Seminar organized
by Doctorates for Doctorates

7th PhD Student seminar

of the German Working group for Analytical Spectroscopy (DAAS) in the GDCh Division of Analytical Chemistry

and ETV Workshop

15-17 November 2023, Berlin

www.bam.de/daas2023

BAM Bundesanstalt für Materialforschung und -prüfung

DAAS Deutscher Arbeitskreis für Analytische Spektroskopie

GDCh Analytische Chemie

Program at glance

ETV workshop

15 Nov Wednesday	12:00 – 13:00	**Registration & Opening**
	13:00 - 14:15	**Presentation talks & Discussion**
	14:15 - 15:00	**Coffee break & Networking**
	15:00 - 15:45	**Presentation talks & Discussion**
	16:00 - 18:00	**Lab tour**

PhD Seminar

16 Nov Thursday	08:00 – 09:15	**Registration & Opening**
	09:15 - 10:15	**Presentation talks**
	10:15 - 10:45	**Coffee break & Poster session**
	10:45 - 12:00	**Presentation talks**
	12:00 - 13:00	**Lunch break**
	13:00 - 14:15	**Presentation talks**
	14:15 - 15:15	**Discussion about Career paths**
	15:15 - 15:45	**Coffee break & Poster session**
	15:45 - 17:00	**Presentation talks**
	18:00 - 20:00	**Social event: Pub quiz**
17 Nov Friday	09:00 - 10:00	**Presentation talks**
	10:00 - 10:30	**Coffee break**
	10:30 - 11:30	**Presentation talks**
	11:30 - 12:00	**Coffee break**
	12:00 - 12:30	**Closing & Awards**

Welcoming words

Dear Participants,

We would like to express our heartfelt gratitude for your presence at our event. This gathering is not only a platform for PhDs to share their research and connect with accomplished scientists and leading experts, but also an opportunity to network and build lasting connections with your peers. We hope you find this event fulfilling both professionally and personally.

Thank you for making it a memorable and enriching experience.

Best regards,

Organizing team

Working group of Dr. Björn Meermann
MSc. Dariya Tukhmetova
MSc. Michail Ioannis Chronakis
MSc. Vera Scharek

phdseminar2023@bam.de

Federal Institute for Materials Research and Testing (BAM),
Division 1.1 Inorganic Trace Analysis,
Berlin, Germany

Join our social event

Join us for a delightful evening of socializing, networking, and fun at our post-seminar **Pub Quiz**, organized by DAAS organizing team. After a day of enriching discussions, unwind with fellow participants, enjoy drinks with delicious pizza, and put your knowledge to the test in a friendly competition. We look forward to sharing great moments and laughter with you.

We will gather at the entrance of BAM (Building 8.05) at 17:30 to walk together to the pub. Participation (including beer & food) is free of cost.

Please bring your name budge to enter the venue.

Program in detail

15 Nov Wednesday: ETV workshop

12:00 - 12:50	Registration
12:50 - 13:00	Opening & Welcoming
13:00 - 13:30	Dr. Thomas Vogt, TU Bergakademie Freiberg, "Carbon based samples – a problem for element analysis, but not with ETV"
13:30 - 14:00	Dr. Dirk Wuestkamp, Spectro, "New features and possibilities for ETV – with ICP Analyser Pro from research to routine"
14:00 - 14:15	Discussion with Dr. Thomas Vogt & Dr. Wuestkamp
14:15 - 15:00	Coffee break + Networking
15:00 - 15:30	Prof. Martín Resano, University of Saragossa, "Graphite furnace techniques for atomic, molecular and isotopic analysis"
15:30 - 15:45	Discussion with Prof. Martín Resano, University of Saragossa
15:45 - 16:00	Group photo (ground floor of BAM)
16:00 - 18:00	Lab tour with Dr. Peter Perzl, instrument presentation

16 Nov Thursday: PhD seminar

08:00 - 09:05		Registration
09:05 - 09:15		Opening & Welcoming
09:15 - 09:45	Key-01	Dr. Thibaut Van Acker, Gent University, "The road to fast elemental mapping with laser ablation-ICP-mass spectrometry"
09:45 - 10:00	PhD-01	Iker Basabe Mendizabal, Gent University , "Evaluation of the analytical capabilities of a nanosecond 193 nm kHz laser for LA-ICP-MS elemental mapping"
10:00 - 10:15	PhD-02	Daniel Paszek, Johannes Gutenberg-Universität Mainz , "Development of an on-chip DOD aerosol generator for sample introduction in ICP MS"
10:15 - 10:45		Coffee break & Poster Session
10:45 - 11:15	Key-02	Dr. Jan Lisec, BAM, "When drowning in data, start swimming"
11:15 - 11:30	PhD-03	René Klauer, Johannes Gutenberg-Universität Mainz, "Development of a tungsten-based ETV-unit for the direct determination of trace metals in green tea"
11:30 - 11:45	PhD-04	Frederik Droste-Rehling, TU Clausthal , "Challenges and approaches on characterisation of LIB recycling slag by ETV-ICP-OES"
11:45 - 12:00	PhD-05	Teres Pietschner, TU Bergakademie Freiberg, "Investigations of phosphorus release behavior from sewage sludge by ETV-ICP-OES to optimize phosphorus recovery processes"
12:00 - 13:00		Lunch break

13:00 - 13:30	Key-03	Sofia Pazzagli, HU Berlin
13:30 - 13:45	PhD-06	Anna Przibilla, Helmholtz-Zentrum Hereon, "$\delta^{98/95}$Mo as tracer for past and current redox conditions in sediment samples from the Skagerrak"
13:45 - 14:00	PhD-07	Pascal Hoppe, University of Hamburg, "How pollutants are transported - Distribution of organic and inorganic pollutants in different Elbe compartments"
14:00 - 14:15	PhD-08	Dominik Wippermann, University of Hamburg, "Using ICP-MS/MS to study the impact of offshore wind farms on the marine environment"
14:15 - 15:15		Discussion about career paths for PhDs (Dr. Stefanie Fingerhut from Merck, Dr. Björn Meermann from BAM, Dr. Petra Metz from HU, Lennart Gehrenkemper from UBA)
15:15 - 15:45		Coffee break & Poster Session
15:45 - 16:15	Key-04	Lennart Gehrenkemper, UBA, "Working for UBA – Research meets Regulatory"
16:15 - 16:30	PhD-09	Dominik Blaimer, Ulm university , "Greenness of analytical methods for the study of metal-containing nanoparticles in complex matrices"
16:30 - 16:45	PhD-10	Fabian Simon, BAM, "HR-CS-GFMAS for PFAS analysis - an optimized method for fluorine sum parameters"
16:45 - 17:00	PhD-11	Viktoria Mueller, University of Graz, "Per – and polyfluoroalkyl substances in wild boars"
17:00 - 17:15		Group photo (ground floor of BAM)
18:00 - 20:00		Pub Quiz by DAAS Organizing team

17 Nov Friday: PhD seminar

09:00 - 09:30	Key-05	Dr. Mario Corte Rodriguez, University of Oviedo, "Single-particle and single-cell elemental analysis by ICP-MS as tools for biomedical analysis:
09:30 - 09:45	PhD-12	Tim Steinwachs, University of Münster, "Exploring the Potential of Single Particle ICP-MS for the Analysis of Nanoparticles in Organic Solvents"
09:45 - 10:00	PhD-13	Andrés Suárez Priede, University of Oviedo, "Evaluating the Biogenic Production of Selenium Nanoparticles by Edible Mushrooms"
10:00 - 10:30		Coffee break
10:30 - 11:00	Key-06	Heinrich Kipphard, BAM, "Introduction to Metrology "
11:00 - 11:15	PhD-14	Frithjof Mähler, TU Clausthal, "Determination of diffusion inside ionometric membranes with micro XRF"
11:15 - 11:30	PhD-15	Riccarda Müller, Ulm university , "Mirco X-ray fluorescence spectrometry for quantitative and distribution analysis of metals in POMbranes"
11:30 - 12:00		Coffee & Snacks break & Voting
12:00 - 12:30		Closing & Awards

