-MS, Yeast

Effect of gas species and flow rate on desolvation in droplet sample injection ICP- MS for single cell analysis

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The analysis of trace elements in single cells is expected to contribute to the fields of regenerative medicine and drug discovery. We have developed a droplet sample injection system that enables single cell analysis by injecting droplets of approximately 70 μm in diameter containing a single cell into an ICP- MS (1). However, the solvent should be removed from the droplet because it adversely affects ionization efficiency and reduces the analytical sensitivity. Therefore, we have developed an infrared-based desolvation system.

In this study, the optimum condition for droplet transport in this sample injection system was determined by investigating the effect of gas species and flow rate on desolvation. A schematic of the experimental apparatus is shown in Fig 1. Linear infrared light was focused on the central axis of the quartz glass tube by a reflective focusing optical system. Droplets were introduced into the desolvation apparatus from the top of the tube with the gas. The effect of desolvation was evaluated by measuring the diameter of the droplet that passed through the apparatus. In the presentation, the influence of gas species and flow rate on desolvation effect will be reported.

Fig.1 schematic of the experimental apparatus

Mass spectrometry, Single cell analysis, Desolvation

Shigeta et.al., J. Anal. At. Spectrom., 28, pp.637-645 (2013).

Elemental speciation analysis and molecular mass spectrometry for investigation of metal homeostasis in allergic subjects

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We previously reported that subjects with allergic rhinitis suffer from a functional iron-deficiency having elevated levels of the copper-containing ferroxidase ceruloplasmin which correlated also with the allergic symptom burden [1]. In humans, copper and iron metabolism are intertwined with under iron-deficient conditions elevated copper-levels being reported in the intestinal mucosa and influencing iron transport. As such, in the present work we assessed the contribution of copper complexes in the gut of subjects with or without allergies.

Trace elements in serum and stool samples as well as the microbial composition of stool samples were assessed. Trace elements were correlated with the microbial composition, ceruloplasmin and the allergic state of the investigated subjects. A more detailed investigation of stool was envisaged aiming at elemental speciation analysis of the aqueous stool extracts. LC-HRMS analysis was applied for structural elucidation of the detected, putative copper complexes. As stationary phase we employed a fully wettable reversed phase material with a methanol gradient, which is compatible with both LC-ICPMS and electrospray ionization utilized in LC-HRMS.

In addition, data from a state-of-the-art non-targeted analytical workflow which has been performed with the same samples via LC-HRMS was evaluated with regard to the findings made. First results will be presented and the potential of the approach will be discussed.

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Intracellular elemental content of CHO cells in batch versus fed-batch conditions

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Metals play a crucial role in biologic production, influencing mammalian cell growth, product titer, and critical quality attributes of protein therapeutics. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has been extensively used to determine elemental content in cell culture media to understand the role of metals in manufacturing biologic therapeutics. Further information about intracellular metal content is needed to determine the dynamics of cellular metal uptake during cell growth and the influence of media composition on this process. At present it is not fully understood how much metal is taken up from the media and internalized in the cell to participate as crucial cofactors for metabolic processes. The use of ICP-MS in measuring intracellular metal content is limited in bioproduction, possibly due to the lack of a robust method for this highly specialized application. Here we describe the development of a method for quantifying intracellular metals in bulk Chinese Hamster Ovary (CHO) K1 cells using a Thermo Scientific iCAP TQTM ICP-MS. A protocol for bulk cell harvesting and digestion with either microwave or hot block digestion was developed. The protocol was further optimized for samples containing as low as 1 million cells to make it suitable for small-scale culture studies. The accuracy of the method was confirmed with spike recovery studies. This newly developed method was successfully deployed in a cell culture time-course study, where both abundant and critical trace elements levels were reported, during exponential and stationary growth phases. Future implementation of this method will explore the holistic uptake of metals with other media components, potentially providing insight into metal speciation in cell culture media. This information may pave the way for custom metal balanced media solutions, tailored to performance attributes of interest to biologic therapeutics manufacturers.

Cell analysis, Metallomics, Cell culture, TQ-ICP-MS

Fate and impact of iodinated contrast media in exposed aquatic organisms - a metallomic approach

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Iodinated contrast media (ICM) used in X-ray imaging for diagnosis purpose are released into waste water and then encountered in natural water at usually several dozen of µg.L-1 and sometimes up to hundred µg.L-1. ICM are considered as emerging pollutants as the knowledge about their occurrence and impact on ecosystems and environment is extremely limited. Even so they are synthesized in order to be not toxic for human, aquatic organisms are continuously exposed and therefore their potential deleterious effect is questioned.

