10th Nordic Conference on Plasma Spectrochemistry

June 12 - 15, 2022
Loen, Norway

Programme and Abstracts

1 Table of Contents

2 Welcome Letter

Dear colleagues,
On behalf of the Analytical Section of the Norwegian Chemical Society and the Organising Committee it is an honour and pleasure to welcome you to Loen and the 2022 Nordic Conference on Plasma Spectrochemistry. This conference provides both an international and regional forum by which researchers and users can share their knowledge and exchange ideas.

The plenary programme has been planned with a view of furnishing a comprehensive overview of the latest developments in this scientific field. Since some of the world's leading authorities will be present, the conference will hopefully be a stimulating forum for communication across boarders and between scientific disciplines.

In contrast to other plasma spectrochemistry meetings, short tutorial courses will be offered to all participants during the three and a half day meeting which may be attractive to participants who can learn about or to be updated on plasma spectrochemistry and applications. This concept is meant to stimulate especially Nordic users of plasma-based techniques to learn more about theoretical and practical issues as well as to obtain specialists recommendations for method improvements.

We know that the natural beauty of the area will captivate you, but we also hope that the conference excursions, social events, and outdoor farewell dinner may complement the scientific endeavours. We promise you an exciting and memorable conference and stay in Loen!

On behalf of the Organising Committee

Yngvar Thomassen
Chairman

3 Organising and Scientific Committee

Yngvar Thomassen (Chairman), National Institute of Occupational Health, Oslo and
Norwegian University of Life Sciences, Ås, Norway
Elin Gjengedal, Norwegian University of Life Sciences, Ås, Norway
Balazs Berlinger, University of Veterinary Medicine, Budapest, Hungary
Ivar Martinsen, GE Healthcare, Oslo, Norway
Arne Åsheim (Exhibition coordinator), 3A pro analysi, Porsgrunn, Norway
Oddvar Røyseth (Treasurer), Røyseth AS, Oslo, Norway
Jens Sloth, Technical University of Denmark, National Food Institute, Denmark
Ari Väisänen, University of Jyväskylä, Finland

4 General Information

Conference Desk

The conference desk is situated in the conference foyer of Hotel Alexandra. It will operate as follows:

Saturday	June 11	15:00 - 18:00
Sunday	June 12	07:30 - 08:15
Monday	June 13	07:30 - 08:00
Tuesday	June 14	07:30 - 08:00
Wednesday	June 15	08:30 - 09:00

Participants are requested to register as soon as possible upon arrival to the conference venue, Hotel Alexandra, Loen.

Conference Venue

All oral and poster sessions will be held in the various auditoriums of Hotel Alexandra.

Tel: +47 57 87 50 00 Fax: +47 57 87 50 51 Email: alex@alexandra.no
Homepage: www.alexandra.no

Meals

Participants staying at Hotel Alexandra are served breakfast, lunch and dinner (all included in their accommodation package).

5 Social Programme

Saturday, June 11, 17:00 - 19:00 Informal get-together in the Hotel Alexandra Bath & Spa

All delegates and accompanying persons are invited to enjoy the heated outdoor swimming pool and refreshments. *This event is kindly sponsored by PerkinElmer.*

Sunday, June 12, 14:00: Half-day excursion to Geiranger

This tour encompasses a mountain plateau above the tree and snow lines, the summit of Dalsnibba (1746 m), and a sail of 25 km along the spectacular Geirangerfjord.

Sunday, June 12, 14:15: Guided walk to Bødal Glacier

On the Bødal Glacier in Loen Valley you can enjoy a genuine walking experience in beautiful West Norwegian surroundings. The whole trip, rated a moderately difficult hike, takes from five to six hours.

The Bødal Valley, with the Bødalseter summer pasture farms and the Bødal Glacier, is one of the gems of the Jostedalsbreen National Park. Take a rucksack, clothes, food and drink for a half day walk. Good strong mountain boots will be an advantage.

Sunday, June 12, 14:15: Mountain hiking for fit spectroscopists: The Skåla Challenge

Those who want to challenge the Norwegian mountains after lunch may climb to the Klaumann Tower at Skåla Mountain. This is the hardest uphill walk in entire Norway, approx. 1800 m straight up. Presently there is much snow above 1000 meters. Hikers are advised to bring appropriate footwear and clothing for this walk. Free of charge, but we promise; you will sweat!

Sunday, June 12, 14:15: Loen Skylift

Loen Skylift is a spectacular attraction and adventure arena in the inner part of the Nordfjord. A cable car will lift you from the fjord to 1011 m above sea level. Here you can enjoy the views of the fjord landscape – from the restaurant table, or while exploring in the mountains.

Monday, June 13, 21:30: Bring your own wine to the poster viewing and wine tasting

The cork fee charged by the hotel to allow you to bring your own wine is kindly sponsored by *Agilent Technologies and Matriks AS.*

Tuesday, June 14, 16:30: Excursion to the Briksdal Glacier with a conference outdoor dinner

You are invited to visit the heart of Norway - an **Unforgettable** trip to the Briksdal Glacier. Participants can enjoy a walk to view the enormous cascade of ice where you will be able to test the best aquavite in the world; *Gilde Aqua Ultra Plus*, or the local *Loen Apple Juice* sponsored by *HolgerHartmann/Milestone.*

Afterwards there will be the famous outdoor barbeque at "Kleivane" (weather permitting - otherwise the grill party will be held at Briksdalen Inn).
The well-known Norwegian gourmet chef Frode Aga will once again be in charge of the kitchen to ensure your best outdoor food experience.
This event is kindly sponsored by Shimadzu, Thermo Fischer Scientific, NU and HolgerHartmann/Milestone.

6 Scientific Programme

Oral presentations
Invited plenary lectures and submitted oral contributions will be 25 and 15 minutes in length, respectively (including discussion).
Video projectors will be provided in all lecture rooms.

Posters
The posters should be mounted early Sunday morning June 12, in the poster area located next to the lecture room. Materials for poster mounting are available either from the conference desk or in the poster mounting area.

Language
The working language of the conference is english.

7 Liability

The Organising Committee declines any responsibility whatsoever for injuries or damages to persons or their property during the conference.

8 Sponsors and exhibitors

The conference is sponsored by:

The Research Council of Norway

matriks KJEMISK TEKNOLOGI

Agilent Technologies

The exhibition of scientific instrumentation, literature and consumables is located next to the auditorium at the first floor.

The following companies have registered for display and demonstration:

Holger Hartmann AS / Milestone
Houm AS
LAB Norway AS
Matriks AS/Agilent Technologies
Nu Instruments
Perkin Elmer
Shimadzu Europa GmbH
Thermo Fisher Scientific

9 Correspondence after the conference

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National Institute of Occupational Health
Gydas vei 8, N-0033 Oslo, Norway
Tel: +47 23 10 53 20 +47 99 51 05 21
E-mail: Yngvar.Thomassen@stami.no

10 Schedule of events

Saturday, June 11, 2022	
15:00 - 18:00	**Registration**
17:00 - 19:00	**Informal get-together in the Hotel Alexandra Bath & Spa** This event is kindly sponsored by PerkinElmer
From 19:00	**Dinner**

Sunday, June 12, 2022	
07:30 - 08:15	**Registration**
08:00 - 08:15	**Welcome and opening remarks**
08:15 - 10:05	**Plenary session I: Progress in plasma spectrochemistry** **Poster viewing and exhibition**
10:05 - 10:20	**Coffee break, poster viewing and exhibition**
10:20 - 13:00	**Plenary session I continues: Progress in plasma spectrochemistry** **Poster viewing and exhibition**
13:00 - 14:00	**Lunch**
14:00 -	**Excursion to Geiranger, The Skåla Challenge, Loen Skylift and guided walk to Bødal Glacier**
From 19:00	**Dinner**

<table>
<tr><th colspan="6">Monday, June 13, 2022</th></tr>
<tr><td>08:00 - 09:45</td><td colspan="5">Plenary session II: Bio-imaging and speciation
Poster viewing and exhibition</td></tr>
<tr><td>09:45 - 10:05</td><td colspan="5">Coffee break, poster viewing and exhibition</td></tr>
<tr><td>10:05 – 12:55</td><td colspan="5">Plenary session II continues: Bio-imaging and speciation
Poster viewing and exhibition</td></tr>
<tr><td>13:00 - 14:15</td><td colspan="5">Lunch</td></tr>
<tr><td>14:15 - 15:45</td><td colspan="5">Plenary session III: Applications of plasma spectrochemistry
Poster viewing and exhibition</td></tr>
<tr><td>15:45 -16:00</td><td colspan="5">Coffee break, poster viewing and exhibition</td></tr>
<tr><td colspan="6">Short course session I</td></tr>
<tr><td>16:00 - 17:45</td><td>Short course A1</td><td>Short course A2</td><td>Short course A3</td><td>Short course A4</td><td>Short course A5</td></tr>
<tr><td colspan="6">Short course session II</td></tr>
<tr><td>17:55 -19:40</td><td>Short course B1</td><td>Short course B2</td><td>Short course B3</td><td>Short course B4</td><td>Short course B5</td></tr>
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From 19:00	**Dinner**
21:00	**Poster viewing and discussions with wine tasting** **(Bring your own wine)** This event is sponsored by Matriks AS and Agilent Technologies

<table>
<tr><th colspan="6">Tuesday, June 14, 2022</th></tr>
<tr><td>08:00 - 08:15</td><td colspan="5">The Nordic Plasma Torch Award</td></tr>
<tr><td>08:15 - 10:25</td><td colspan="5">Plenary Session IV: Single particle and single cell analysis by plasma spectrochemistry
Poster viewing and exhibition</td></tr>
<tr><td>10:25 - 10:40</td><td colspan="5">Coffee break, poster viewing and exhibition</td></tr>
<tr><td>10:40 - 13:35</td><td colspan="5">Plenary Session V: New analytical capabilities</td></tr>
<tr><td>13:35 - 14:30</td><td colspan="5">Lunch</td></tr>
<tr><td colspan="6">Short course session III</td></tr>
<tr><td>14:30 - 16:15</td><td>Short course C1</td><td>Short course C2</td><td>Short course C3</td><td>Short course C4</td><td>Shor course C5</td></tr>
<tr><td>16:30</td><td colspan="5">Excursion to Briksdal Glacier and conference outdoor dinner</td></tr>
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<table>
<tr><th colspan="3">Wednesday, June 15, 2022</th></tr>
<tr><td>08:30 - 09:30</td><td colspan="2">Plenary Session VI: Applications of plasma spectrochemistry</td></tr>
<tr><td>09:30 - 09:45</td><td colspan="2">Coffee break, poster viewing and exhibition</td></tr>
<tr><td colspan="3">Short course session IV</td></tr>
<tr><td>09:45 - 11:30</td><td>Short course D1</td><td>Short course D2</td></tr>
<tr><td>11:30 - 11:45</td><td colspan="2">Closing remarks and farewell</td></tr>
<tr><td>12:00</td><td colspan="2">Lunch</td></tr>
</table>