Poster presentation by PhDs

PhD-16	Saksia Stopp, TU Bergakasdemie Freiberg, "The Potential of Mid-Infrared Spectroscopy and LIBS for Characterization of Soil Quality Parameters"
PhD-17	Benedikt Keitel, Ulm university, "Specific Extraction of Bioavailable Proanthocyanidins from Grape Seed Extracts by Molecular Imprints"
PhD-18	Silke Lehner, Hahn Schickard Ulm, "Detection of Thin-Film Contaminants at Metal Surfaces via PM-IRRAS"
PhD-19	Amelie Huber, Ulm University, "Revolutionizing Diclofenac Sodium Salt Quantification: Molecularly Imprinted Polymers for Preconcentration Facilitating On-Line IR-ATR Analysis in Aqueous Matrices"
PhD-20	Matthias Schmitt, Philipps-Universität Marburg, "Characterization of functionalized polymer microparticles using single particle ICP-MS"
PhD-21	Dennis Kessen, University of Münster, "Method development for direct elemental analysis of lithium ion battery materials by means of ETV-ICP-OES"
PhD-22	Marc Vahnstiege, University of Münster, "Implementation of Single Particle ICP-OES to Quantify the State-of-Charge of Lithium-Ion Battery Active Materials"
PhD-23	Jialu Yu, BAM, "Isotopic and Elemental Screening Analysis of Biofilm on Microbiologically Influenced Corrosion on Using LASS-MC-ICP-MS/ICP-ToF-MS/HR-ICP-MS"
PhD-24	Pranav Seena Prem, BAM, "Investigation of Instrumental Isotope Fractionation in ICP-MS"
PhD-25	Michail Ioannis Chronakis, BAM, "MDG-ICP-ToF-MS: A Versatile Tool for Quantification in the field of Single Particle ICP-MS Using Isotopic Dilution"
PhD-26	Michail Ioannis Chronakis, BAM, "Single cell-asymmetrical flow field-flow fractionation/ICP-time of flight-mass spectrometry (sc-AF4/ICP-ToF-MS): an efficient alternative for the cleaning and multielemental analysis of individual cells "

Award for the best presentation

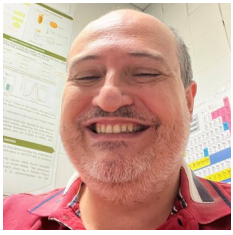
Two best oral presentations and one best poster presentation will be awarded with a prize sponsored by **Analytical and Bioanalytical Chemistry**.

Each winner will get 100 € voucher for Springer books.

All participants of the event are invited to vote for the best speaker. Voting will be done online by following the link https://forms.gle/gwCC2QDm3QyqatQP7 on Friday at 11:30.
Scan the QR code to vote.

Invited speakers

Dr. Martin Resano, University of Zaragoza, Spain



Dr. Martín Resano Ezcaray (PhD 1999, University of Zaragoza; Post-Doc at University of Gent (Belgium)) is a Professor at the University of Zaragoza where he leads the research group MARTE (Rapid Analysis Methods with Spectroscopic Techniques, DGA Reference E43_20R) since 2008. MARTE develops new methodologies with high-resolution molecular and atomic absorption spectrometry (HR CS MAS/AAS) and inductively coupled plasma mass spectrometry (ICP-MS) to undertake the direct trace elemental and isotopic analysis of solids and complex samples of all types, although with increasing emphasis on biomedical applications and nanoanalysis. Dr. M. Resano has chaired the Editorial Board of the Journal of Analytical Atomic Spectrometry (Royal Society of Chemistry) between July 2016 and July 2020 and is a Fellow Member of the Royal Society of Chemistry. His work has been awarded (26/03/2015) with the Bunsen-Kirchhoff Prize of the German Working Group for Analytical Spectroscopy (AK DAAS) of the German Chemical Society (GDCh). (mresano@unizar.es)

Dr. Thomas Vogt, TU Bergakademie Freiberg, Germany

Dr. Thomas Vogt is currently a senior scientist at the Institute of Analytical Chemistry at the TU Bergakademie Freiberg. After the qualification as electrian, he studied Applied Natural Science with focus on environmental analysis and his growing interest in analytical chemistry led to a diploma thesis in the field of atomic spectroscopy to analyze solar silicone with ETV-ICP-OES. Solid sampling with ETV was also the main topic of his doctorial theses as part of the DER (Deutsches EnergieRohstoffzentrum), in which he developed methods for the process accompanying analysis of fuels for energetic and material use. Direct solid sampling methods like ETV, LIBS and LA remain the focus of his research to this day. (thomas.vogt@chemie.tu-freiberg.de)

Dr. Thibaut Van Acker, Gent University, Belgium

Dr. Thibaut Van Acker obtained his Master of Science degree in Bioscience Engineering: Environmental Technology at Ghent University (Belgium) in 2015. He carried out his Master thesis in the Atomic & Mass Spectrometry (A&MS) research unit under the supervision of Dr. Eduardo Bolea-Fernandez and Prof. Dr. Frank Vanhaecke and it was in that period that he developed his interest in Analytical Chemistry. As a result, he started his PhD in the A&MS research unit on the topic "Method development for high-resolution elemental bio-imaging via laser ablation-ICP-mass spectrometry (LA-ICP-MS)". After obtaining his PhD degree in Chemistry in 2019, he continued his journey as postdoctoral researcher further exploring the LA-ICP-MS for elemental bio-imaging applications in interdisciplinary contexts. Thibaut is (co-)author of 24 publications in peer-reviewed scientific journals (h-index: 14, total number of citations: 711) and recently was awarded the 2023 European Rising Star Award for Plasma Spectrochemistry at the European Winter Conference on Plasma Spectrochemistry organized by the National Institute of Chemistry in Ljubljana, Slovenia. (thibaut.vanacker@ugent.be)

Dr. Jan Lisec, BAM, Germany

Dr. Jan Lisec studied Biotechnology at the TU Berlin, preparing his diploma thesis at Murdoch University (Perth, Australia). He investigated the metabolome of model plants to shed light on the heterosis phenomenon using quantitative genetics approaches at the Max-Planck-Institute for Molecular Plant Physiology and obtained his PhD from U Potsdam (2009). Mass spectrometry, programming and statistics remained in the focus of his research that led him to the Molecular Cancer Center of the Charité Berlin, investigating cellular metabolic fluxes, and ultimately to BAM where he currently is co-heading a mass spec facility. Dr. Lisec is the (co-)author of numerous publications (https://scholar.google.de/citations?user=NP6Jv14AAAAJ) and R packages (https://github.com/janlisec), working continuously on improving all steps of non-targeted metabolomics analyses and compound annotation in particular. (jan.lisec@bam.de)

Sofia Pazzagli, Humboldt University, Germany

Dr. Sofia Pazzagli received her PhD in Physics in 2018 at the University of Florence in Italy. Since 2019, she is a researcher at the Humboldt Universität zu Berlin, where she set up an optical lab for integrated quantum nanophotonics using organic molecules. Her ambition is to make future photonic technologies economically and environmentally sustainable. She is developing a strong interest in entrepreneurship, and in 2022 her team was awarded the 1st prize in the category "Digital & Technologies" in the "Research to Market Challenge," a competition organized by the Berlin University Alliance. Sofia is a proud member of the network of Women in Natural Science Adlershof (WiNS) and since 2021 she co-organizes events for students and early-stage career researchers, such as the Berlin PostDoc Day and the Friday Light Talks. For her, any opportunity is a good occasion to test her communication skills: from pitching at the Falling Walls Lab competition to surfing (and not drowning!) social media. (sofia.pazzagli@hu-berlin.de)

Lennart Gehrenkemper, UBA, Germany

Lennart Gehrenkemper is a scientist at the German Federal Environment Agency. Previously, he studied education (B.A.) and chemistry (B.Sc. & M.Sc.) with a focus on analytical chemistry at the University of Münster. From 2020 to 2023, he conducted research on PFAS sum parameters as part of his PhD project at the German Federal Institute for Materials Research and Testing in the group of Dr Björn Meermann. Since February this year, Lennart has been working on the derivation of soil safty values for PFAS in the group of Dr Annegret Biegel-Engler. His intersectional research is supported by a group of experts in the fields of environmental sciences, analytics, toxicology and plant physiology. (lennart.gehrenkemper@uba.de)

Dr. Mario Corte Rodriguez, University of Oviedo, Spain

Dr. Mario Corte-Rodríguez obtained his PhD in 2017 at the University of Oviedo. His Doctoral Thesis was about the application of ICP-MS to study the incorporation of metallodrugs at the cellular level. In this time, he started to work in the analysis of single particles and cells (SP and SC-ICP-MS). In his postdoc, his research has been focused on the development of ICP-MS based methods for the analysis of single particles and, specially, cells, in combination with metal labels for the quantification of biomarkers at the single cell level. During the last years, he has carried out research stays at BAM in Berlin and the University of Vienna to learn and apply new concepts to single cell analysis. He is currently an Assistant Professor at the University of Oviedo and his current research goes towards the elemental characterization of cell populations in terms of biomarker expression, elemental content and metal and nanoparticles uptake, and the application of SP-ICP-MS analysis to the quantification of specific nucleic acid sequences. (macortero@gmail.com)

Heinrich Kipphardt, BAM, Germany

Heinrich Kipphardt graduated from University Dortmund in collaboration with ISAS (Institute for Analytical Science) and Max-Planck-Laboratory for ultrapure materials analysis with focus on inorganic chemical analysis. During his three years stay at IRMM (Institute for Reference Materials and Measurements) he discovered his passion for metrology when working on gas isotopes. He joined BAM (Federal Institute for Materials research and Testing) in 1999 with the main task of developing primary standards for element determination, which technically requires to characterise a high purity metal with respect to all other possible impurities mainly by atomic spectrometry. In 2012 he joined BAM's gas analysis group, being now head of the subject area and technically responsible for the automotive and energy gases. Heinrich is also active in metrology as well as in national and international standardisation bodies. (heinrich.kipphardt@bam.de)

Invited career representatives

Dear Participants,

We are excited to invite you to an insightful discussion session on "**Career Possibilities for PhDs**." We have gathered a diverse panel of experts, each with a PhD, who have taken their research careers in different directions. Our panelists include individuals from research academia, regulatory offices, industry, and mentoring programs. They will share their invaluable experiences and offer guidance to help fellow PhDs explore the wide array of career options available.