This communication presents the study of the determination of the occurrence and fate of two ICM, i.e diatrizoic acid and iohexol of different osmolality, in two types of aquatic organisms a bivalve (dresseina polymorpha) and a fish (gasterosteus aculeatus). The organisms were exposed under laboratory conditions at different concentrations and duration representative of the environmental ones. Total iodine content was first determined by ICP MS in several organs of the 2 organisms. Then, organs with highest levels of iodine were selected to get deeper insights of iodine fate at the subcellular level. For that purpose, iodine interaction with biomolecules were studied in the cytosolic fraction using size exclusion chromatography coupled to ICP MS. For fish, iodine tends to be slightly enriched in liver, brain and gonads. Although the speciation analysis didn't reveal an increase of iodine content in high molecular weight proteins fractions, iodine was mainly found associated in the metabolites fraction after ICM exposure. For bivalves, iodine content increased slightly in digestive gland, gonads and gills. In the cytosolic fraction of these three organs, the ICM exposure didn't tend to modify the iodine distribution among high molecular weight proteins, beside the detection of iodine peaks in the metabolites fraction compare to control conditions. Reversed phase chromatography coupled to ICP MS allowed confirming the presence of ICM in these cytosolic fractions. The two ICM tended to reveal different behavior during the exposure and depuration phases.

pharmaceutical compounds, Iodinated contrast media, aquatic organisms, accumulation, SEC-ICP MS, organs, cytosol

Metallobiomolecule profiling in gilthead seabream and European seabass blood serum by online SEC – ICP – MS

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Currently fish welfare depending on environmental status, as well as the risk associated with seafood consumption, are evaluated mainly by determining total metal concentrations in fish tissue.(1) The analytical chemical techniques used to determine total metal concentrations, mainly microwave digestion with ICP-MS, are well established and have become relatively routine. However, knowledge of total metal concentrations does not reveal much about metal distribution amongst biomolecules and thus metal function in an organism. (2) Also, the analysis of fish muscle tissue does not allow for the systematic study of the same subjects and significantly limits the frequency of carrying out corresponding analyses.

In order to overcome the aforementioned problems a novel online SEC-ICP-MS approach, for multielement metallobiomolecule profiling in fish blood serum, has been developed. This approach was applied for the analysis of As, Se, Ni, Zn, Cu, Fe, Co, Mn, Cr, Cd and Pb in blood serum of two commercially important fish species from the same aquaculture facility: the gilthead seabream (Sparus aurata) and European seabass (Dicentrarchus labrax). These species have been studied before for the determination of total metal concentrations in their tissues and intestines, but no information about the corresponding metallobiomolecules has been provided.(3)

The preliminary results of this study indicate the correlation of fish blood serum metallobiomolecule profile with fish species. In addition, data on the metallobiomolecule profiles as a function of fish weight, length and environmental factors such as total metal concentrations in borehole seawater supplying the aquaculture facility will be presented. This approach is expected to contribute to further studies related to fish welfare and seafood consumption nutritional value and risk assessment.

Metallomics, Metallobiomolecules, Multielement analysis, SEC-ICP-MS, Serum, Fish

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Can Single Cell ICP-MS improve our understanding of the role of iron on our immune system?

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Deficiency or over exposure to elements are recognised to have noticeable effects on human health.The effect of an element is determined by several characteristics, including absorption, metabolism, and degree of interaction with physiological processes (1).Iron is essential for oxygen transport, generation of energy, synthesis of DNA and several enzymatic systems.The concentration of iron and distribution in the body is tightly regulated for homeostasis by multiple genes that control its transport across cell membranes, redox state and storage.Iron deficiency impairs these functions and a familiar and important manifestation of advanced iron deficiency is anaemia. Around a quarter of a billion children worldwide are anaemic (2).Recent findings have shown that iron is a powerful regulator of immune responses which is of concern as iron deficiency is so prevalent.The underlying reasons why iron is needed by lymphocytes is unclear and requires further investigation (3).