11 Daily Programme

Sunday, June 12, 2022

Time	Abstr.	
08:00- 08:15		**Welcome/Opening remarks** Yngvar Thomassen, Conference chairman
		Session I: Progress in plasma spectrochemistry Chairman: Jens Sloth
08:15 08:50	O-1	**Distinguished Speaker Lecture: And Now What?** Gary M. Hieftje *Indiana University, USA*
08:50- 09:15	O-2	**New possibilities in single cell analysis via ICP-TOF-MS – Zooming into the region where materials meet environment** Björn Meermann *Federal Institute for Materials Research and Testing (BAM) – Berlin, Germany*
09:15- 09:40	O-3	**Exploring unique chemistry in plasmas and droplets to better understand the chemical origins of life** Jacob T. Shelley,[1,2,3] Brian T. Molnar,[1] Sunil P. Badal,[1] Samantha E. Pryor,[2,3] Elly A. Breves,[1,3] Julia L. Danischewski,[1] and Morgan F. Schaller[2,3] [1]*Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute,* [2]*Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute,* [3]*Rensselaer Astrobiology Research and Education Center, Rensselaer Polytechnic Institute, Troy, NY 12180 USA*
09:40- 10:05	O-4	**High-precision MC-ICP-MS isotopic analysis of essential mineral elements as a tool in biomedical research** Frank Vanhaecke, Yulia Anoshkina, Marta Costas-Rodriguez, Rosa Grigoryan, Agustina A.M.B. Hastuti, Kasper Hobin and Lana Van Heghe *Atomic & Mass Spectrometry – A&MS research unit, Department of Chemistry, Ghent University, Belgium*
10:05- 10:20		**Coffee, exhibition and poster viewing**
		Session I continues: Progress in plasma spectrochemistry Chairman: Jacob T. Shelley
10.20- 11:45	O-5	**Laser Ablation Research & Development: 60 Years Strong** Richard E. Russo *Applied Spectra, Inc., West Sacramento, CA, USA* *Lawrence Berkeley National Laboratory, Berkeley, CA, USA*
10:45- 11:10	O-6	**Improving the solution cathode glow discharge atomic emission spectrometry source through discharge-liquid interaction studies and novel instrumental approaches** Jaime Orejas[1], Nicholas V. Hazel[2], Yinchenxi Zhang[1],Cristian Soto Gancedo[1], Jorge Pisonero[1], Steven J. Ray[2] and Nerea Bordel[1] [1]*Grupo de Espectroscopia, Láseres y Plasmas, Universidad de Oviedo, Mieres, Spain* [2]*Department of Chemistry, University at Buffalo, Buffalo NY, USA*

Time	Abstr.	
11:10-11:35	O-7	**Intracellular element and nanoparticle analysis by nanoscale secondary ion mass spectrometry** Dirk Schaumlöffel and Maria Angels Subirana *CNRS/Université de Pau et des Pays des l'Adour, Pau, France*
11:35-12:00	O-8	**The LS-APGD microplasma: A versatile ionization source for elemental, isotopic and molecular species determinations** R. Kenneth Marcus, *Department of Chemistry, Clemson University, Clemson, USA*
12:00-12:15	O-9	**Thin-layer chromatography surfaces for enhanced plasma-based ambient desorption/ionization mass spectrometry** Maximilian Heide, Cristian C. Escobar-Carranza, Manuel Heinelt, Désirée A.-M. Schütz and Carsten Engelhard *University of Siegen, Department of Chemisty and Biology, Germany*
12:15-12:30	O-10	**Glow discharge-mass spectrometry in the field of lithium batteries-Overcoming challenges in method development** Malina Helling [1], Maximilian Mense [1], Simon Wiemers-Meyer [1], Martin Winter [1,2], Sascha Nowak [1] [1] *University of Münster, MEET Battery Research Center, Münster, Germany* [2] *Helmholtz-Institute Münster, IEK 12, Forschungszentrum Jülich GmbH, Münster, Germany*
12:30-12:45	O-11	**Isobaric dilution analysis as a tool for the internal quantification of ^{99}Technetium in aqueous samples** M. Horstmann[a], C. Derrick Quarles Jr.[b], S. Happel[c], A. Faust[d], U. Karst[a] [a] *University of Münster, Institute of Inorganic and Analytical Chemistry, Münster, Germany,* [b]*Elemental Scientific, Inc., 7277 World Communications Dr., Omaha, NE, USA* [c] *Triskem International, Rue Maryse Bastié, Campus de Ker Lann, Bruz, France,* [d] *European Institute for Molecular Imaging, Münster, Germany*
12:45-13:00	O-12	**High precision in-situ Rb-Sr dating using the Thermo Scientific Neoma MS/MS MC-ICP-MS** G. Craig[1], S. Dalby[1], C. Bouman[1], J. Roberts[1], N. S. Lloyd[1] and J. Schwieters[1] [1]*Thermo Fisher Scientific, Bremen, Germany*
13:00-14:00		**Lunch**
14:00		**Excursion to Geiranger, the Skåla challenge, guided walk to Bødal Glacier and Loen Skylift**
From 19:00		**Dinner**

Monday, June 13, 2022

Time	Abstr.	
		Session II: Bio-imaging and speciation Chairman: Björn Meermann
08:00-08:25	O-13	**High-resolution and high-speed imaging by LA-ICP-TOF-MS** Sarah Theiner[a], Andreas Schweikert[a,b] Oana Voloaca[c], M. Clench[c], L. Cole[c], S. Haywood-Small[c], Bernhard K. Keppler[b], Gunda Koellensperger[a] *[a] Institute of Analytical Chemistry, Faculty of Chemistry, University of Vienna, Austria,[b] Institute of Inorganic Chemistry, Faculty of Chemistry, University of Vienna, Austria,[c] Biomolecular Sciences Research Centre, Sheffield Hallam University, Sheffield, U.K*
08:25-08:50	O-14	**Quantitative bioimaging by LA-ICP-MS as a tool to study genetic disorders of the iron and copper metabolism** Michael Sperling, Jennifer-Christin Müller and Uwe Karst *University of Münster, Institute of Inorganic and Analytical Chemistry, Germany*
08:50-09:15	O-15	**ICP-MS as a workhorse to study how nanoparticles can be tailored to efficiently deliver nutrients to agricultural plants** Søren Husted *University of Copenhagen, Department of Plant and Environmental Sciences, Frederiksberg C, Denmark*
09:15-09:30	O-16	**Bioimaging of Zn and Cd in leaves of hyperaccumulator *Arabidopsis halleri* using laser ablation-inductively coupled plasma-mass spectrometry with referencing strategies** Maximilian von Bremen-Kühne[1], Hassan Ahmadi[2], Michael Sperling[1,3], Ute Krämer[2] and Uwe Karst[1] *[1]Institue of Inorganic and Analytical Chemistry, University of Münster,* *[2]Molecular Genetics and Physiology of Plants, Ruhr University Bochum,* *[3]European Virtual Institute for Speciation Analysis (EVISA), Münster, Germany*
09:30-09:45	O-17	**Elemental bioimaging for the simultaneous quantification of cisplatin and a gadolinium-based contrast agent in liver tissue** Katharina Kronenberg[1], Julia Werner[2], Peter Bohrer[2], Fabian Lohöfer[2], Rickmer Braren[2], Philipp Paprottka[2], Uwe Karst[1] *[1]University of Münster, Institute of Inorganic and Analytical Chemistry,* *[2]Technical University of Munich, Department of Diagnostic and Interventional Radiology, Faculty of Medicine, Germany*
09:45-10:05		**Coffee break, exhibition and poster viewing**
		Session II continues: Bio-imaging and speciation Chairman: Michael Sperling
10:05-10:30	O-18	**Fluorine speciation using ICP-MS: Is that necessary and useful?** Jörg Feldmann[1,2], Viktoria Mueller[1,3], Amnah Al Zbedy[2], Tengetile Nxumalo[2] *[1]TESLA-Analytical Chemistry, University of Graz, Austria* *[2]TESLA-Department of Chemistry, University of Aberdeen, Scotland* *[3]James Hutton Institute, Craigiebuckler, Aberdeen, Scotland*