This is a great opportunity to gain insights, ask questions, and connect with professionals who have successfully navigated various career paths.

We look forward to your participation in this discussion, where you discover new possibilities and make informed decisions about your future.

At 14:15–15:15 on 16 Nov Thursday. Moderated by Michail Ioannis Chronakis

Dr. Björn Meermann, BAM, Germany

Science & **Research**

Dr. Björn Meermann studied chemistry at the University of Münster and obtained his doctorate in analytical chemistry in 2009 in the working group of Prof. Dr. Uwe Karst (University of Münster). He then spent almost 2 years as a post-doc at the University of Ghent (Belgium) in the working group of Prof. Dr. Frank Vanhaecke. In 2012, he moved to the Federal Institute of Hydrology (BfG, Koblenz) as a research assistant. Since June 2019, he has been Head of Department 1.1 "Inorganic Trace Analysis" at the Federal Institute for Materials Research and Testing (BAM) in Berlin. His current research focuses on the interface between materials and the environment as well as the life sciences. He investigates the release of elements, element species and (nano)-particles from materials into the environment, organisms and cells. The focus is on coupling techniques, single particle/cell-ICP-ToF-MS and HR-CS-GFMAS (for non-metals) methods. (bjoern.meermann@bam.de)

Dr. Stefanie Fingerhut, Merck, Germany

Science & **Industry**

Dr. Stefanie Fingerhut obtained her bachelor's and master's degrees in chemistry from the University of Münster. She then pursued her passion for analytical chemistry and completed her PhD under the supervision of Prof. Karst, focusing on ICP-MS hyphenation techniques. After completing her PhD, Stefanie joined a middle-sized company as a Project Manager in the quality control department before she joined Merck in 2019 as a Senior Scientist in the Central Analytics department. She took over the position of lab manager for Elemental Impurity Profiling in 2021. Furthermore, Stefanie is an active member of the GDCh, specifically in the *Fachgruppe Analytische Chemie* as a Board member of the DAAS since 2023. (stefanie.fingerhut@merckgroup.com)

Dr. Petra Metz, Humboldt University, Germany

Science & **Mentoring**

Dr. Petra Metz is currently a Head of WINS Adlershof Program: a Career Development and Mentoring Program for Female Scientists. Since 2023 she is a Head of Center for Career Development Adlershof, Humboldt-Universität zu Berlin, Germany. She supports doctoral students and postdocs on campus with regard to a scientific career, to acquire key qualifications, exchange ideas and network with leaders from academia and research. He career path started as a DAAD Lecturer in Ecole des Hautes Etudes en Sciences Sociales in Paris, France between 1996-2001. In 2005 she obtained her PhD in German Literature at the Humboldt-Universität zu Berlin, Germany. Between 2002-2016 she worked as an Advisor and Curator of Cultural and Scientific Events, Berlin, Germany, and 2009-2017 as a Head of Department, LIFE e.V., Berlin, Germany. (petra.metz@hu-berlin.de)

Lennart Gehrenkemper, UBA, Germany

Science & **Regulations**

Lennart Gehrenkemper is a scientist at the German Federal Environment Agency. Previously, he studied education (B.A.) and chemistry (B.Sc. & M.Sc.) with a focus on analytical chemistry at the University of Münster. From 2020 to 2023, he conducted research on PFAS sum parameters as part of his PhD project at the German Federal Institute for Materials Research and Testing in the group of Dr Björn Meermann. Since February this year, Lennart has been working on the derivation of soil safty values for PFAS in the group of Dr Annegret Biegel-Engler. His intersectional research is supported by a group of experts in the fields of environmental sciences, analytics, toxicology and plant physiology. (lennart.gehrenkemper@uba.de)

Evaluation of the analytical capabilities of a nanosecond 193 nm kHz laser for LA-ICP-MS elemental mapping

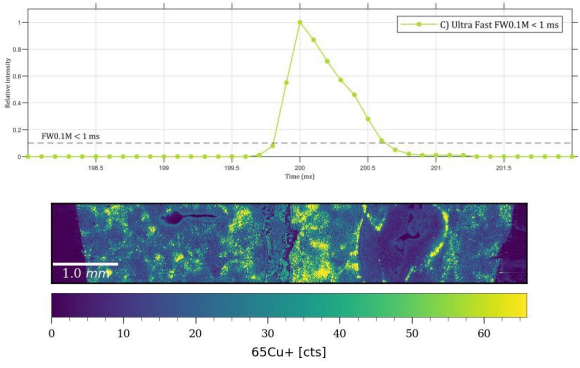
Iker Basabe Mendizabal*, Tom Van Helden, Frank Vanhaecke, Thibaut Van Acker

(*iker.basabemendizabal@ugent.be)

Department of Chemistry, Atomic & Mass Spectrometry, A&MS Research Unit, Ghent University, B-9000 Ghent, Belgium.

Lately, new developments in LA-ICP-MS technology such as, novel low-dispersion designs of ablation cells[1] and highly efficient aerosol transport systems[2] , have enabled fast elemental mapping at high spatial resolution and its application in various research fields. Nowadays, low-dispersion setups are capable of producing very narrow peak profiles of less than 1 ms duration, improving the signal-to-noise ratio and requiring a laser capable of operating at high repetition rates.

In this work, the analytical performance of a nanosecond 193 nm kHz laser, housed in an Iridia LA-unit with Cobalt ablation chamber was evaluated for LA-ICP-MS elemental mapping with a variety of instrumental setups characterized by single pulse response (SPR) profiles in the range of 100 down to <1 ms duration (defined as full peak width at 10% of the peak maximum, FW0.1M). The slowest setup was composed of a cup-type ablation cell with a cross-flow mixing bulb and the fastest setup housed a tube-type ablation cell[3] together with an Aerosol Rapid Introduction System (ARIS). The pulse-to-pulse laser energy stability, the linearity of the signal response, elemental fractionation effects and oxide formation were evaluated over a wide range of laser repetition rates (10-1000 Hz). With all instrumental setups, elemental maps of chondritic meteorite samples were generated at a laser repetition rate of 1 kHz and the pixel acquisition rate was matched to the SPR durations. Finally, with the fastest instrumental set-up, for the first-time pulse-resolved mapping at 1,000 pixels s^{-1} and several elemental maps of a mice liver tissue section and a chondritic meteorite sample were produced to showcase the capabilities.



References:

(1) Becker, P.; Koch, J.; Günther, D. Impact of Ablation Cell Design in LA-ICP-MS Quantification. *J Anal At Spectrom* **2022**, *37* (9), 1846–1854. https://doi.org/10.1039/d2ja00167e.

(2) Van Acker, T.; Van Malderen, S. J. M.; Van Helden, T.; Stremtan, C.; Šala, M.; Van Elteren, J. T.; Vanhaecke, F. Analytical Figures of Merit of a Low-Dispersion Aerosol Transport System for High-Throughput LA-ICP-MS Analysis. *J Anal At Spectrom* **2021**, *36* (6), 1201–1209. https://doi.org/10.1039/d1ja00110h.

(3) Van Malderen, S. J. M.; Van Acker, T.; Vanhaecke, F. Sub-Micrometer Nanosecond LA-ICP-MS Imaging at Pixel Acquisition Rates above 250 Hz

Development of anon-chip DOD aerosol generator for sample introduction in ICP-MS

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The introduction of liquid samples into inductively coupled plasmas is predominantly done with pneumatic nebulizers. The task of such sample introduction systems is the conversion of liquid sample solutions into an aerosol. However, the aerosol produced in this process does not have ideal properties for use with ICPs, which is why spray chambers are used to optimize and filter the aerosol. As a result, the primary, polydisperse aerosol is converted into a tertiary aerosol with reduced polydispersity. Unfortunately, the use of spray chambers also has some disadvantages: A loss of up to 98% of the sample material leads to reduced sensitivity and decreased detection capability. There is also the risk of memory effects, which makes rinsing processes necessary between individual measurements, thus increasing the analysis duration.[1]

A sample introduction system designed to address some of the mentioned disadvantages is the drop-on -demand aerosol generator (DOD) developed by the Bings group. This system operates based on the thermal inkjet principle and is capable of generating a gas bubble using heating pulses, thereby ejecting discrete droplets through a nozzle. By adjusting the frequency of the heating pulses, less polydisperse droplets can be produced at a range of different dosing rates, which can then be introduced into the plasma. In addition to the direct generation of the aerosol, the DOD offers the possibility of frequency-based calibration. In previous studies, this principle of droplet generation using modified printer cartridges has already been demonstrated.[2,3]

The current focus of this work is the development and testing of a microchip-based system for aerosol generation. The further development of the system towards a microchip allows for operation as a flow cell, which in the future should enable coupling the DOD with chromatographic and electrophoretic separation systems. Current challenges include reducing the droplet diameter of the generated droplets and improving the stability of droplet generation at higher frequencies.