The first commercially available Single Cell ICP-MS (SC-ICP-MS) system was introduced by PerkinElmer in 2016.This innovation allows a cell suspension to be nebulised through a dedicated SC-ICP-MS introduction system designed to ensure that cells arrive at the argon plasma intact.As each cell enters the plasma, it is ionised and the resulting ion plume detected as a single event.The larger the response the higher the concentration in the individual cell.SC-ICP-MS has been identified as a key tool to help better understand cellular uptake of iron as it allows rapid quantification of the iron content of individual cells.

This presentation will explain the hardware and software used at the University of Oxford, the benefits of pairing advanced cell technology and short dwell times, together with results demonstrating the measurement of iron in individual T cells to help investigate the role of iron on our immune system.

Single cell ICP-MS, Immune system, Anaemia

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Meta-analysis of blood serum Zn stable isotope compositions from healthy subjects using individual participant data

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In the last twenty years, studies on the use of Fe, Cu, and Zn isotope ratios in blood serum as diagnostic and prognostic markers of disease have become increasingly prevalent [1]. These studies typically include up to several tens of samples from a diseased population and a similar number of presumed-healthy subjects (or cited the control group of another study [2]). Sample preparation for isotopic analysis is labour-intensive and limits the number of measurements that can reasonably be performed. When considered in the broader context of clinical research, these investigations are small and can contain biases that make statistical analysis and data interpretation challenging. Initial investigations sought to establish whether factors, such as age, sex, diet, and menopausal status must be controlled for healthy subjects [3]. However, with only a limited number of healthy subjects assessed in each study, these questions are still not fully resolved. To that end, a meta-analysis using individual participant and aggregate data was conducted. This involved an extensive search for relevant articles in the databases of PubMed, EBSCOhost, and SCOPUS up to January 2022. Relevant articles were screened and validated by three independent reviewers. Serum Fe, Cu, and Zn isotope datasets were identified, spanning North America, Europe, and Asia, with six studies for Fe (173 healthy subjects), 13 studies and one unpublished dataset for Cu (305 healthy subjects), and six studies and one unpublished dataset for Zn (127 healthy subjects). When unavailable in-text or in supplementary files, sex, age, and serum Fe, Cu, and Zn concentrations were requested from corresponding authors. In this poster, the results for Zn will be discussed. Potential geographic differences and the causes of inter-study variability will be explored, and reference ranges established for healthy subjects. Ultimately, this meta-analysis will ensure patient cohorts are compared against appropriately-matched control groups, thereby enhancing the ability of isotope metallomics researchers to develop metal isotope ratio-based markers of disease.

Isotopic analysis, Zn, MC-ICP-MS, Metallomics,

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Spectral interferences as the reason of signals "amplification" on trace concentration of elements determination by ICP-AES

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To ensure the high quality of the results of the analysis, special attention in the ICP analysis should be paid to trace concentrations, since each stage of the analytical scheme introduces an error into the final result and the sum of errors is more reflected in trace concentrations. Significant errors in ICP analysis usually arise from spectral and matrix (non-spectral) interferences. The variety of analytical tasks is a guarantee that the analyst will face the task of identifying and accounting for interference.

So, during the analysis of the real solutions containing Sc, Fe, S and C we observed a double increase in the scandium signal at a wavelength of 361.3 nm (concentration of Sc 1 ppb). A doubling of the scandium intensity value was recorded on two ICP-AES spectrometers. For 10 ppb scandium concentration, this effect was absent. To find the reasons of the signal amplification, we carried out experiments on model solutions containing 1–10 ppb Sc, 10–30 ppb Fe, 30–100 ppm S, and 950–2850 ppm C.

We proposed that the reason for the amplification of the scandium signal is spectral interferences, which are not observed at scandium concentrations of 10 ppb and higher. To confirm this hypothesis, the theoretical values of the intensities of Sc and Fe, as well as Sc and S, were calculated. The calculations were shown that, starting from the concentration ratio of 0.1 : 99.9 (Sc : Fe), and 0.00001 : 99.99999 (Sc : S), correct detection of the scandium signal at a wavelength of 361.3 nm is impossible. It follows from the calculations that iron is the main interference, but the contribution of sulfur at the indicated ratio of analyte and interferent concentrations cannot be ruled out either. It should be noted that in the library of spectral overlays included in the instrument software, sulfur line 361.3 nm is not indicated as an interferent.