Time	Abstr.	
10:30- 10:55	0-19	**Potential toxic elements and arsenic species in new aquafeed ingredients - are there concerns in terms of feed and food safety?** Veronika Sele[a], Jojo Tibon[a,b], Anne-Katrine Lundebye[a], Tore Strohmeier[a], Marta Silva[a], Robin Ørnsrud[a] & Jens J. Sloth[a,b] [a] *Institute of Marine Research, Bergen, Norway* [b] *National Food Institute, Technical University of Denmark, KGS Lyngby,* Denmark
10:55- 11:10	O-20	**Speciation analysis of arsenic in seafood and seaweed at the U.S. Food and Drug Administration** Mesay Mulugeta Wolle, Sean D. Conklin and Todor Todorov *Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, College Park, MD, USA*
11:10- 11:25	O-21	**Arsenic speciation in mesopelagic biomass – An insight into arsenic behavior during aquafeed processing** Jojo Tibon[1,2], Heidi Amlund[2], Ana I. Gomez-Delgado[1], Marc H. G. Berntssen[1], Marta S. Silva[1], Martin Wiech[1], Jens J. Sloth[1,2], and Veronika Sele[1] [1]*Institute of Marine Research, Bergen, Norway* [2]*National Food Institute, Technical University of Denmark, KGS Lyngby, Denmark*
11:25- 11:40	O-22	**Fast and automated total arsenic and arsenic speciation by inductively coupled plasma mass spectrometry** C Derrick Quarles Jr.[1], Patrick Sullivan[1], Nick Bohlim[1], Nathan Saetveit[1], Michael Szoltysik[2] [1]*Elemental Scientific, Inc., Omaha, NE, USA* [2]*Elemental Scientific Sweden, Lidköping, Sweden*
11:40- 11:55	O-23	**Occupational exposure to organotin substances: Speciation of organotin compounds in workplace air samples via HPLC-ICP-MS** T. Schwank[1*], C. Claesgens[1], K. Pitzke[1], D. Breuer[1] [1]*Institute for Occupational Safety and Health of the German Social Accident Insurances – IFA, Sankt Augustin, Germany*
11:55- 12:10	O-24	**Identification and quantification of metal complexes by isotope dilution HPLC - ICP MS / ESI MS** Katarzyna Kińska, Luluil Maknun, Katarzyna Bierla, Ryszard Lobinski. Joanna Szpunar *Institute of Analytical and Physical Chemistry for the Environment and Materials Pau, France*
12:10- 12:25	O-25	**Utilization of ICP-MS technique for investigation of bovine lactoferrin interactions with metals and characterization of respective metal-rich protein complexes** Oleksandra Pryshchepa[1,2], Katarzyna Rafińska[1,2], Adrian Gołębiowski[1,2], Agnieszka Rogowska[1,2], Philippe Schmidt-Koplin[3,4], Bernhard Michalke[4], Bogusław Buszewski[1,2], Paweł Pomastowski[1]. [1] *Centre for Modern Interdisciplinary Technologies Nicolaus Copernicus University in Torun, Poland* [2] *Department of Environmental Chemistry and Bioanalytics, Faculty of Chemistry, Nicolaus Copernicus University in Torun, Poland* [3] *Comprehensive Foodomics Platform, Chair of Analytical Food Chemistry, TUM School of Life Sciences, Technical University of Munich, Freising, Germany* [4] *Helmholtz Zentrum Muenchen, Analytical BioGeoChemistry, Neuherberg, Germany*

Time	Abstr.	
12:25- 12:40	O-26	**Challenges of ultra-trace speciation analysis of chromium in foodstuffs by species-specific isotope dilution and HPLC-ICP-MS** Petru Jitaru[1*], Marina Saraiva[1,2], Thierry Guerin[3] and Jens Sloth[2] *[1] French Agency for Food, Environmental and Occupational Health & Safety (ANSES), Laboratory for food safety, Maisons-Alfort, France,[2]National Food Institute, Technical University of Denmark, Kemitorvet, KGS Lyngby, Denmark,[3] French Agency for Food, Environmental and Occupational Health & Safety (ANSES), Directorate of Strategy and Programs, Maisons-Alfort, France*
12:40- 12:55	O-27	**Rapid speciation analysis of anthropogenic gadolinium in surface and drinking water** Marcel Macke,[1] Mathis Athmer,[1] C. Derrick Quarles Jr.,[2] Michael Sperling[1] and Uwe Karst[1] *[1] University of Münster, Institute of Inorganic and Analytical Chemistry, Germany* *[2] Elemental Scientific Inc., 7277 World Communications Dr., Omaha, NE, USA*
13:00- 14:15		**Lunch**
		Session III: Applications of plasma spectrochemistry Chairman: Balazs Berlinger
14:15- 14:30	O-28	**A metrological journey into the high accuracy determination of total arsenic in biological materials by ICP-MS** John Entwisle, Christian Ward-Deitrich, Sarah Hill and Heidi Goenaga-Infante *LGC National Measurement Laboratory, Teddington, UK*
14:30- 14:45	O-29	**Using ICP-TOFMS to significantly reduce measurement uncertainty for Pd, Pt and Rh in autocatalysts** Stanislav Strekopytov, John Entwisle, Christian Ward-Deitrich, Sarah Hill and Heidi Goenaga-Infante *LGC National Measurement Laboratory, Teddington, Middlesex, UK*
14:45- 15:00	O-30	**Evaluating multi-energy calibration as a potential tool for regulatory analysis of nutrient elements in food ICP-OES** Jake A. Carter, Patrick J. Gray, and Todor I. Todorov *Center for Food Safety and Applied Nutrition, United States Food and Drug Administration, College Park, MD, 20740, USA*
15:00- 15:15	O-31	**Rapid and accurate determination of uranium and neodymium concentrations in environmental and urine samples using standards addition HPIC-SF-ICP-MS** Nancy N. Wanna, Andrew Dobney, Mirela Vasile, Karen Van Hoecke and Ingrid Geuens *Belgian Nuclear Research Centre SCK CEN, Mol, Belgium*
15:15- 15:30	O-32	**Distribution of inorganic nanoparticles in a Norwegian fjord** Are S. Bruvold[1,2], André Marcel Bienfait[2], Torunn Kringlen Ervik[3], Katrin Loeschner[4], Stig Valdersnes[1,2] *[1]University of Bergen, Department of Chemistry, Bergen,* *[2]Institute of Marine Research, Bergen, Norway* *[3] Norwegian Institute of Occupational Health, Oslo, Norway* *[4]National Food Institute, Technical University of Denmark, KGS Lyngby, Denmark*

Time	Abstr.	
15:30-15:45	O-33	**Reflections on the first decade of triple Quadrupole ICP-MS: Addressing challenging applications using ICP-MS/MS** Uwe Noetzel[1], Glenn Woods[2], and Ed McCurdy[2] [1]Agilent Technologies Germany; [2]Agilent Technologies LDA (UK) Ltd
15:45-16:00		**Coffee break, exhibition and poster viewing**

Short Course Session I

16:00-17:45	A1-A5	**A1** Ilia Roduskhin **Sources of contamination and remedial strategies**	**A2** Rick Russo **Eliminate sample digestion**	**A3** Jörg Feldmann **Arsenic speciation, how to it for rice and seafood: routine and affordable options**	**A4** Kenneth Marcus **Use of the orbitrap as an analyzer for isotope ratio mass spectrometry**
		A5 Carsten Engelhard **Nanomaterials characterization by ICP-MS in single particle mode and related techniques**			

Short Course Session II

17:55-19:40	B1-B5	**B1**	**B2**	**B3**	**B4**
		Jacob Shelley **Modern plasma-based desorption/ ionization: From molecular analysis to chemical synthesis**	Gary Hieftje **Glow discharge: The most versatile source**	Sasha Novak **Surface analysis of Li ion batteries-Challenges and opportunities**	Michael Sperling **LA-ICP-MS as a tool for bioimaging**
		B5 Björn Meermann and Marcus von der Au **From ICP-Quads to ToF & single particles to cells – Theory, applications, future possibilities**			

From 19:00	**Dinner**
21:00	**Poster viewing and discussions with wine tasting and exhibition. (Bring your own wine)** *This event is sponsored by Matriks AS and Agilent Technologies*

Tuesday, June 14, 2022

Time	**Abstr.**	
08:00- 08:15		**The Nordic Plasma Torch Award** Organising Committee
		Session IV: Single particle and single cell analysis by plasma spectrochemistry Chairman: Dirk Schaumlöffel
08:15- 08:40	O-34	**Detection of nanoparticles and microplastics in environmental samples with atomic and molecular mass spectrometry** Carsten Engelhard, Darya Mozhayeva, Annika Schardt, Cristian C. Escobar-Carranza, *Maximilian Heide, Manuel Heinelt, Johannes Schmitt, Ingo Strenge* *University of Siegen, Department of Chemistry and Biology, Siegen, Germany*
08:40- 08:55	O-35	**Influence of sample handling on the quality of single cell ICP-MS data** Alexander Köhrer[1], Matthias Elinkmann[1], C. Derrick Quarles jr.[2], Uwe Karst[1] [1]*University of Münster, Institute of Inorganic and Analytical Chemistry, Germany* [2]*Elemental Scientific, Inc., Omaha, NE, USA*
08:55- 09:10	O-36	**Endogenous metal analysis in labelled single cells using time of flight ICP-MS for the elucidation of a cells metalome on a per cell level** Lukas Schlatt *Nu Instruments, Unit 74 Clywedog Road South, Wrexham Industrial Estate, Wrexham LL13 9XS, United Kingdom*
09:10- 09:25	O-37	**Automated single cell ICP-MS for the quantification of trace metals in beer samples** Matthias Elinkmann[1], Patrick Sullivan[2], Tyler Herek[2], C. Derrick Quarles Jr.[2], Uwe Karst[1] [1]*Institute of Inorganic and Analytical Chemistry, University of Münster, Germany* [2]*Elemental Scientific, Inc., Omaha, NE, USA*
09:25- 09:40	O-38	**MDG-ICP-MS - A versatile tool for quantification in the field of single particle ICP-MS using isotopic dilution** M. von der Au, S. Faßbender, M. Chronakis and B. Meermann *Federal Institute for Materials Research and Testing (BAM), Berlin, Germany*