References:

[1] N. H. Bings, J. O. Orlandini von Niessen and J. N. Schaper, Spectrochimica Acta Part B: Atomic Spectroscopy, 2014, 100, 14–37.

[2] J. O. Orlandini v. Niessen, J. N. Schaper, J. H. Petersen and N. H. Bings, J. Anal. At. Spectrom., 2011, 26, 1781.

[3] J. O. Orlandini v. Niessen, J. H. Petersen, J. N. Schaper and N. H. Bings, J. Anal. At. Spectrom., 2012, 27, 1234.

Development of a tungsten-based ETV-unit for the direct determination of trace metals in green tea

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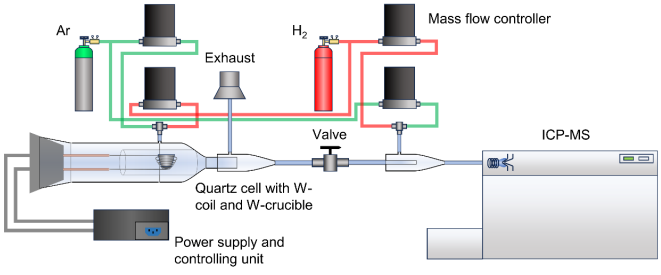
[1]Johannes Gutenberg-Universität Mainz, Department Chemie, Saarstraße 21, 55122 Mainz

For the multielemental determination of trace metals in samples with complex matrices like oils, metal powders, food and environmental samples, the matrix commonly has to be digested prior to the analysis using e.g. ICP-MS or -OES. However, the digestion procedure has several disadvantages: it is time-consuming from various points of view, it bears the risk of contamination due to the used chemicals and the resulting digested sample is diluted, possibly below the limit of quantification achievable with the selected analytical procedure. Also with respect to environmental protection and sustainability, this procedure is at least suboptimal, due to the use of additional chemicals and the production of chemical waste.

Therefore, an electrothermal vaporization unit with a basket-shaped heatable tungsten-coil and an inserted crucible also made of tungsten as evaporation vessel (see figure below, not to scale) was developed in the Bings group. This unit allows the direct sampling of e.g. aforementioned samples and it does not require complex sample preparation procedures. The crucible can be easily removed for weighing liquid and powdered samples (max. 3 mg). A controlling unit consisting of a standard computer power supply and an Arduino microcontroller is connected to the coil. A sequence of voltage-dependent temperatures combined to a temperature program could then be used to dry, pyrolyze and evaporate the sample resulting in a dry aerosol ready to be analyzed. The analytical performance of this lab-made W-ETV-system coupled to an ICP-MS was proven for the direct determination of trace metals in green tea.



Challenges and approaches on characterisation of LIB recycling slag by ETV-ICP-OES

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Recycling of end-of-life lithium-ion batteries (LIB) is commonly done in a combination of pyro- and hydro-metallurgy. The recovery of lithium (Li) especially in the presence of manganese (Mn) in pyro-metallurgical processing is challenging [1], with Li passing into the slag, resulting in lower recovery rates. A strategy for higher recovery rates is the modification of slag phases, forming engineered artificial minerals (EnAM) [2]. In this context artificial recycling slags are surveyed by means of ETV-ICP-OES to support a systematic development of new recycling processes and routines for a circular economy.

Measuring main and matrix elements by ETV-ICP-OES bears a challenge in the operating parameters and the selection of suitable element emission wavelengths. Of main interest is the elemental release behaviour from these slags, foremost of Li and Mn. With Mn forming different phases with deviating oxidation states in the slag, optimal parameters are searched for defined release peaks.

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Investigations of phosphorus release behavior from sewage sludge by ETV-ICP-OES to optimize phosphorus recovery processes

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The energetic and material use of various substitute fuels has increasingly become the focus of research in the last few years. For the development and implementation of suitable thermal conversion processes, in-process or process-accompanying analysis is essential. In addition to the quantification of various components, the release behavior of individual elements during the thermal conversion is also of great interest. This contributes to a better understanding of the transformation of the samples during the process, in terms of deposit formation, corrosion or emission. The method of electrothermal vaporization with inductively coupled plasma optical emission spectrometry (ETV-ICP-OES) is suitable for simulating these processes, by varying the gas atmosphere and the temperature program.

The presentation will focus on phosphorus release from various sewage sludges. A method was developed for the ETV-ICP-OES to distinguish between different chemical forms of phosphorus on the base of their release behaviour. This enables both the quantification of the elements contained and additional indications to their binding forms. For the assignment of individual signals, a targeted extraction of different P-fractions and solid-state NMR-measurement were applied.

In addition, the gas atmosphere can be modified, e.g., by addition of O_2, to simulate similar conditions to real conversion processes. Therefore, a coating of the graphite parts of the furnace and an adjustment of all parameters is necessary. This includes the temperature program and the selection of suitable emission lines. In dependence of O_2 concentration and composition of the sewage sludge samples, different signals in the phosphorus release were observed.

$\delta^{98/95}$Mo as tracer for past and current redox conditions in sediment samples from the Skagerrak

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The Skagerrak is the major depot-center for organic carbon produced in the North Sea. Remineralization and burial pathways of organic carbon highly depend on the prevailing redox conditions. To evaluate the past and future carbon storage capacity of the Skagerrak, it is hence important to investigate the redox conditions within Skagerrak sediments. However, in-situ measured parameters like the oxygen saturation only reflect the situation during sampling and not the conditions under which the sediments were formed. In contrast, $\delta^{98/95}$Mo values have proven to be a suitable tracer of the redox conditions that prevailed during sedimentation [1].

In our study, we investigated the $\delta^{98/95}$Mo values of three sediment cores from different locations within the Skagerrak, analyzed via MC-ICP-MS. Mass bias correction was based on a $^{92/98}$Mo double spike added prior to sample processing and measurement [2] and NIST SRM 3134 was used as reference. In addition to the analysis of the unaltered sediments and pore waters, sediments were incubated with seawater under aerobic and anaerobic conditions for up to one year to simulate changing oxygen conditions within the Skagerrak.

In agreement with previous studies at the same locations [3], our results show that there are distinct differences in redox conditions between the three sampling stations. The deepest station (680 m) exhibited Mo mass fractions of up to 54.6 ± 2.4 mg kg^{-1} that were associated with high mass fractions of Mn (30.3 ± 1.6 g kg^{-1}), suggesting that the Mo coprecipitated with Mn oxides. Below the layer of highest Mn mass fractions, dissolved Mn concentrations of more than 15 mg L-1 occurred in the porewater, indicating Mn reduction at this site. During the incubations, Mo and Mn were released from this sediment under both aerobic and anerobic conditions. The $\delta^{98/95}$Mo of the sediment was as low as -0.48 ± 0.14 ‰. Especially during anaerobic incubations, the $\delta^{98/95}$Mo of the sediment increased, indicating the reduction of the Mn oxides and release of associated Mo. Both shallower stations (450-510 m) showed distinctively less Mo and Mn (up to 4.6 ± 0.4 mg kg^{-1} and 4.65 ± 0.12 g kg^{-1}, respectively) but the $\delta^{98/95}$Mo values were still lower than for seawater (~2.0 ‰).

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How pollutants are transported - Distribution of organic and inorganic pollutants in different Elbe compartments

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The Elbe River is an important ship traffic route for cities like Hamburg, Berlin, and Dresden. Despite being an economical important transport route, the Elbe River belongs to the most heavily polluted rivers in the EU. The Elbe Estuary reaches from Geesthacht, located to the southeast of Hamburg, up to Cuxhaven where it flows into the North Sea. The Elbe Estuary is influenced by tidal changes and carries a salt gradient where fresh- and saltwater mix. The harbor region as well as parts of the tidal region are strongly impacted by sedimentation of material originating from upstream regions as well as material from the North Sea, which is transported upstream by tidal pumping. To allow the operation of Hamburg Harbor, continuous dredging of the polluted sediments is necessary. Due to the pollution load sediment management, which also includes its dumping into the North Sea or at a different Elbe site gets more and more difficult. Many studies monitor legacy pollutants such as Zn, Cu, or Pb in Elbe sediment and water, but not possible transport pathways of these pollutants and the effects of changes in tidal, salinity or pH values [1, 2]. However, such information combined with numerical models focusing on sediment and suspended particulate matter (SPM) transport and related pollutants could be a valuable tool for improved sediment management and a better understanding of the transport, distribution, and fate of pollutants.