ICP-AES, trace element concentration, interferences

Grebneva-Balyuk. J. of Anal.Chem., 2022, V. 77, No. 1, 66-80.

Uncertainty evaluation in double isotope dilution inductively coupled plasma mass spectrometry

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This presentation provides a detailed approach for the evaluation of measurement uncertainty in reference material characterization by double isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). This study particularly focuses on the treatment of the instrumental isotope fractionation (IIF) phenomenon and correlated components of uncertainty. It is discussed that the IIF cancels out in double ID-ICP-MS so that the IIF effect needs to be excluded from consideration in uncertainty budgets. It is also discussed that by carefully removing uncorrelated components of uncertainty from characterization uncertainty and combining it with between-sample standard deviation, the uncertainty of a certified value can be obtained conveniently without double counting issues and complicated statistical analyses to assess homogeneity.

Certified reference material, measurement uncertainty, isotope dilution, inductively coupled plasma mass spectrometry

Improving valuable metals recycling: quantifying Technology Critical Elements in the urban mine

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Technology critical elements (TCE) are key materials for high level technology but their supply to the EU is challenging. A sustainable solution to this problem is through recovery and recycling, but the analysis of waste streams is difficult and a complicating factor.

In an effort to improve the reliability of TCE analysis in wastes with high recycling potential, certified reference materials are being developed within the EMPIR project MetroCycleEU, where 14 TCE are targeted. One of the main challenges in producing reference material lies in the homogeneous crushing of a large amount of material down to a size suitable for analysis. In the present study waste printed circuit boards crushed down to 200 µm were analysed for TCE with primary reference methods, recognised internationally: ID-ICP-MS and INAA. In the case of ID-ICP-MS, the first step is to optimize the digestion method to the targeted elements.

In this work, we compared the performances of acidic digestion, with and without HF, and alkali fusion digestion, all followed by HR-ICP-MS measurements. The first results show a fairly good agreement between the TCE concentrations obtained with acidic digestion and alkali fusion, however using a single digestion for all elements increases the difficulties in the resolution of interferences.

These results will help producing and certifying a reference material which will later be available to validate TCE analysis in the framework of quality control and analytical innovation.

Technology critical elements, Urban mine, ICP-MS

A Novel Isotope Dilution ICP-MS Approach for Validating Mercury Gas Generators

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Mercury (Hg) is a global pollutant that poses significant threats to both human health and the environment. Mercury is distributed globally by air, sequestered into soils, waters, and plants, and readily re-volatilised. Current atmospheric Hg concentrations are 500% above natural levels and anthropogenic Hg sources are responsible for 50% of emissions[1]. Thus, legislation such as the Industrial Emissions Directive (IED) 2010/75/EU and the Minamata Convention regulate Hg emissions from high emission industries such as coal-fired power plants. Traceable Hg measurements are therefore vital for controlling global Hg emissions. Field testing laboratories use Hg gas generators to calibrate analysers for Hg measurements. The most common mercury gas generators produce a continuous flow of Hg gas by either a permeation tube, the flow of inert gas over a stationary phase loaded with Hg, or the evaporation of a liquid Hg standard. The Hg concentration can be controlled by changing the gas flow rate and/or the liquid Hg standard concentration. However, these generators and related field measurements currently lack metrological traceability to SI units.

This work discusses a novel approach for the direct quantification and validation of Hg gas generators. The method employs gas phase isotope dilution (IDMS) for the accurate quantification of Hg using a triple quadrupole tandem mass spectrometer (ICP-MS/MS). The new approach is applicable to Hg gas generators with span gases between 10 ng/m^3 and 100 µg/m^3. It is based on mixing the gaseous Hg output of the generator with a Hg standard enriched with ^{199}Hg of known concentration and isotopic composition. To achieve this, the ^{199}Hg standard is introduced as a gas via a continuous cold vapour system. The gaseous Hg blend is measured by ICP-MS/MS, and the Hg generator output quantified using gas phase IDMS calculations. The combined expanded measurement uncertainty (k=2) for concentrations of gaseous Hg between 1 µg/m^3 and 35 µg/m^3 was found to be less than 5%. This method has the potential to improve the uncertainty and traceability of Hg measurements to the SI in the field and will support the standardisation work of the European Committee for Standardization (CEN).

mercury, gas, isotope dilution, ICP-MS/MS

United Nations Environment Programme (UNEP), 2019. Global Mercury Assessment 2018 Geneva, Switzerland. ISBN: 978-92-807-3744-8, https://www.unenvironment.org/resources/publication/global-mercury- assessment- 2018.