Time	Abstr.	
09:40- 09:55	O-39	**LA-ICP-MS and proteins: Utilization on nanoparticle-based biorecognition elements** Tomáš Vaculovič[1], Markéta Vejvodová[1], Kristýna Zemánková[2,3], Kristýna Pavelicová[2,3], Marcela Vlčnovská[2,3], Vratislav Horák[4], Viktor Kanický[1], Vojtěch Adam[2,3], Markéta Vaculovičová[2,3] *[1] Masaryk University, Brno, [2] Mendel University in Brno,* *[3] Central European Institute of Technology, Brno University of Technology, Brno,* *[4] Laboratory of Applied Proteome Analyses, Institute of Animal Physiology and Genetics of the Czech Academy of Sciences, Libechov, Czech Republic*
09:55- 10:10	O-40	**Single particle ICP-OES analysis of battery materials determining particle inactivation and its consequences for the battery** Till-Niklas Kröger[a], Patrick Harte[a], Marc Vahnstiege[a], Thomas Beuse[a], Mathis Jan Wölke[a], Sven Klein[a], Markus Börner[a], Martin Wintera,[b], Sascha Nowak[a] and Simon Wiemers-Meyer[a] *[a] University of Münster, MEET Battery Research Center, Münster,* *[b] Helmholtz-Institute Münster, Münster, Germany*
10:10- 10:25	O-41	**Capabilities of fast single particle ICP-MS with nanosecond time resolution as a new tool for nanomaterial analysis** Annika Schardt, Johannes Schmitt, and Carsten Engelhard *University of Siegen, Department of Chemistry and Biology, Siegen, Germany*
10:25- 10:40		**Coffee break, exhibition and poster viewing**
		Session V: New analytical capabilities of plasma spectrochemistry Chairwoman: Veronica Sele
10:40- 11:05	O-42	**Multi-isotope approach within environmental forensics** Ilia Rodushkin[a,b], Emma Engström[a,b], Cora Paulukat[b] and Simon Pontér[a] *[a] Division of Geosciences, Luleå University of Technology, Luleå, Sweden* *[b]ALS Laboratory Group, ALS Scandinavia AB, Luleå, Sweden*
11:05- 11:30	O-43	**Common use of LA-ICP-MS in earth science & new approaches with laser ablation, ICP-MS, ICP-OES, SEM, EMPA and optical microscopy** Tonny B. Thomsen, Benjamin D. Heredia, Sebastian N. Mallki, Nynke Keulen *The Geological Survey of Denmark and Greenland (GEUS)*
11:30- 11:55	O-44	**Analysis of permanent gases and light hydrocarbons evolving during operation of lithium ion batteries with a barrier discharge ionization detector** Marco Leißing[1], Martin Winter[1,2], Simon-Wiemers-Meyer[1] and Sascha Nowak[1], *[a] MEET Battery Research Center, Münster, Germany* *[b] Helmholtz-Institute Münster, Forschungszentrum Jülich GmbH, Germany*
11:55- 12:20	O-45	**ICP-MS/MS analysis of technologically critical elements in printed circuitboard waste** Timo Sara-Aho *Finnish Environment Institute (SYKE), Helsinki, Finland*
12:20- 12:35	O-46	**Materials mapping, what laser induced breakdown spectroscopy can afford in order to help us?** C.-P. Lienemann[1], L. Jolivet[1], V. Motto-Ros[2], L.Sorbier[1] *[1] IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, Solaize, France* *[2] Institut Lumière Matière, UMR5306 Université Lyon,Villeurbanne, France*

Time	Abstr.	
12:35- 12:50	O-47	**Evaluation methods for LIBS data in industrial on-line applications** Arne Bengtson, Jonas Petersson, Melina Gilbert-Gatty, Krister Ekström, Louise Hagesjö *Swerim AB, Kista, Sweden*
12:50- 13:05	O-48	**LA-ICP-MS imaging method: Can make a geologist happy?** Markéta Holá[1], Martin Kubeš[2], Jan Dobeš[1], Vojtěch Wertich[2], Jaromír Leichmann[2], Viktor Kanický[1] *[1]Department of Chemistry, Faculty of Science, Masaryk University, Brno* *[2]Department of Geological Sciences, Faculty of Science, Masaryk University, Brno, Czech Republic*
13:05- 13:20	O-49	**Application of analytical techniques for the characterization of battery materials** Mikael Axelsson, *Thermo Fisher Scientific, Stockholm, Sweden*
13:20- 13:35	O-50	**Do we still have to worry about interferences in ICP-MS?** Ewa Pruszkowski, Chady Stephan and Liyan Xing *PerkinElmer Inc., Shelton, CT, USA*
13:35- 14:30		**Lunch**

Short Course Session III

Time	Abstr.	C1	C2	C3
14:30- 16:15	C1 – C5	Jaime Orejas **Liquid-Electrode Discharges**	Dirk Schaumlöffel **SIMS and related techniques for elemental and isotopic imaging at nanometer scale**	Frank Vanhaecke **An introduction to isotopic analysis using single- and multi-collector ICP-MS**
		C4	**C5**	
		Sarah Theiner **Calibration strategies for quantitative bioimaging by LA-ICP-MS**	Stefano Paggio **Choosing the right sample preparation technique for your elemental analysis: what are the key factors?**	

16:30		**Excursion to Briksdalen Glacier and conference outdoor dinner**

Wednesday, June 15, 2022

Time	Abstr.	
		Session VI: Applications of plasma spectrochemistry Chairman: Yngvar Thomassen
08:30- 08:45	O-51	**Seaweed for food and feed applications – need for elemental analysis** Jens J. Sloth, David J. Jensen, Katarina Kreissig, Cecilie W. Nielsen, Susan L. Holdt *National Food Institute, Technical University of Denmark, KGS Lyngby, Denmark*
08:45- 09:00	O-52	**ICP-MS determination of metals in sodium hypochlorite solutions used for disinfection of drinking waters** André Miranda; João Miguel Paiva; Rui Neves Carneiro *Empresa Portuguesa das Águas Livres, S.A., Lisbon, Portugal*
09:00- 09:15	O-53	**Utilization of 3D printed metal scavengers for precious metal recovery and for pre-concentration and speciation of mercury** Ari Väisänen, Suvi Kulomäki and Siiri Perämäki *Department of Chemistry, University of Jyväskylä, Finland*
09:15- 09:30	O-54	**Technology–critical elements (TCE) in soils in areas around waste electrical and electronic equipment (WEEE) recycling plant** Magdalena Jabłońska-Czapla[1]*, Katarzyna Grygoyć[1], Marzena Rachwał[1,3], Agnieszka Fornalczyk[2], Joanna Willner[2] [1] *Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze, Poland* [2] *Faculty of Materials Engineering and Metallurgy, Silesian University of Technology, Katowice, Poland* [3] *Institute of Safety Engineering, Warsaw, Poland*
09:30- 09:45	O-55	**Determination of cadmium and other elemental contaminant in cocoa/chocolate products and their packaging by ICP-MS** Lucas Givelet, Heidi Amlund, Yuka Omura Lund, Katrin Löschner, and Jens J. Sloth *Research group for analytical food chemistry, National Food Institute, Technical University of Denmark, Lyngby, Denmark*
09:45- 10:00		**Coffee break, exhibition and poster viewing**

Short Course Session IV

Time	Abstr.	D1	D2
10:00- 11:40	D1- D2	Gary Hieftje **Make your own lecture counts!**	Karl Andreas Jensen **Practical approaches to use reaction gases in ICP-MS triple quadrupole**
11:45- 12:00		**Closing remarks and farewell**	
12:00		**Lunch**	

Poster Presentations

Sunday, June 12 - Wednesday, June 15, 2022

Abstr.

P-1 **CADMIUM LEVELS IN WHELKS FROM DANISH WATERS – INFLUENCE OF SIZE, SAMPLING LOCATION AND SEASON**
Florian Brulfert[1], Heidi Amlund[1], Johan W. Nielsen[2], Bent Wismann[3] and Jens J. Sloth[1]
[1] *Research group for Analytical Food Chemistry, National Food Institute, Technical University of Denmark, Lyngby, Denmark*
[2] *Department of Biology, Marine Biological Section, University of Copenhagen, Copenhagen, Denmark*
[3] *Aquamind, Hellerup, Denmark*

P-2 **AN AUTOMATED SINGLE ALGAE-ICP-TOF-MS APPROACH FOR THE QUANTIFICATION OF METAL UPTAKE IN DIATOMS**
Marcus von der Au[1], Olga Borovinskaya[2], Luca Flamigni[2], Katharina Kuhlmeier[3], Claudia Büchel[3], Björn Meermann[1]
[1]*Federal Institute for Materials Research and Testing (BAM) - Division 1.1 Inorganic Trace Analysis, Berlin, Germany*
[2]*TOFWERK AG, Uttigenstrasse 22, 3600 Thun, Switzerland*
[3]*Institute of Molecular Biosciences, University of Frankfurt, Max von Laue Str. 9, 60438 Frankfurt, Germany*

P-3 **FAST, HIGH-RESOLUTION FULL ELEMENTAL LASER ABLATION IMAGING USING TIME-OF-FLIGHT ICP-MS FOR ENDOGENOUS METAL ANALYSIS AND LABEL IDENTIFICATION IN BIOLOGICAL SAMPLES**
Lukas Schlatt
Nu Instruments, Wrexham, United Kingdom

P-4 **THE USE OF TIME OF FLIGHT ICP-MS AND VERY FAST WASHOUT LASER ABLATION SYSTEMS TO ACCURATELY IMAGE MAJOR AND MINOR ISOTOPES AS WELL AS ELEMENTAL RATIOS IN GEOLOGICAL SAMPLES**
Lukas Schlatt
Nu Instruments, Wrexham,United Kingdom

P-5 **ACCURATE IDENTIFICATION, EXAMINATION AND DIFFERENTIATION OF MULTIELEMENT NANOPARTICLES USING TIME OF FLIGHT ICP-MS AND SUB-MILISECOND SPECTRAL ACQUISITION TIMES**
Lukas Schlatt
Nu Instruments, Wrexham, United Kingdom

P-6 **TOTALQUANT TECHNIQUE – MORE THAN SEMI-QUANTITATIVE ANALYSIS**
Ewa Pruszkowski, Chady Stephan and Liyan Xing
PerkinElmer Inc., Shelton, USA

P-7 **ANALYSIS OF TOXIC AND NUTRITIONAL ELEMENTS IN BABY FOODS BY ICP-MS**
Liyan Xing, Ewa Pruszkowski, Chady Stephan
PerkinElmer Inc., Woodbridge, ON, Canada

P-8 **QUANTITATIVE DETERMINATION OF LITHIUM PLATING ON GRAPHITE ANODE SURFACES UTILIZING GC-BID**
Tobias Brake[a], Martin Winter[a,b], Sascha Nowak[a] and Simon Wiemers-Meyer[a]
[a] *University of Münster, MEET Battery Research Center, Münster, Germany*
[b] *Helmholtz-Institute Münster, IEK-12, FZ Jülich, Münster, Germany*

Abstr. Poster Presentations Cont.