The goal of the cooperative interdisciplinary project Contaminants Transport Modelling in the Elbe Estuary (CTM-Elbe) of the Federal Waterways Engineering and Research Institute (BAW) and Helmholtz-Zentrum Hereon, to determine and accurately model the transport pathways of selected inorganic and organic pollutants such as copper (Cu), zinc (Zn), mercury (Hg), cadmium (Cd) in different compartments (water, SPM, and sediments) of the Elbe River.

To obtain a preliminary overview of the degree of pollution of the relevant compartments, as well as to obtain first information on the partitioning of the selected pollutants between the different compartments, environmental samples collected on a campaign with the Ludwig Prandtl research vessel in April 2023 were analyzed for their trace metal composition according to Zimmermann et al. (2020) [3]. The digests were analyzed via ICP-MS/MS and the mass fractions of the selected pollutants were calculated. This contribution will provide a first insight into the data collected from the sampling campaign in April 2023, which includes data on the inorganic pollutants in two of the three compartments (water and sediment) ranging from level of quantification (LOQ) to 310 ± 90 µg kg-1 up to 35.9 ± 2.3 mg kg-1 to 162 ± 8 mg kg-1 for Hg and Zn, respectively. Furthermore, the planned work and method development for the determination of organic pollutants by means of QuEChERS extraction and GC-MS/MS and laboratory experiments to investigate the pollutant pathways in case of changes in pH, SPM concentration or salinity as well as the benefits of the interdisciplinary cooperation project for sediment management and the understanding of pollutant distribution in the Elbe Estuary are presented.

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Using ICP-MS/MS to study the impact of offshore wind farms on the marine environment.

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The demand for renewable and independent energy sources in Europe gained high attention during the last years. Within this context, offshore wind farms (OWF) are a key technology towards a sustainable future and a decreased use of fossil fuels. The harsh conditions, to which OWFs are exposed, require the use of corrosion protection systems, such as coatings and/or galvanic anodes. Galvanic anodes are made of AlZnIn alloys and contain different other elements as supplement or contamination (e.g., Ga, Cd, In, Pb), whose possible release and impact on the marine environment is not sufficiently understood yet.

In collaboration with the German Federal Maritime and Hydrographic Agency the OffChEm and its successor project OffChEm II aimed on the study of potential impacts of corrosion protection by galvanic anodes. Al based galvanic anodes contain significant amounts of different toxicological relevant trace metals such as Cd (>0.255 mg kg^{-1}), Pb (>6.7 mg kg^{-1}), and Zn (>26200 mg kg^{-1}) aside other supplements like Ga (>78.5 mg kg^{-1}) and In (>143 mg kg^{-1}), therefore a special focus was set on the analysis of these previously proposed tracers by Reese et al. (2020) [1].

This contribution presents the first results from a large-scale investigation (2016-2022) of sediment samples from OWFs within the German North Sea. Sediment samples were digested following the protocol of Zimmermann et al. (2020) [2] and analyzed via ICP-MS/MS using different reaction/collision cell modes (no gas, He, N_2O, H_2, H_2 HMI) for mass fractions of 68 elements. For the first time data on sediment mass fractions of Ga and In within OWFs of the German Bight are determined. Mass fractions of the proposed tracer elements are predominantly within the range of the known variability of the North Sea. Some Cd and Pb mass fractions are above the reference values of 0.08 mg kg^{-1} - 0.87 mg kg^{-1} for Cd and 12 mg kg^{-1} - 182 mg kg^{-1} for Pb, indicating locally elevated mass fractions. Ga and In mass fractions range between 8.6 mg kg^{-1} ± 0.5 mg kg^{-1} and 27 mg kg^{-1} ± 14 mg kg^{-1} and 65 µg kg^{-1} ± 9 µg kg^{-1} and 270 µg kg^{-1} ± 30 µg kg^{-1}, respectively. This results in median mass fractions of Ga and In in good accordance with data published by Klein et al. (2022) [3]. Overall, this study shows that 13 years after the operational start of the first OWF within the German Bight no significant release of Cd, Pb, Zn, Ga and In from OWF corrosion protection systems into marine sediments is measurable so far. However, the used galvanic anodes will continuously release metals and are therefore a source of contamination that needs to be monitored further. Within the context of general precautionary principles as well as the drastically changed targets in terms of the future numbers of installed OWFs in either German but also EU waters the potential environmental impacts of such a large scale Experiment has to be further investigated to avoid any unwanted side effects on the long term.

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Greenness of analytical methods for the study of metal-containing nanoparticles in complex matrices

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Nanotechnology is still an emerging field and applications of metal-containing nanoparticles (MNPs) in all day products are widely spread. However, knowledge of their possible impact on human health is still not comprehensive. Lately, concerns on their safety have led to stricter regulations including the ban on TiO2-NPs for the use in food by 2022. Therefore, analytical methods for MNP analysis in food and personal care products – as possible sources of human exposure – as well as in biomedical samples to study potential accumulation and effects, are required. Yet, no standard methods are defined and a broad variety of analytical methods has been proposed in literature. Apart from analytical performance of these methods, greenness will play an important role when it comes to provision of standard methods suitable for monitoring of MNPs. A guideline for the development of sustainable analytical methods are the 12 principles of green analytical chemistry (GAC) proposed by Gałuszka et al. [1] in 2013. Since then, several approaches have been developed to evaluate and rate the greenness of analytical methods. In this work, we evaluated greenness of methods for MNP analysis in biomedical samples, food and personal care products that were published within the last 10 years in peer-reviewed journals in English language. Greenness metrics Analytical GREEnness calculator AGREE [2] and AGREEprep [3] were applied to a selection of 30 individual methods and analytical performance of 9 methods is discussed in comparison to greenness. AGREE summarizes the result in an easily understandable pictogram and is the only approach that considers each of the 12 principles of GAC separately. Moreover, as sample preparation is often the most time- and reagent-consuming part of the analytical procedure, we also applied AGREEprep to score greenness. It is an analytical greenness metric for sustainability evaluation of sample preparation procedures which utilizes the same rating and type of pictogram as well as similar criteria as AGREE. Our evaluation revealed no correlation between size detection limits and AGREE values. Nevertheless, issues that potentially help improving sustainability of methods for MNP analysis are presented as well as tips that might help researchers to rank their approaches to reported scores.

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Abstract PhD-10, Oral presentation

HR-CS-GFMAS for PFAS analysis - an optimized method for fluorine sum parameters

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Per- and polyfluorinated alkyl substances (PFASs) are a group of several million individual compounds [1]. Several PFASs are extremely persistent, bioaccumulative and toxic [2]. The analysis of PFASs is challenging because of their various chemical and physical properties as well as the high number of compounds. Target-based approaches (e.g., LC-MS/MS) are limited to the availability of analytical grade standards and are not suitable for the analysis of new/unknown PFASs and transformation products. Therefore, PFAS sum parameter methods become increasingly important to indicate realistic PFAS pollution levels.

For the instrumental analysis of such sum parameters, a fluorine selective detector is needed. In our study we used high resolution-continuum source-graphite furnace molecular absorption spectrometry (HR-CS-GFMAS) which is a sensitive and highly selective tool for fluorine determination. The method is based on the in situ formation of diatomic gallium-mono fluoride (GaF) in a graphite furnace at a temperature of 1550°C. The molecular absorption of GaF can be detected at its most sensitive wavelength at 211.248 nm providing limits of quantification of β(F) 2.7 µg/L [3].

Here, we present an improved method for the determination of PFASs using HR-CS-GFMAS via GaF detection. The optimized method includes a modifier dry pretreatment step using a mixture of Ga, Mg, Pd and Zr and a correction measurement using perfluorooctanoic acid. The combination of both resulted in increased accuracy and precision as well as overall lower detection limits. Furthermore, during optimization the influence of species-specific responses during HR-CS-GFMAS analysis was reduced resulting in a more accurate determination of fluorine sum parameters. To validate the method instrumental standard recoveries and matrix effects were evaluated.

Innovative aspects

· Highly sensitive and selective method for fluorine/PFASs analysis based on HR-CS-GFMAS

· Increased accuracy for the determination of EOF

· Reduction of PFAS species-specific responses by optimized modifier conditions

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Per – and polyfluoroalkyl substances in wild boars

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Wild boars have been reported as bioindicators for per- and polyfluoroalkyl substances (PFAS) in a variety of studies. However, data about PFAS levels in wild boars from sites with limited industrial and general human activity is scarce. In this study, wild boar organs from Šumava National Park (Czech Republic) were used as bioindicators for PFAS pollution. 29 liver and 24 kidney samples were investigated using high performance liquid chromatography with electrospray ionisation tandem mass spectrometry (HPLC-ESI-MS/MS) and combustion ion chromatography (CIC) for targeted PFAS, total – and extractable organic fluorine content (TF and EOF). Additionally, direct total oxidisable precursor assay (dTOPA) was used to estimate the amount of precursor PFAS in the organs. Perfluoro carboxylic acids between C4 and C7 and perfluorooctansulfonic acid (PFOS) were detected in more than 50% of the samples, while dTOPA showed that the amount of precursor PFAS is minimal. PFOA and PFNA levels are one order of magnitude higher than in a background contamination site from northeastern Germany. The dominance of PFCAs over PFSAs indicates that atmospheric deposition might be the main PFAS source in the national park. The elevated concentration of PFCAs may indicate differences in biomagnification for different habitats or an unidentified PFAS source in proximity to the national park.