Harmonisation of measurement of environmental pollutants in Europe: Introduction to a European Metrology Project

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The European Green Deal’s ambition for zero pollution requires the detection of ultra-low concentrations of pollutants and to determine their isotopic ratio values for source attribution. Mass spectrometry is a key method for stable element determination and is increasingly applied to detection of long-lived radionuclides.

A European metrology project on ‘Metrology for Harmonisation of measurement of environmental pollutants in Europe’ (MetroPOEM) started in October 2022 and will run for three years. The aim is to bridge the gap between decay counting and atom counting methods and establishing new tools for tracing pollutants. Understanding of the advantages, limitations, measurement uncertainties and detection limits achievable by different mass spectrometer designs will be significantly improved using newly developed reference materials, SI-traceable measurement procedures and interlaboratory comparison exercises with an immediate impact for tracking pollution sources by commonly available mass spectrometers. The project consists of 21 European partners, with scientific work falling into four main areas: (i) Establishing and comparing the capabilities of different mass spectrometer designs using radionuclide standard solutions. The focus will be on relative instrument performance with respect to current measurement challenges around detection limits. (ii) Advancing stable and long-lived radiogenic isotope ratio measurements of environmental pollutants through the development of new and improved methods for stable and long-lived radioactive isotope ratio measurements by mass spectrometry with uncertainties that allow resolving natural mass dependent isotope fractionation. (iii) Development of two radioactive reference materials, one liquid and one solid, containing radioactive pollutants (237Np, 234,235,236,238U, 239,240Pu, 241Am and possibly 226Ra and 90Sr) addressing end user and stakeholders needs. (iv) Development of a traceable certified reference material for inorganic environmental pollutants which will be designed according to the needs of the end users performing environmental analysis and monitoring.The scientific outputs of the project will be disseminated via the scientific literature and by using the outcomes from the project through standards committees concerned with the determination of environmental pollutants.

The project (21GRD09 MetroPOEM) has received funding from the European Partnership on Metrology, co-financed by the European Union’s Horizon Europe Research and Innovation Programme and from by the Participating States.

Mass spectrometry, metrology, traceability, standards, reference materials, comparison exercises, stable pollutants, radioactive pollutants

Applying chemometric tools to search for relationships between elements in herb roots determined by ICP-MS

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Herbs are a source of microelements, vitamins, proteins and other pro-health compounds, such as polyphenols, carotenoids or flavonoids. Fast urbanization and growing agricultural and industrial production often lead to soil contamination. Consequently, toxic and potentially carcinogenic elements (e.g. Pb, Cd, As, Ni, Cr) are absorbed by plants cultivated in contaminated areas. Element toxicity may vary depending on the dose, administration route, chemical form of element and time of exposure; additionally, certain correlations between elements (antagonistic, synergistic, both simultaneously or without correlation) were also observed. According to the European pharmaceutical laws, herbs are not drugs but rather food supplements and the pharmaceutical safety regulations do not apply to them. The World Health Organization (WHO) proposed a strategy for 2014–2023 to regulate practices and products related to herbs. The European Pharmacopoeia proposes tests of heavy metals, mycotoxins, pesticides and microbial contamination in herbal products that help to assess their safety before introduction to the market. The purpose of this research was to determine the elements, both toxic and physiological, in herb roots by ICP-MS and to evaluate the multivariate data using chemometric tools: multiple regression analysis and canonical variate analysis (CVA) with interaction effects. An analytical procedure was developed, which included the preparation and digestion of samples, calibration, validation and quantitative analysis by ICP-MS with spectral and non-spectral interference removal methods. The analytical procedure was validated and traceability was established through the use of matrix-matched certified reference materials (CRM). The herbs were purchased in two batches 1 year apart to verify the variability of the elemental content over time. The maximum permissible concentration (MPC) of Cd (0.3 mg kg−1) was exceeded in 7 herb roots, which represents 13% of all samples. Multiple regression analysis revealed the significant relationships between elements, including Mg with Sr; V with Pb, As and Ba, Mn with Pb. The CVA showed that the statistical inference should not be based solely on the type of herb or number of batch, due to the underlying interaction effects between those two variables that may be a source of variability of the content of elements. Also, CVA showed the magnitude of differences between two batches of herbs, taking into account each determined element and showing that for some herbs the differences were much more prominent than in others.