P-9 ASSESSING LITHIUM MIGRATION IN LITHIUM ION BATTERIES AT DIFFERENT STATES OF CHARGE BY COMBINING ISOTOPE DILUTION ANALYSIS WITH PLASMA-BASED TECHNIQUES
Stephen Lars Dorn [1], Marcel Diehl [1], Martin Winter [1,2], Simon Wiemers-Meyer[1], Sascha Nowak [1].
[1] University of Münster, MEET Battery Research Center, Münster, Germany,
[2] Helmholtz-Institute Münster, IEK 12, Forschungszentrum Jülich GmbH, Münster, Germany

P-10 INVESTIGATION OF THE C-RATE DEPENDENT GASSING DURING FORMATION OF LITHIUM-ION BATTERIES UTILIZING GAS CHROMATOGRAPHY - BARRIER DISCHARGE IONIZATION DETECTOR
Marco Leißing[1], Fabian Horsthemke[1], Simon Wiemers-Meyer[1], Martin Winter[1,2], Philip *Niehoff[1] and Sascha Nowak[1]*
[1] University of Münster, MEET Battery Research Center, Münster, Germany
[2] Helmholtz Institute Münster, IEK-12 of Forschungszentrum Jülich, Münster, Germany

P-11 THE INFLUENCE OF ADDITIVES ON PRIMARY SEI-DEVELOPMENT ON LITHIUM METAL – AN ACCUMULATION STUDY
Bastian von Holtum [a], Martin Winter [a,b], Sascha Nowak [a] and Simon Wiemers-Meyer [a]
[a] MEET Battery Research Center, Münster, Germany
[b] Helmholtz-Institute Münster, IEK-12, Forschungszentrum Jülich GmbH, Münster, Germany

P-12 SPATIALLY RESOLVED *POST-MORTEM* ANALYSIS OF LITHIUM DISTRIBUTION AND TRANSITION METAL DEPOSITIONS ON CYCLED ELECTRODES *VIA* LASER ABLATION-ICP-OES / -MS METHODS
Constantin Lürenbaum[1], Patrick Harte[1], Martin Winter[1,2], Simon Wiemers-Meyer[1] and Sascha Nowak[1]
[1]University of Münster, MEET Battery Research Center, Münster, Germany
[2]Helmholtz-Institute Münster (HI MS), IEK-12, Forschungszentrum Jülich GmbH, Münster,

P-13 INVESTIGATION OF THE MESOSCALE STATE-OF-CHARGE DISTRIBUTION IN LITHIUM ION BATTERY CATHODE MATERIALS BY MEANS OF SINGLE-PARTICLE INDUCTIVELY COUPLED PLASMA-BASED ANALYTICAL TECHNIQUES
Till-Niklas Kröger[1], Sascha Nowak[1], Martin Winter[2,1], and Simon Wiemers-Meyer[1]
[1]University of Münster, MEET Battery Research Center, Institute of Physical Chemistry (MEET)
[2]Helmholtz-Institute Münster, IEK 12, Forschungszentrum Jülich GmbH (HIMS) - Corrensstraße 46, 48149 Münster, Germany

P-14 ANALYSIS OF HETEROGENEOUS WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT SAMPLES BY ICP-OES
Jutta Koskinen and Ari Väisänen
Department of Chemistry, University of Jyväskylä, Finland

P-15 "ICP-MS IN A BOX"
Torill Kalfoss[1], Bente Sæten[1], Ørjan Espeseth[2] and Thor Lichtenthaler[2],
[1]Bayer AS, Oslo, Norway
[2]Matriks AS, Oslo, Norway

P-16 ANALYTICAL PLASMA CHEMISTRY IN A MINI-PILOT SCALE HYDROMETALLURGICAL LABORATORY
Antti Tiihonen and Ari Väisänen,
Department of Chemistry, University of Jyväskylä, Finland

Poster Presentations Cont.

Abstr. **Poster Presentations Cont.**

P-17 **OPTIMIZATION OF ANALYTICAL METHOD FOR SELENIUM SPECIATION IN FISH FEED AND FEED INGREDIENTS USING A CHEMOMETRIC APPROACH**
Kjersti E. Vaksdal[1,2], Marta S. Silva[1], Svein A. Mjøs[2], Snorri Gunnarsson[1], Marita Eide Kristoffersen[1] and Veronika Sele[1]
[1] *Institute of Marine Research (IMR), Bergen.*
[2] *Department of Chemistry, University of Bergen, Norway.*

P-18 **INVESTIGATION ON THE BIOACCUMULATION AND TRANSLOCATION OF RARE EARTH ELEMENTS IN THE SOIL-RICE SYSTEM**
Andrea Mara[1], Mario Deroma[2], Ilaria Langasco[1], Maria Itria Pilo[1], Antonino Spanu[2], Nadia Spano[1] and Gavino Sanna[1]
[1] *Department of Chemistry and Pharmacy, University of Sassari, Italy.*
[2] *Department of Agricultural Sciences, University of Sassari, Italy.*

P-19 **NANOGRAM LEVEL ANALYSIS OF MERCURY IN HUMIC-RICH NATURAL WATERS BY ICP-MS**
Suvi Kulomäki, Elmeri Lahtinen, Siiri Perämäki, Ari Väisänen
Department of Chemistry, University of Jyväskylä, Finland

P-20 **DETERMINATION OF XANTHATES IN AQUEOUS SOLUTIONS BY HPLC-ICP-MS/MS**
Ronja Suvela, Matti Niemelä, Paavo Perämäki
Research Unit of Sustainable Chemistry, University of Oulu, Finland

P-21 **METHOD DEVELOPMENT AND OPTIMISATION FOR THE ELEMENTAL ANALYSIS OF ACETIC ACID LEACHATES OF NEODYMIUM MAGNETS**
Joni Niskanen, Virva Kinnunen, Siiri Perämäki
Department of Chemistry, University of Jyväskylä, Finland

P-22 **ALUMINIUM MEASURMENTS BY ICP-MS: INFLUENCE OF MICROWAVE DIGESTION PARAMETERS ON THE RECOVERY**
Lucas Givelet, Heidi Amlund, Yuka Omura Lund, Florian Brulfert and Jens J. Sloth
Research group for analytical food chemistry, National Food Institute, Technical University of Denmark, Lyngby

P-23 **CLASSIFICATION OF FERMENTED BEAN PASTE PRODUCTS USING PLASMA-BASED ELEMENTAL ANALYSIS TECHNIQUES**
Sang-Ho Nam and Yonghoon Lee
Department of Chemistry, Mokpo National University, Muan-gun, Jeonnam, Republic of Korea.

P-24 **TWO-STEP PARTIAL LEAST SQUARES-DISCRIMINANT ANALYSIS TO OVERCOME THE LIMIT OF GLOBAL MODELING APPROACH: APPLICATION TO CLASSIFICATION OF EDIBLE SALT PRODUCTS USING LASER-INDUCED BREAKDOWN SPECTRROSCOPY**
Yonghoon Lee and Sang-Ho Nam
Department of Chemistry, Mokpo National University, Muan-gun, Jeonnam Republic of Korea

P-25 **A NOVEL ICP-MS METHOD FOR SENSITIVE, ACCURATE AND HIGH-THROUGHPUT ANALYSIS OF BABY FOOD**
Mikael Axelsson, Marshall Allin, Sukanya Sengupta, Daniel Kutscher
Thermo Fisher Scientific, Stockholm, Sweden

Abstr. Poster Presentations Cont.

P-26 SENSITIVE DETERMINATION OF IMPURITIES IN LITHIUM BATTERIES USING THE THERMO SCIENTIFIC ICAP PRO XP ICP-OES
Mikael Axelsson and Simon Nelms,
Thermo Fisher Scientific, Stockholm, Sweden

P-27 DEVELOPMENT OF GERMANIUM SPECIATION STUDY USING IC-ICP-MS TECHNIQUE IN SOIL SAMPLES
Magdalena Jabłońska-Czapla, Katarzyna Grygoyć
Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze, Poland

P-28 IMPROVED ENVIRONMENTAL IMPACT ASSESSMENT OF HIGH SALINITY PRODUCED WATER
Neri Bonciani, Matteo Ottaviani, Karen Louise Feilberg
Technical University of Denmark, Danish Offshore Technology Centre, Lyngby, Denmark.

P-29 DIGESTATE FROM ANAEROBIC DIGESTION AND POWER PLANT FLY ASH AS A CIRCULAR ECONOMY FERTILIZER: EVALUATION OF HEAVY METAL CONCENTRATIONS
Sylva Larsson, Virva Kinnunen, Siiri Perämäki
Department of Chemistry, University of Jyväskylä, Finland

P-30 COMPARISSON OF DIFFERENT PLASMA VIEWS FOR THE ANALYSIS OF COMPLEX SAMPLES
Petar Ivanov and Olaf Schulz
Spectro Analytical Instruments GmbH, Kleve, Germany

P-31 FEED-TO-FISH TRANSFER OF ARSENIC AND ARSENIC SPECIES IN ATLANTIC SALMON FED ON DIETS CONTAINING NORWEGIAN FARMED BLUE MUSSEL AND KELP
Marta S Silva[a], Jojo Tibon[a,b], Sahar Sartipiyarahmadi[a,c], Sofie C. Remø[a], Veronika Sele[a], Liv Søfteland[a], Harald Sveier[d], Martin Wiech[a], Antony J. Prabhu Philip[a], Marc Berntssen[a]
[a] Institute of Marine Research, Bergen, Norway, [b] National Food Institute, Technical University of Denmark, Lyngby, Denmark,[c] Department of Biological Sciences, University of Bergen, Norway
[d] Lerøy Seafood Group ASA, Bergen, Norway

P-32 STUDYING THE MECHANISM OF SILVER IONS BINDING TO CASEIN
Tetiana Dyrda-Terniuk[1,2], Adrian Gołębiowski[1,2], Oleksandra Pryshchepa[1,2], Katarzyna Rafińska[1,2], Magdalena Buszewska-Forajta[3], Paweł Pomastowski[2], Bogusław Buszewski[1,2]
[1] *Department of Environmental Chemistry and Bioanalytics, Faculty of Chemistry, Nicolaus Copernicus University in Torun*
[2] *Interdisciplinary Centre of Modern Technologies, Nicolaus Copernicus University in Torun,*
[3] *Institute of Veterinary Medicine, Nicolaus Copernicus University in Torun, Torun, Poland*

P-33 SPECIATION OF ELEVEN ORGANOTIN COMPOUNDS VIA HPLC-ICP-MS USING THE COMPLEXING AGENT A-TROPOLONE
C. Claesgens[1], T. Schwank[1], K. Pitzke[1], D. Breuer[1]*
[1]Institute for Occupational Safety and Health of the German Social Accident Insurances – IFA, Sankt Augustin, Germany

Abstr. Poster Presentations Cont.