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Exploring the Potential of Single Particle ICP-MS for the Analysis of Nanoparticles in Organic Solvents

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In recent years, single particle ICP-MS (spICP-MS) has been established as an additional method for the analysis of nanoparticles (NP). The use of spICP-MS allows both a versatile characterization of NPs with respect to their size, composition, and concentration as well as the discrimination between intact NPs and dissolved ionic species in one measurement. Most applications of spICP-MS have been limited to the study of aqueous systems. However, a large proportion of engineered NPs are synthesized and stored in organic solvents, or naturally occurring NPs can be found in organic solvents which can be challenging to analyze using ICP-MS.

To address this challenge, a series of analyses were performed comparing spICP-MS analysis of citrate-stabilized gold nanoparticles (AuNPs) in organic and aqueous solvents using a quadrupole ICP-MS equipped with three different sample introduction systems: a scott spray chamber, a two-stage desolvation system, and a total consumption spray chamber. These systems were evaluated in terms of their signal intensity, sensitivity, and transport efficiency.

Using the Scott spray chamber, the sensitivity of AuNPs in water was 2.65 times larger than in acetonitrile (MeCN). However, by using the total consumption nebulizer system or the two-stage desolvation system in combination with lower sample flow rates, it was possible to reduce and optimize the oxygen flow. Thus, the sensitivity for MeCN could be increased almost to the same level with water, accompanied by an increased linear range.

Building on these results, it is possible to extend the optimized system to the characterization of other nanoparticles dispersed in organic solvents including the analysis of magnetite nanoparticles as potential impurities in process chemicals of importance to the semiconductor industry, as isopropyl alcohol and xylene, to demonstrate the capability of the spICP-MS analysis in organic solvents.

Evaluating the Biogenic Production of Selenium Nanoparticles by Edible Mushrooms

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Selenium (Se) is considered an essential element in human diet which compounds have been reported as antimicrobial, antioxidant and anticarcinogenic agents. The non-uniform distribution of it in soils worldwide has resulted in selenium deficiency in the diets of many populations, which has been related to health problems such as increased risks of cancer development [1]. Thus, selenium dietary supplementation turns to be a key and interesting endeavor for research.

Among different Se compounds, selenium nanoparticles stand out due to their particular physicochemical characteristics which grant them lower toxicity and greater bioavailability, among others. Specifically, biogenic SeNPs, which are synthesized by biological systems such as plants, bacteria, or fungi, present a greater biocompatibility and stability compared to those chemically manufactured [2]. Furthermore, their biological origin can confer them special behavior and physiological properties. This can grant them great relevance from a biomedical point of view and represents a clear advantage for dietary fortification aims. Thus, in this work, two different species of edible mushrooms, *Ganoderma lingzhi* and *Pleurotus ostreatus*, cultivated in a selenite enriched medium, have been studied as potential biogenic nanoparticulated selenium producers.

For the determination of the presence and characterization of biogenic nanoparticles in biological systems, different analytical techniques can be employed. Among them, single particle analysis by ICP-MS (SP-ICP-MS) has been suggested and principally allows the characterization of the mass of selenium in individual nanostructures [3]. Then, after an optimization of the extraction method to isolate the nanoparticles following different strategies, SP-ICP-MS was applied in this work to address the presence, characteristics, and number concentration of SeNPs in the mentioned fungi samples. Additionally, high performance liquid chromatography coupled to ICP-MS (HPLC-ICP-MS) and transmission electron microscopy (TEM) were employed as complementary techniques for a complete characterization.

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Determination of diffusion inside ionomeric membranes with micro XRF

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Polymer electrolyte membranes (PEM) are commonly used in Vanadium redox flow batteries (VFB) as separators of the half-cells. VFB's are promising candidates for large scale stationary storage of renewable energy. The most common PEM is Nafion™, but this membrane has a poor ion selectivity and allows V -diffusion. Understanding and measuring the diffusion of the V-species in the membrane is important to improve the materials and theoretical models of these. The diffusion coefficients (D) known to literature spread over a large range between 10^{-10} - 10^{-12} m^2 s^{-1}. These values are all determined at different conditions and with different methods which are mainly based on investigations of the electrolytes and not the Vanadium inside the membrane.

In this work we present an in situ approach on the determination of D´s of V-species inside Nafion™ 117 with micro-XRF analysis. Another aspect of this work is the successful transfer of synchrotron based micro-XRF diffusion coefficient determination to lab-based setups. Lab-based approaches are much more affordable and accessible compared to synchrotron studies.

The measured concentration profiles were evaluated with two different approaches. Both methods are based on one dimensional diffusion in a semi-infinite solid and the calculations are derived from FICKs second law. The measured concentration profiles can be described with a step profile based on an error function. Jakes et al. used the width at the half maximum of the concentration profile as mean square displacement (MSD) [1]. Malhotra et al. solved FICKs law to obtain a D for every measured line scan [2].

Synchrotron-radiation (SR) based measurements were done in *through plane* orientation [3]. The lab-based experiments were realized in in plane direction. The applicability of the MSD approach shows no dependency of the wetting time of the membrane in the V-electrolyte. The second method is suspected to have deviating results for wetting times longer than 4 hr. The values of the D for the V-species are comparable between the two evaluation methods in the range of 9 -22 · 10^{-12} m^2 s^{-1}. With wetting times of 4 hrs, it is recognizable that the D of V(III) is 44% smaller than with wetting times of 8 hr. The results of the SR-based measurements, with wetting times in the range of minutes are at 2% of the value with 8 hrs. This decline in the D is suspected to be connected to the V-concentration inside the membrane.

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Mirco X-ray fluorescence spectrometry for quantitative and distribution analysis of metals in POMbranes

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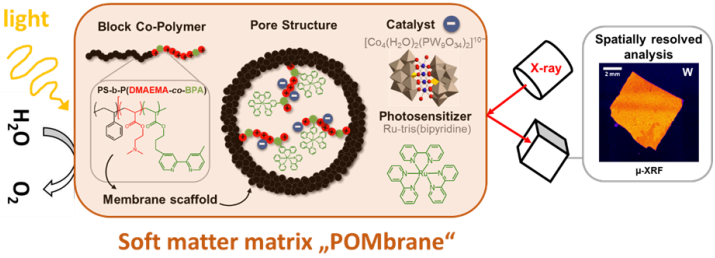

An attractive and renewable energy strategy is the light-driven catalytic splitting of water to produce solar hydrogen and/or oxygen. Here, a photocatalytic soft matter system is considered that consists of a block copolymer membrane functionalized with a polyoxometalate (POM) catalyst (CAT) and a photosensitizer (PS). These so-called "POMbranes" hold great potential for the conversion and storage of solar energy [1].
The development of such artificial photocatalytic systems involves thorough characterisation and testing of functionality [2]. Besides the determination of the catalytic activity as well as other aspects, the POMbranes have to be analysed with regard to loading, homogeneity and stability of CAT and PS. For this purpose, two-dimensional micro X- ray fluorescence spectrometry (2D µXRF; M4 Tornado (Bruker Nano GmbH, Berlin, Germany)) seems ideal. µXRF bears the possibility of non-destructive elemental determination in different kind of samples with areas of up to several cm^2. For the measurements a specially designed set up is developed to make in situ analysis of wet membranes possible. Additionally, to enable thickness determination of membranes and quantification of elements of interest in the membranes using µXRF, suitable calibration strategies are investigated.

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The Potential of Mid-Infrared Spectroscopy and LIBS for Characterization of Soil Quality Parameters

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The quality of soil plays a crucial role to achieve the largest possible harvest. Therefore, the determination of soil quality parameters is essential. In addition to soil nutrients and soil moisture, the organic matter (humus) essentially determines soil fertility. Soil organic matter is not only important for fertility, but also as a conversion place for greenhouse gases. The soil stores carbon in humus and thus forms the largest terrestrial sink for carbon dioxide. A report on changes in stocks of organically sequestrated carbon in agricultural and forestry soils is of great interest [1].

Due to the inhomogeneous composition of arable land in terms of chemical, physical and biological properties, characterization of the most important soil parameters with high spatial resolution is required in order to avoid negative consequences from overfertilization. Instead of performing time-consuming sampling, the concept of precision farming is based on capturing heterogeneities and specifically targeting differences by the use of in-situ sensors.