Elemental analysis, ICP-MS, herbs, toxic elements, metrology, validation, chemometrics, multivariate analysis

Sajnóg et.al, Scientific Reports, 2021, 11, 20683
Kayzer et.al., Biometrical Letters, 2019, 56, 89–104

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Menero-Valdes, Paula, et. al., Talanta, 2023, 123974

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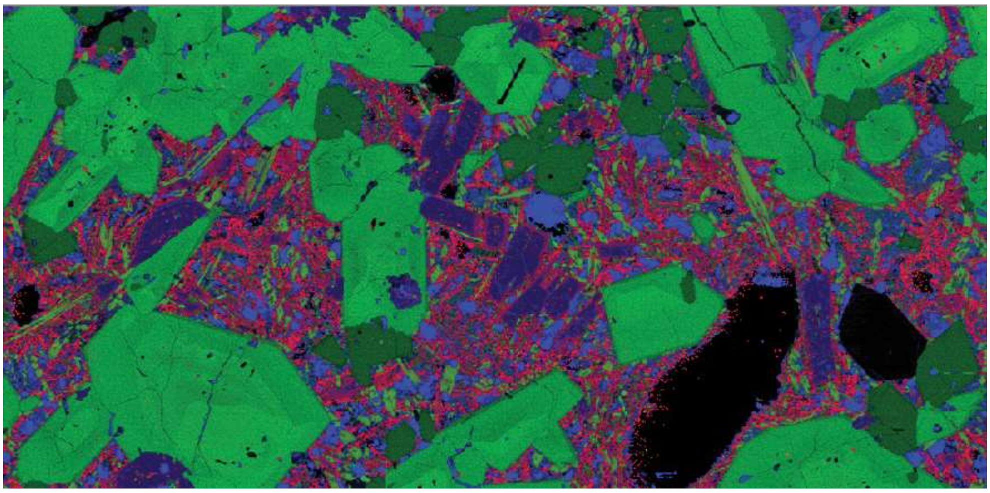

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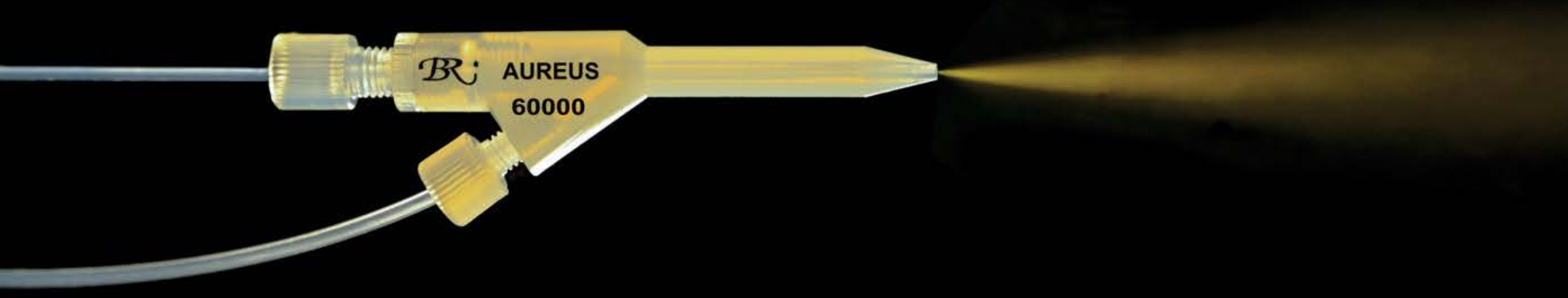
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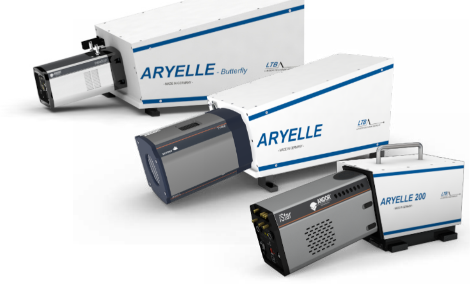

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