P-34 ANALYSIS OF ARSENIC AT ULTRA TRACE LEVEL IN HYDROCHLORIC ACID USING INNOVATIVE ICP-MS TECHNOLOGIES

Alexandre Labet[1], Nadège Tudela[1], Peio Riss[2]
[1] *CEA, DES, IRESNE, DEC, Cadarache F-13108 Saint-Paul-Lez-Durance, France*
[2] *Analytik Jena France, L'Orme des Merisiers, 91190 Saint-Aubin, France*

P-35 A METHOD TO DETERMINE NUTRIENT AND OTHER ELEMENTS IN FOODS USING CLOSED VESSEL MICROWAVE ASSISTED DIGESTION AND INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY: SINGLE LAB VALIDATION

Jake A. Carter, Patrick J. Gray, and Todor I. Todorov
Center for Food Safety and Applied Nutrition, United States Food and Drug Administration, College Park, MD, 20740, USA

P-36 INVESTIGATION OF GRAPHITE-BASED ANODES FOR LIB USING GD-OES – IMPACT OF PLASMA PARAMETERS AND ELECTRODE PROPERTIES

Frauke Langer[1,2], Anggraini Utami[1,3], Jochen Kirres[1], Elisabeth Krämer[1], Julien Bachmann[2]
[1]*Mercedes-Benz Group AG, Stuttgart, Germany*
[2]*Friedrich-Alexander-Universität Erlangen-Nürnberg, Lehrstuhl Chemistry of Thin Film Materials, IZNF, Erlangen, Germany*
[3]*Hochschule Darmstadt, Darmstadt, Germany*

P-37 TOTAL MERCURY IN SNOW COLLECTED ON JAN MAYEN

Thobias Hans Østvedt[1], Elin Gjengedal[1], Stephan Weinbruch[2&4], William Hartz[3], Roland Kallenborn[1], Stine Eriksen Hammer[4] and Øyvind Enger[1]
[1]*Norwegian University of Life Sciences (NMBU), N-1432 Ås, Norway,*
[2]*Technical University of Darmstadt, Germany,*
[3]*University of Oxford, OX-2, UK,*
[4]*National Institute of Occupational Health, N-0033 Oslo, Norway*

12 Oral Abstracts

(O-1)
AND NOW WHAT?

Gary M. Hieftje

Indiana University, 980 Cape Marco Drive, #1205, Marco Island, FL 34145, USA

Compared to fields such as art, philosophy and mathematics, atomic spectrometry is a very young discipline. The foundations of atomic spectrophysics and atomic spectrochemistry can be traced back to such scientific giants as Newton, Bunsen, and Kirchhoff. However, it can be argued that many aspects of current practice in *analytical* atomic spectrometry were introduced in the 19th, 20th and 21st centuries. Such developments include modern ways of producing and detecting atomic optical and mass spectra, the introduction of alternative sources for generating neutral atoms and atomic ions, advanced understanding of fundamental events that affect analytical figures of merit, an almost continuous improvement of such figures of merit, the melding of atomic and molecular spectrometry, and the application of atomic spectrometric methods to an almost unfathomable range of contemporary problems. However, even the most up-to-date methods, applications, and instrumentation for atomic spectrometry exhibit shortcomings.

In this presentation, some of these limitations will be outlined and possible means to overcome them offered. These considerations will in turn suggest future directions that research in atomic spectrometry might profitably take.

(O-2)

NEW POSSIBILITIES IN SINGLE CELL ANALYSIS VIA ICP-TOF-MS – ZOOMING INTO THE REGION WHERE MATERIALS MEET ENVIRONMENT

Björn Meermann

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Materials are key for our modern communities; current life seems nearly impossible without concrete, plastic and metal. In particular metals play important roles in all areas of our daily life - from building materials to high tech products.

However, due to the increasing consumption of metals and corresponding waste production, an elevated release of metals from buildings and consumer goods into the environment takes place. Furthermore, metals in direct contact with the environment undergo corrosion processes which leads also to a release of metals into the (aquatic) environment. Besides this immediate metal release, the lifespan of products/buildings are substantially reduced – hence unnecessary economic costs arise. Thus, research in this regard is needed within the force field of metal/material ⇔ environment.

However, to evaluate the environmental impact of materials as well as developing “safe” materials, new analytical methods are highly needed. One promising powerful tool in this regard is single cell-ICP-ToF-MS for multi-elemental analysis on a single cell/organism level.

Within this presentation the concept, strength as well as challenge of single cell-ICP-MS are briefly introduced. Afterwards, two application examples are presented: (i) assessing the environmental impact of metals and (ii) the impact of the environment on metal-based materials and the derivation of potential environmental-friendly material protection strategies. These applications highlight the strength of new analytical approaches to explore the durability and safety of newly developed materials. Thus, analytical chemistry is one corner stone to transformation of modern society into circular economy (CEco).

(i) Diatoms are located at the bottom of the food chain. Thus, toxicological relevant metals taken up by diatoms can possibly accumulate within the food web and cause harmful effects. Diatoms are a common test system in ecotoxicology. To investigate potential metal uptake and harmful effects on a single cell level, we developed an on-line single cell-ICP-ToF-MS approach for multi-elemental diatom analysis. Our approach is a new potential tool in ecotoxicological testing for metal-based materials.[1,2]

(ii) Next to classical corrosion processes, microorganisms are responsible for so called microbially influenced corrosion (MIC). MIC is a highly unpredictable process relying on the interaction pathways between cells and the metal surface. To shed light on MIC processes and derivate potential metal protection strategies, we applied single cell-ICP-ToF-MS for MIC research on a single bacteria/archaea level.[3] It turned out that microorganism are taking up particular metals from alloys - thus, single bacteria-ICP-ToF-MS will enable the development of environmental friendly corrosion protection strategies.

[1] M. Von der Au, M. Schwinn, K. Kuhlmeier, C. Büchel, B. Meermann, Anal. Chim. Acta 2019, 1077, 87-94.

[2] M. Von der Au, O. Borovinskaya, L. Flamigni, K. Kuhlmeier, C. Büchel, B. Meermann B., Algal Res. 2020, 49, 101964.

(O-3)

EXPLORING UNIQUE CHEMISTRY IN PLASMAS AND DROPLETS TO BETTER UNDERSTAND THE CHEMICAL ORIGINS OF LIFE

Jacob T. Shelley[1,2,3] Brian T. Molnar,[1] Sunil P. Badal,[1] Samantha E. Pryor[2,3] Elly A. Breves[1,3] Julia L. Danischewski,[1] and Morgan F. Schaller[2,3]

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[3]Rensselaer Astrobiology Research and Education Center, Rensselaer Polytechnic Institute, Troy, NY 12180 USA

Determining or theorizing the origins of life on Earth has been a long-standing philosophical and scientific endeavor for humans. Many efforts of the past several decades have focused on the chemistry that could have existed on the early Earth to yield complex molecules seen in modern life and often viewed as necessary precursors for life formation (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.*, CO_2, CO, H_2O, N_2). Such energy sources include UV radiation from the Sun, hydrothermal vents, aerosols from crashing waves, impactor-induced shockwaves, lightning, and wet-dry cycling in shallow ponds/lakes.

The classic Miller-Urey experiments of the 1950s, which utilized a spark discharge in a mixture of reduced gases, demonstrated that lightning could have been a viable means to synthesize complex organic molecules from atmospheric precursors. In fact, nearly all of life’s monomers have been detected in the complex mixtures from these experiments. Unfortunately, those experiments were only successful in a reduced atmosphere, while the modern geological consensus is that Hadean Earth atmosphere was oxidized. In addition, those experiments did not offer a mechanism to accumulate enough bio-organic monomers to eventually produce higher order structures (e.g., peptides, oligonucleotides, vesicles).

This presentation will focus on a different approach to find and understand more viable pre-biotic synthesis routes. Specifically, we apply realistic early Earth conditions (i.e. oxidized atmospheres and high pressures) 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. Eventually, those pathways will be mapped onto realistic early Earth environments with appropriate chemical reagents and tested in the absence of plasma.

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. Products formed from plasma-droplet interaction can be recorded in real-time with mass spectrometry (MS). Lastly, these results will be discussed in the context of the astrobiology literature to postulate scenarios for complex (bio)molecule formation on the early Earth.

(O-4)

HIGH-PRECISION MC-ICP-MS ISOTOPIC ANALYSIS OF ESSENTIAL MINERAL ELEMENTS AS A TOOL IN BIOMEDICAL RESEARCH

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Improvement in mass spectrometric instrumentation has led to the awareness that all elements with ≥2 isotopes show natural variation in their isotopic composition as a result of isotope fractionation. Multi-collector ICP-mass spectrometry (MC-ICP-MS) shows a sufficient isotope ratio precision to reveal and quantify such differences. Since its introduction, MC-ICP-MS is frequently used by geo- and cosmochemists, but 15 years of research has demonstrated that also in a biomedical context, high-precision isotopic analysis is a powerful tool as isotope ratios of essential mineral elements have been proven to pick up some metabolic changes more sensitively and more reproducibly than element concentrations do and/or may contain information not embedded in element concentrations.

Examples from the authors' lab involving isotopic analysis of essential mineral elements such as Cu, Fe, Zn, Mg and K in the context of conditions, such as anemia, liver cirrhosis, cancer, diabetes and neurological disorders, will be discussed. The diagnostic and/or prognostic capabilities of MC-ICP-MS isotopic analysis of human body fluids will be demonstrated and it will be shown how the combination of isotopic analysis with *in vitro* experiments with cell lines and *in vivo* experiments relying on animal (murine) models provide information on the biochemical processes driving the isotope fractionation.

[1] High-precision isotopic analysis of essential mineral elements: capabilities as a diagnostic/prognostic tool, F. Vanhaecke and M. Costas-Rodríguez, View, 2, paper nr: 20200094, 2021. DOI: 10.1002/VIW.20200094.