This work focuses on two techniques with the potential of in-situ analysis of soil quality parameters. IR spectroscopy offers the possibility of predicting soil type and binding forms of soils nutrients [2]. Reflection techniques, which involve the detection of reflected radiation, require little to no sample preparation and spectra are obtained within a few seconds. These are the main advantages of IR spectroscopy that enable field application. This work describes IR investigations of soil samples using ATR technology (attenuated total reflection) in the mid-IR range (4000 - 400 cm-1). Attention was paid to the development of a method for determining soil moisture. A fast and direct method for the analysis of solids is required for the direct characterization of element contents. As a robust solid sample method, the Laser-induced breakdown spectroscopy (LIBS) is found to be qualified [3]. In our work a prototype LIBS setup is used to determine element contents in soil profiles under laboratory conditions and a prototype LIBS setup for in-situ field measurements is developed.

The superordinate aim is to combine LIBS and IR spectroscopy in an appropriate way and correlate these techniques to get comprehensive information of soil quality parameters. By attaching them to farming vehicles for online characterization the analyzation process can be accomplished directly in the field in the future.

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Specific Extraction of Bioavailable Proanthocyanidins from Grape Seed Extracts by Molecular Imprints

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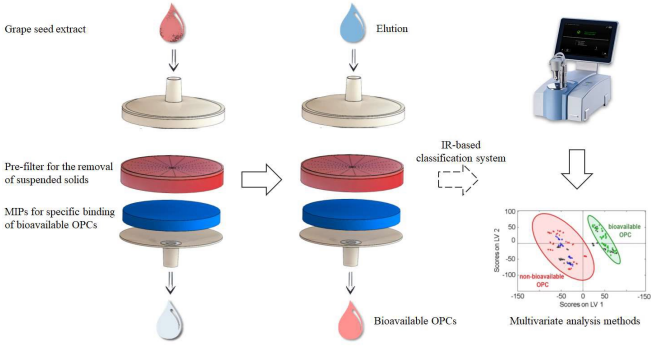
As tailored artificial receptors for molecular recognition, so-called molecularly imprinted polymers (MIPs) have the potential to efficiently purify complex proanthocyanidin-rich grape seed extracts and specifically enrich the health-promoting and bioavailable oligomeric proanthocyanidins (OPCs) thereof. This research presents initial investigations into the development of MIPs as cartridge inserts to extract antioxidant phytochemicals. The goal is to produce blends enriched with low-molecular-weight OPCs, as they are known for their high bioavailability. Due to its wide commercial availability, the proanthocyanidin monomer (+)-catechin was used as a model template for low-molecular-weight OPCs in a non-covalent imprinting strategy. Incubation studies revealed that the MIPs exhibit a significantly higher binding capacity for catechin than the non-imprinted control polymers. After optimization, the preparation method needs to be transferred to other low-molecular-weight OPCs of interest. Using the resulting MIPs in sample preparation, a classification system based on infrared spectroscopy combined with multivariate analysis methods will be developed in the future. This method should allow the straightforward and reproducible detection of grape seed extracts with predominantly bioavailable OPCs.



Detection of Thin-Film Contaminants at Metal Surfaces via PM-IRRAS

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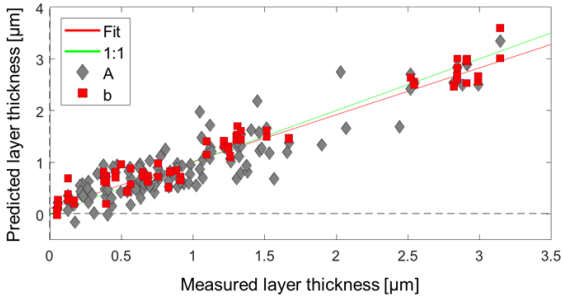
In metal industry, rolling steps are essential for further processing of metal sheets. Using high temperature and pressure, the sheet thickness and formability is modified to ensure optimum readiness for later use. To prevent friction during processing, lubricants or hydraulic oils are applied. However, these organic agents frequently remain at the metal surface, which may affect further processing steps. Hence, residues remaining at the surface should be detected immediately in order to reduce production errors. While monitoring of contaminants is apparently relevant, currently used methods are limited owing to their reduced surface sensitivity.[1–3]

Herein, a solution for the quality control of aluminum surfaces using photonic techniques is demonstrated based on polarization-modulation infrared reflection-absorption spectroscopy (PM-IRRAS). Within this study, a database was generated comprising experimental PM-IRRAS spectra, mass, and thin-film thickness. In combination with multivariate data evaluation strategies, several lubricants at aluminum surfaces were identified and quantified. The obtained results demonstrate the potential of this approach for at-line contamination monitoring of aluminum surfaces during rolling processes and even for roll-finished surfaces.[1]

Figure 1: Multivariate calibration model for the determination of thin-film contamination thicknesses at metal sheet surfaces.



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Revolutionizing Diclofenac Sodium Salt Quantification: Molecularly Imprinted Polymers for Preconcentration Facilitating On-Line IR-ATR Analysis in Aqueous Matrices

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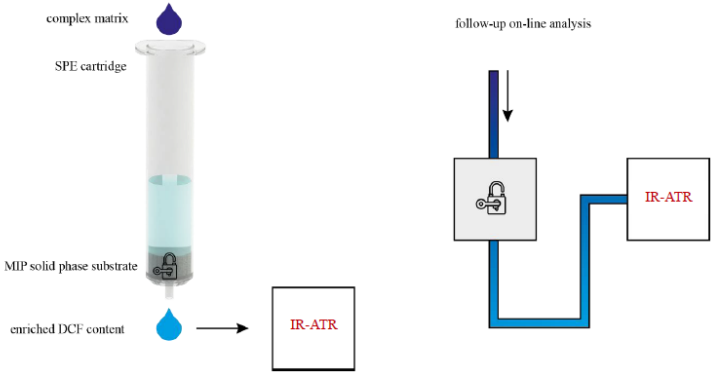
In the pursuit of precise quantification of diclofenac sodium salt (DCF) in aqueous matrices, we introduce an approach that leverages molecularly imprinted polymers (MIPs) for selective enrichment prior to analysis. DCF - a widely used nonsteroidal anti-inflammatory drug – frequently finds its way into aquatic environments posing risks to aquatic life and potentially entering drinking water sources. Monitoring its presence is vital for both environmental protection and human health considerations. With DCF concentrations often in the microgram per liter range, there is a need to amplify and preconcentrate the analyte prior to on-line quantification via infrared attenuated total reflection spectroscopy (IR-ATR). In this study, molecularly imprinted solid phase extraction (MISPE) is conceptually tested during laboratory.

The overarching goal is to facilitate the analysis of samples sourced from diverse environments including but not limited to, e.g., sewage treatment plants for the presence of DCF. By leveraging selective DCF enrichment capabilities of correspondingly synthesized MIPs, we aim at achieving target concentrations amenable for on-line IR-ATR analysis.



Characterization of functionalized polymer microparticles using single particle inductively coupled plasma mass spectrometry

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Single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) is a well-established tool for the analysis of metal nanoparticles. However, the application of sp-ICP-MS to the analysis of polymer-based microparticles, which are critical to the environment and important technical products, is challenging. Major limitations are the low sensitivity of carbon in the ICP, the lack of available certified reference materials and the low transport efficiency of micrometer-sized particles from the suspension into the plasma.

This study presents methodology for the heteroatom-based analysis of polymeric particles in sp-ICP-MS. A series of polymeric cation-exchange particles with adjustable properties is analyzed using diverse sample introduction techniques to enable a broader set of applications [1,2].

Microparticles with a diameter of 4 and 10 µm are detected by using both covalently attached heteroatoms and electrostatically labeled metal cations. Barium cations improve sensitivity compared to the direct detection of sulfur and are found to be the optimal metal tag due to the high affinity to the polymeric particles. Transport efficiency is optimized using infrared heating of the sample introduction system, whilst flow injection facilitates the ease of measurements and data evaluation. As proof of concept, the homogeneity and degree of particle functionalization is determined for a series of resins. Results are compared to reference data obtained from microscopy and combustion ion chromatography experiments.