(O-5)

LASER ABLATION RESEARCH & DEVELOPMENT: 60 YEARS STRONG

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A miniature explosion is created when a focused laser beam energy exceeds the dielectric breakdown of a material, a process known as laser ablation. Laser ablation science began around the same time as the invention of the laser in the early 1960’s. Since that time, the international scientific community has investigated fundamental mechanisms to understand and control this intriguing transient physics and chemistry phenomenon – which has become a comprehensive field of study. Fundamentals studies are imperative, and they still are addressed as there are no first-principle models to describe the ablation process or predict performance for an application. However, empirical R&D is predominant as the goal is to achieve reproducible behavior – the backbone for applications. Applications can be to process the ablated material itself, like surface texturing, drilling, shaping (medical), discover new material phases that are formed in the high temperature and rapidly cooling plasma plume, nano-particle formation, pulsed laser deposition, modeling of nuclear events, plasma emission spectroscopy, and many others.

Spectroscopy serves a dual purpose, optical emission measurements provide fundamental knowledge of the plasma (temperature, electron number density, shockwaves, etc,) and the luminous optical plasma spectroscopically represents the elemental and isotopic content of the material composition. The process is commonly referred to as laser induced breakdown spectroscopy (LIBS). The atomic and ionic emission wavelengths represent the samples’ elemental content and their concentrations. A new technology LAMIS (Laser Ablation Molecular Isotopic Spectroscopy) measures isotopes in laser plasmas at atmospheric pressure from molecular emission band spectra. Laser plasma spectroscopy is the underlying technology of the ChemCam instrument on the NASA Mars Curiosity Rover. The benefits of this technology are significant for many industrial measurements including energy (battery, solar), environmental, medical, materials, food safety, nuclear nonproliferation and essentially every aspect of society where chemistry is important in defining a material.

This presentation will provide an overview of the accomplishments in laser plasma R&D, fundamental behavior, several unique applications, and the ability to measure isotope ratios in field-based instruments. Early (1970’s) instrumentation was developed but could not meet the needs of industrial requirements; not because of the technology itself, but because lasers, spectrometers (optical and mass), and computers also were just being developed, and were unreliable. The components have been advanced (always more to come) to the point that sensitive, accurate and precise laser plasma spectrochemical analysis is becoming mainstay. Companies now commercializing instruments for spectrochemical analysis are seeing increased demand for products as the world awakens to the use of this 21st century technology.

(O-6)

IMPROVING THE SOLUTION CATHODE GLOW DISCHARGE ATOMIC EMISSION SPECTROMETRY SOURCE THROUGH DISCHARGE-LIQUID INTERACTION STUDIES AND NOVEL INSTRUMENTAL APPROACHES

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Elemental analysis at trace levels in aqueous solutions is a widely demanded analytical procedure in varied fields (e.g., environmental, clinical and food analysis or material characterization). For the determination of a broad range of elements, traditional techniques such as Atomic Absorption Spectrometry (AAS) or Inductively Coupled Plasma (ICP) coupled with Optical Emission Spectrometry (OES), or Mass Spectrometry (MS) provide robust analysis results and are widely used by routine analytical laboratories. Nevertheless, its instrumentation is complex and restricted to laboratory environments, and require high consumption of pressurized gases and/or electrical power, increasing their implementation costs.

The advent of atmospheric pressure glow discharges (APGDs) and other micro-discharges during the last twenty years has opened new possibilities on the development of alternative optical emission sources, targeting miniaturization and reduced consumption. In this sense, they can be implemented as portable instruments that can lead to novel in-situ elemental analysis applications.

One such source is the Solution-Cathode Glow Discharge (SCGD), an APGD sustained without plasma gas between a metallic electrode and an aqueous solution electrode, the sample. The SCGD plasma has the distinctive feature to directly transfer the analytes dissolved in the incoming solution into the plasma for its excitation, through a complex plasma-liquid interaction that, among other phenomena, eject droplets directly from the solution surface.

The present communication shows and discusses the behavior of the SCGD at short-time frames (10s of µs), detailing the discharge filamentary structure and the interaction of these filaments with the solution electrode surface. A similar set-up was used to characterize the ejection of droplets through laser scattering videos. The information obtained with these fundamental studies led to the envision and implementation of novel instrumental approaches for the SCGD in order to improve its analytical features.

(O-7)

INTRACELLULAR ELEMENT AND NANOPARTICLE ANALYSIS BY NANOSCALE SECONDARY ION MASS SPECTROMETRY

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Chemical bioimaging provides an important contribution to the investigation of biochemical functions, biosorption and bioaccumulation processes 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. Nanoscale secondary ion mass spectrometry (NanoSIMS) 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. NanoSIMS allows chemical imaging of a sample surface with lateral resolution down to 50 nm pixel size combined with high sensitivity and thus it is perfectly suited to localize the distribution of chemical elements with high spatial resolution at cellular level. A novel radio frequency plasma oxygen primary ion source provides high sensitivity and high spatial resolution for trace metal detection. Correlative imaging can be realized with transmission electron microscopy, synchrotron-based µXRF as well as µ-X-ray tomography and Laser Ablation ICPMS.

This lecture highlights the application of NanoSIMS and related techniques for intracellular element and nanoparticle analysis. Challenges and limitations including sample preparation will be discussed. Sophisticated sample preparation techniques are necessary basing on by chemical fixation or cryofixation, followed by resin embedding and ultramicrotomy. Recent examples for (trace) metal and nanoparticle localization in single cells will be presented such as distribution and dissolution of barium sulfate nanoparticles in human lungs cells, the first NanoSIMS detection of HgSe particles in whale liver, arsenic accumulation in marine algae, and an outlook of trace element imaging in animal nutrition research.

(O-8)

THE LS-APGD MICROPLASMA: A VERSATILE IONIZATION SOURCE FOR ELEMENTAL, ISOTOPIC, AND MOLECULAR SPECIES DETERMINATIONS

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In a world where information-rich methods of analysis are often sought over those with superior figures of merit, there is a constant search for ionization methods which can be applied across diverse analytical systems. To be sure, the advent of the inductively-coupled plasma (ICP) source brought tremendous versatility to the world of atomic spectrometry, in terms of its multielement capabilities, its sensitivity, and the diverse means of sample introduction. Sample can be introduced as ‘bulk liquids’, through gas and liquid chromatography, capillary electrophoresis, and following a laser ablation event. Of course, the coupling to mass spectrometric analyzers (i.e., ICP-MS) has only increased the power of the methods. There is no question that ICP-MS provides the greatest analytical versatility of the tools available for elemental analysis. The word ‘atomic’ is key here as all analytes are determined following processes which decompose the initial analytes from molecular down to atomic forms, with no memory or evidence of their chemical states in the primary sample.

The liquid sampling-atmospheric pressure glow discharge (LS-APGD) is a microplasma device which has the inherent capabilities to operate as a combined atomic and molecular (CAM) ionization source. That is, spectra can be acquired in which a greater, more comprehensive picture of the chemical state of the primary sample can be obtained. The plasma is sustained by placement of a high voltage (~500 V, dc) onto an electrolytic solution through which the analyte is generally delivered to the discharge. Judicious choice of the solvent provides a means of obtaining atomic/elemental and/or molecular mass spectra; and combinations thereof. Thus the amount of information density can be much higher than the ICP, where elemental and isotopic analysis are the primary products. Representative spectra and figures of merit are presented towards elemental and isotope ratio measurements, as well as application to small organic molecules, organometallic complexes, and intact proteins. Presented here are the diverse modes of sample introduction that have been realized, including the ‘bulk liquids’, tgas and liquid chromatography, capillary electrophoresis, and laser ablation employed in the ICP case, but as well the use of the microplasma ion an ambient desorption mode. In addition to the diversity in information types and sample introduction means, the diversity of mass spectrometer platforms to which the LS-APGD has been interfaced brings increase performance relative to ICP-MS. In general terms, the plasma can be interfaced to any mass analyzer system which has been designed to sample standard electrospray (ESI) and atmospheric pressure chemical ionization (APCI) sources common to organic mass spectrometry. Most significantly, the coupling with commercial orbitrap mass analyzers yields mass resolution values ranging from 70 k – 1.5 M! a factor not exercised in the organic world is the ability to acquire very high precision isotope ratio measurements as all target ions are trapped and analyzed simultaneously. It is believed that the diversity of analytical applications (via the range of sample introduction and information density) and ready implementation across the entirety of MS platforms portends a level of versatility not realized with other plasma-based ionization sources.

(O-9)

THIN-LAYER CHROMATOGRAPHY SURFACES FOR ENHANCED PLASMA-BASED AMBIENT DESORPTION/IONIZATION MASS SPECTROMETRY

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Ambient desorption/ionization high-resolution mass spectrometry (ADI-HR-MS) is a fast and efficient tool for the direct molecular analysis of a sample in its native state, preferably without any preceding sample preparation steps. One challenge for ADI-MS is the accurate quantification of analytes in complex samples [1]. Here, the use of chromatographic techniques is still the gold standard.

In this presentation, we will report on the benefits of using thin layer chromatography (TLC) plates as sample substrates for direct analysis of liquids and dried residues by plasma-based ADI-MS. Among the different TLC surfaces investigated, cyano- and dimethyl-modified silica showed promising properties, as both yielded around 100-fold higher analyte signals compared to other surfaces when examined with the flowing atmospheric pressure afterglow (FAPA) source. In terms of sensitivity, applied analyte amounts in the low fmol range were detectable. In general, it was found that the chemical compound class of the analyte of interest plays an important role in the desorption/ionization from the mentioned surfaces.

The capabilities and advantages of the method were not only demonstrated for simple standards and standard mixtures of selected compound classes but could also be observed during analysis of complex samples. Accurate quantification of analytes in matrix-containing samples was feasible without prior planar chromatography using isotopically labeled standards. For result validation, HPLC experiments were performed. Here, a better time efficiency of our presented method was also shown in comparison. The method is considered a promising sampling strategy for direct analysis of analytes in complex matrices by FAPA-MS.