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Method development for direct elemental analysis of lithium ion battery materials by means of ETV-ICP-OES

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In the last three decades, lithium ion batteries (LIBs) have undergone an impressive development and are an integral part of our modern society through their use in portable consumer electronics and the emerging electromobility. The overall aim of achieving higher energy densities and lower material costs has led to the continuous development of new cell chemistries, specifically adapted to the various applications.[1] However, the LIB still suffers from capacity loss due to several aging mechanisms while cycling and storage. The electrolyte is not stable at the occurring electrode potentials and forms passivating layers on anode and cathode, the so called solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI), respectively. These interphases consist of various inorganic lithium salts as well as organic carbonates and phosphates. Structural instability of the cathode active material (lithium transition metal oxide) leads to dissolution of Ni, Co and Mn, which deteriorate the SEI and lead to irreversible lithium loss on the anode. [2]

Elemental analysis, particularly inductively coupled plasma-optical emission spectroscopy (ICP-OES), plays a crucial role in deciphering these aging mechanisms. High requirements are placed on the analysis system for the simultaneous quantification of elements in different concentration ranges from sup-ppm to several percent with high matrix loads. Direct elemental analysis of LIB materials by coupling electrothermal vaporization (ETV) to ICP-OES offers distinct advantages over conventional microwave-assisted digestion approaches. By avoiding the time-consuming and labor-intensive digestion step, analysis time can be significantly reduced, which is accompanied by less risk of cross-contamination and a potential gain in sensitivity and accuracy.[3] Regarding LIB samples, cathode coatings and dopants of compounds like SiO2 and ZrO2 or silicates in anode materials are hard to digest, where direct sample introduction by thermal vaporization could be beneficial. Furthermore, temperature programming might offer possibilities for speciation analysis of the SEI.

Aged anode samples from $Li_1Ni_{0.8}Mn_{0.1}Co_{0.1}$ NMC811||artificial graphite + 10 % SiOx and NMC111||artificial graphite cells were analyzed regarding there Li, Ni. Mn and Co content as well as possibilities for SEI speciation. Method development for the analysis was performed on an ETV (ETV 4000c, Spectral Systems, DE), equipped with an autosampler (AD-50-III, Spectral Systems, DE), which was directly coupled to an ICP Spectrometer (ARCOS, Spectro Analytical Instruments, DE). Sulfur hexafluoride was used as modifier gas. External calibration of the instrument was performed using liquid standards (LabKings B.V., NLD), synthesized matrix-matched standards or certified reference materials, while the Ar 763.5 nm line was used for internal standardization. The analytical performance of the developed method was evaluated by comparison to microwave-assisted ICP-OES and total reflection X-ray fluorescence (TXRF) measurements. As very high lithium contents in the samples had an influence on the plasma conditions, further preliminary experiments using solid sample dilution and dilution of the sample gas flow by an additional sheath gas were performed.

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Implementation of Single Particle ICP-OES to Quantify the State-of-Charge of Lithium-Ion Battery Active Materials

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Since its first introduction in consumer products by Sony in the 1990s, the lithium-ion battery (LIB) has become the most widely used electrochemical energy storage system in the world. Nowadays LIBs are used in portable consumer electronics as well as electric vehicles to overcome fossil fuel based internal combustion engines and reduce greenhouse gas emissions. Consequently, large efforts in scientific research have been made to increase the energy density, cycle as well as calendar life and reduce potential safety hazards of this cell system. Therefore, it is essential to gain an understanding of the redox processes of the cathode active material (CAM) that occur during operation of the battery cell. At the nano- to microscale of the CAM, local inhomogeneities of the electrode, properties of the active material and aging phenomena after prolonged cycling of the cell, can influence such redox processes. Consequently, local inhomogeneities in the state-of-charge (SOC) can emerge, reducing the capacity of the cell and accelerating the aging processes.

To quantify the SOC at this length scale, single particle inductively coupled plasma optical emission spectroscopy (SP-ICP-OES) can be used for the investigation of individual CAM particles.1 For this, the spend battery cell will be opened after cycling, followed by separation of the electrodes and delamination of the CAM from the current collector. Subsequently, the active material is deagglomerated and directly injected into a gravitational counter-flow classifier which is connected to the ICP system. In between the classifier and ICP, a flow-cell particle analyzer (FPA) is located for size-dependent monitoring of the particle number concentration (PNC) that is introduced into the plasma. As the used SPECTRO ARCOS system offers a sampling rate of 10 Hz with a dwell time of 100 ms, high PNCs would lead to multiple particle events in the plasma. By calculating the possibility of multiple particle events using Poisson statistics, time periods of high PNCs can be discarded for the subsequent data analysis. After introduction of the particles into the plasma, simultaneous element-specific analysis of the CAM can be performed.

In this work nickel-rich lithium transition metal oxides with the general formula of $Li[Ni_{0.8}Mn_{0.1}Co_{0.1}]O_2$ are used. For this kind of active material, the Li 670.776 nm to Ni 231.604 nm intensity ratio of the analyzed particles can be determined. To then estimate the SOC of the particles, a matrix-matched external calibration is needed. Therefore, the CAM is delithiated to approx. 20%, 40%, 60% and 80% SOC, resulting in decreasing Li/Ni intensity ratios as the charge state increases. By applying this method, a large quantity of CAM particles from spend battery cells can be analyzed to gain statistical data on the SOC distribution. This was done after cycling in the voltage range of 3.0 to 4.4 V at moderate charging rates of 0.5 C until cell failure, revealing SOC heterogeneities which potentially originate from aging phenomena of the active material.

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Isotopic and Elemental Screening Analysis of Biofilm on Microbiologically Influenced Corrosion on Using LASS-MC-ICP-MS/ICP-ToF-MS/HR-ICP-MS

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Microbiologically influenced corrosion (MIC) is the microbial modification of the chemical environment at the metal surface, causing accelerated corrosion of metals [1, 2]. Rapid corrosion of iron and steel is linked to microbial processes in soil, fresh water, sea water, crude oil and its derivatives, process chemicals and wastewater. It has been reported to cause 20% cost of the total damage due to corrosion. About 10% of corrosion cases in the UK has been attributed to microbial activities [3].

To evaluate the corrosion process, various instrumental techniques have been applied, from morphology (SEM, TEM) to electrochemistry (EN, LPR), from gravimetry to compositional chemistry (XRD, XPS) [4]. However, with the existing analytical methods, it has not yet been possible to identify the corrosion process. The aim of this project is to use a combination of laser ablation (LA) and different types of inductively coupled plasma mass spectrometry (ICP-MS) by split stream to determine spatially resolved isotope ratios and elemental fingerprint in order to elucidate the corrosion process.

Isotope ratios provide not only valuable information of origin and distribution of elements, but also about reaction processes and their timeline. Changes in isotopic compositions have seldom been explored in materials science. Nevertheless, a few studies, which rely solely on bulk analyses with MC-ICP MS and prior wet-chemical sample processing, have revealed remarkable findings, such as the differentiation between electrochemical and microbiologically influenced corrosion through the Fe isotope ratio [5]. However, no information about process sequences and local differences, which are important for process description. Using the laser ablation system with MC-ICP-MS makes it possible to determine isotope ratios in-situ. What's more, investigating what extent MIC leads to an isotopic fractionation of iron, whether the isotope fractionation changes depending on the microorganisms, or whether it differs depending on classic chemical corrosion, which enable to characterize the interaction of biological systems with metals.

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Investigation of Instrumental Isotope Fractionation in ICP-MS

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Instrumental isotope fractionation (IIF) also known as mass bias or instrumental mass discrimination, is the phenomenon which occurs in a mass spectrometer during various stages including sample introduction, ion formation, ion extraction, ion transmission, ion separation, and ion detection, leading to a deviation of the measured isotope ratio from the true isotope ratio in a sample. However, the causes of IIF are not yet completely understood and differ according to the type of the instrument. Therefore, a proper calibration or correction of isotope ratios are necessary for accurate and precise isotope ratio determinations, particularly for absolute isotope ratio measurements.

In our study, we utilize certified isotope reference materials of different elements to assess and compare the IIF in different types of ICP-MS instruments with different mass separation devices including double focusing sector field (single and multi-collector), quadrupole filter and time-of-flight ICP-MS. We investigate the experimental parameters contributing to the accuracy and instrumental precision of isotope ratio measurements. Furthermore, we evaluate different calibration approaches to achieve the highest level of accuracy and precision in the measurement results.

This research emphasizes the importance of using the appropriate correction method for IIF and demonstrates how the choice of instrumentation and calibration techniques can significantly impact the reliability of isotope data and enhance the accuracy and precision of isotope ratio determinations.

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 problems 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.

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Single cell-asymmetrical flow field-flow fractionation/ICP-time of flight-mass spectrometry (sc-AF4/ICP -ToF-MS): an efficient alternative for the cleaning and multielemental analysis of individual cells

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One of the greatest challenges in the analysis of single cells, quite often is the severe ionic background their samples exhibit. 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 effect of untreated cells' samples can be significantly reduced. As a proof of concept, commercial baker's yeast cells were analysed. Their metal content can be determined on a single cell level, for multiple elements at a time. The combination yielded promising results, with the system exhibiting the ability to effectively limit the effect of matrices as severe as 3 × 105 mg per L sodium chloride (NaCl) or 50 mg per 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 (lead, Pb, 0.1–10 mg L-1) 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 potential of the further development and optimization of this fast, robust, and effective coupling and its future applicability to numerous life-science related applications. In addition, new and versatile data treatment tools were developed, and their performance was tested against established methods.[1]

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Event venue:
BAM (Adlershof)
Richard-Willstätter-Str. 11
12489 Berlin, Germany