[1] J.T. Shelley, S.P. Badal, C. Engelhard, and H. Hayen, *Anal. Bioanal. Chem.*, **2018**, 410(17), 4061-4076, https://doi.org/10.1007/s00216-018-1023-9

(O-10)

GLOW DISCHARGE-MASS SPECTROMETRY IN THE FIELD OF LITHIUM BATTERIES – OVERCOMING CHALLENGES IN METHOD DEVELOPMENT

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In order to guarantee a reliable power supply by renewable energy production, the lack of appropriate energy storage systems has to be overcome. The most promising technique in the field of electrochemical energy storage systems are Lithium Batteries. Those can be divided into Lithium Ion Batteries (LIBs) and Lithium Metal Batteries (LMBs). State-of-the-art LIBs consist of a graphitic negative electrode and a lithium transition metal oxides ($\mathrm{Li}M\mathrm{O_2}$: $M = \mathrm{Ni}_x$, Co_y, Mn_z ($x+y+z=1$)) positive electrode, as well as an electrolyte allowing ion transport between the electrodes. LMBs consist of a lithium metal negative electrode in exchange for graphitic materials. However, both systems, LIB and LMB, suffer from battery cell aging mechanisms leading to performance fading.[1]

While operating, different degradation mechanisms occur in lithium batteries, so-called cell aging takes place. An example is the loss of active lithium, which is correlated with capacity fading and is examined by different working groups.[2] For example elemental depth-profiling is used, to create a deeper understanding of the occurring aging phenomena by monitoring the lithium distribution. In contrast to other surface sensitive techniques often used in LIB research (*e.g.*, X-ray Photoelectron Spectroscopy (XPS) or Scanning Electron Microscope-Energy Dispersive X-ray Analysis (SEM-EDX)), Glow Discharge-Sector Field-Mass Spectrometry (GD-SF-MS) offers fast depth-profiling and quantification possibilities as well as a higher sensitivity for lithium.

Non-uniform surfaces and matrixes of negative electrodes represent a challenge for the application of GD-SF-MS, requiring method development and adaptation, respectively. In this work, method development for the analysis of negative electrodes via GD-SF-MS is shown. Starting from standard measurement conditions of the used GD-SF-MS device with a pulsed plasma, different plasma parameters were altered in order to create a reproducible depth profile. Adjustment of plasma voltage and current, pulse frequency and duration were performed considering the elemental depth profile and the resulting crater shape.

References

(1) Dühnen, S.; Betz, J.; Kolek, M.; Schmuch, R.; Winter, M.; Placke, T. Toward Green Battery Cells: Perspective on Materials and Technologies. *Small Methods [Online]* **2020,** *4* (7), 2000039.

(2) Vortmann-Westhoven, B.; Winter, M.; Nowak, S. Where is the lithium? Quantitative determination of the lithium distribution in lithium ion battery cells: Investigations on the influence of the temperature, the C-rate and the cell type. *J. Power Sources [Online]* **2017,** *346*, 63–70.

(O-11)

ISOBARIC DILUTION ANALYSIS AS A TOOL FOR THE INTERNAL QUANTIFICATION OF ^{99}TECHNETIUM IN AQUEOUS SAMPLES

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Ever since its discovery in 1937, the importance of technetium as a frequently observed anthropogenic radiocontaminant has constantly increased. Having a half-life of over 211,000 years, its primary isotope ^{99}Tc accounts for the entire natural and, by now, also a much higher anthropogenic occurrence. Besides its formation as a by-product of nuclear fission in both, the military and the energy sector, the isotope is also actively used as a radiotracer for scintigraphic techniques in medical diagnosis. Here, the features of the metastable form, ^{99m}Tc, specifically its short half-life of only six hours and its property to act as a γ-emitter, can be variably exploited to localize neoplastic tissue within the human body. Nowadays, ^{99m}Tc is applied in an estimated 40 million procedures per year, and makes up for about 85% of all diagnostic scans performed in nuclear medicine worldwide.

Monitoring of ^{99}Tc and its quantification in aqueous media holds intrinsic complications as most samples contain expectedly low concentrations coinciding with difficult matrices such as wastewater, blood or urine. Additionally, due to its radioactivity (β^-), elemental standards for ^{99}Tc are not easily available, therefore expensive and hard to handle. Besides, Tc is virtually monoisotopic as other isotopes, even those with equally high half-lives than ^{99}Tc, are even harder to obtain and therefore do not qualify as internal standards.
To cope with those difficulties, in this work, a quantification strategy called isobaric dilution analysis (IBDA) is used for internal calibration of ^{99}Tc by means of inductively coupled plasma-mass spectrometry (ICP-MS).[1] Exploiting the isobaric interference of naturally occurring ^{99}Ru, ^{99}Tc can be quantified with an elemental Ru standard. To compensate for any difference in elemental sensitivity, for the first time, an isotopic standard of ^{99}Tc was prepared from decayed medical technetium-99m generator eluate by means of solid phase extraction (SPE) and counter-quantified using total reflection X-ray fluorescence spectroscopy (TXRF). With the respective method, ^{99}Tc was quantified in samples of medical origin at concentrations between 200±1 up to 839±1 µg/L.

[1] Clases D, Birka M, Sperling M, Faust A, Karst U. Isobaric dilution analysis as a calibration tool for long lived radionuclides in ICP-MS. J Trace Elem Med Biol. 2017; 40:97-103.

(O-12)

HIGH PRECISION IN-SITU RB-SR DATING USING THE THERMO SCIENTIFIC NEOMA MS/MS MC-ICP-MS

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Radiometric dating of geological materials using the ^{87}Rb–^{87}Sr beta decay system is a well-established geochronological technique which has been exploited for over 80 years. By its nature, beta decay produces a daughter nuclide that isobarically interferes with its parent during mass-spectrometric analysis. At present, no mass spectrometer designed to measure isotope ratios to high precision possesses sufficient mass resolution to resolve ^{87}Rb from ^{87}Sr (required $M/\Delta M \sim 300\,000$). For this reason, *in situ* ^{87}Sr/^{86}Sr analysis has previously been limited to low Rb/Sr phases such as plagioclase or apatite.

The development and coupling of collision cells to inductively-coupled plasma mass spectrometers now permits *in situ* radiogenic Sr isotopic analysis of high Rb/Sr minerals by using a suitable reaction gas within a collision cell to react with the Sr^+ ions but not the interfering Rb^+ ions. Such an approach has been successful in laser ablation Rb–Sr dating using single collector inductively coupled plasma mass spectrometers equipped with collision cells and pre-cell quadrupole mass-filters (CC-ICPMS/MS).

Analytical precision is an important limit in such work and, as a result, many of the previous studies have focused on samples containing minerals with very high Rb/Sr (*e.g.* ^{87}Rb/^{86}Sr ratios >500) or samples that are particularly old (>1 Ga). Here, we demonstrate the potential of the Thermo Scientific™ Neoma MS/MS MC-ICP-MS, a collision cell MC-ICP-MS with a magnetic sector pre-cell mass filter, for in-situ Rb-Sr dating of a wider range of geological targets[1,2].

References:

1. Bevan D, Coath CD, Lewis J, et al. In situ Rb–Sr dating by collision cell, multicollection inductively-coupled plasma mass-spectrometry with pre-cell mass-filter, (CC-MC-ICPMS/MS). *J Anal At Spectrom*. 2021;36(5):917-931. doi:10.1039/D1JA00006C
2. Craig G, Wehrs H, Bevan DG, et al. Project Vienna: A novel pre-cell mass filtre for a collision/reaction cell MC-ICPMS/MS. *Anal Chem*. 2021;93(30):10519–10527.

(O-13)

HIGH-RESOLUTION AND HIGH-SPEED IMAGING BY LA-ICP-TOFMS

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The potential of a low-dispersion laser ablation setup in combination with ICP-TOFMS detection will be highlighted for multi-element imaging of biological samples at the single-cell level. Examples of mapping of endogenous elements with biological key functions within different tissue samples as well novel quantification approaches for bioimaging applications by LA-ICPMS will be presented.

LA-ICP-TOFMS imaging was used to analyze human malignant pleural mesothelioma (MPM) samples at the cellular level [1]. The low-dispersion LA setup employed, provided the high spatial resolution necessary to identify for the first time asbestos and other mineral fibers in lung and pleura tissue samples of MPM patients, based on their multi-element pattern (Si, Mg, Ca, Fe, and Sr) at a pixel size of 2 µm. The laser fluence proved to be the key parameter to simultaneously ablate soft, biological material and hard, mineral fibers without creating artefacts from co-ablation of the glass support.
Insights into the metallome of MPM patients with different pathologies were obtained and significant tissue inflammation was revealed around talc deposit regions in pleura samples. LA–ICP–TOFMS results correlated well with Perls' Prussian blue and histological staining of the corresponding serial sections.

Next to clinical important applications, we discuss calibration in LA-ICPMS as this still represents an Achilles' heel of the technique, lacking appropriate certified reference materials, especially in the field of life sciences (i.e. biological samples). A newly developed multi-point calibration approach will be presented, which is based on gelatin micro-droplets spiked with multi-element standards [2]. Automated and precise droplet deposition was achieved by a micro-spotter resulting in droplet sizes of < 200 µm. This provides the analysis of calibration sequences for LA-ICPMS imaging in less than 10 min. The proposed quantification concept for bioimaging applications was further validated and compared to alternative calibration strategies.

References

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

[2] A. Schweikert, S. Theiner, D. Wernitznig, A. Schoeberl, M. Schaier, S. Neumayer, B. K. Keppler and G. Koellensperger, *Anal. Bioanal. Chem.*, 2022, 414, 485-495

(O-14)

QUANTITATIVE BIOIMAGING BY LA-ICP-MS AS A TOOL TO STUDY GENETIC DISORDERS OF THE IRON AND COPPER METABOLISM

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Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) provides sensitive elemental detection with a spatial resolution down to the low µm range. By using thin tissue sections for bioimaging, quantification is possible by using external calibration with matrix-matched standards. The obtained quantitative distribution maps of target elements provide important information about the transport, metabolism and distribution of these elements between different organs, organ structures, tissue types down to cell types. Such information is crucial in medical investigations and toxicological studies related to elemental species such as metabolic disorders related to metal species.

Here we report about the possibilities of bioimaging by LA-ICP-MS to support such investigations by providing valuable information improving our understanding of interactions and mechanisms targeting at improved diagnostic and therapeutic efficacy. Requirements for sample preparation and quantification will be discussed as well as possibilities and remaining challenges in this field.

(O-15)

ICP-MS AS A WORKHORSE TO STUDY HOW NANOPARTICLES CAN BE TAILORED TO EFFICIENTLY DELIVER NUTRIENTS TO AGRICULTURAL PLANTS

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Conventional strategies for soil fertilization are remarkably inefficient, as only a fraction of most mineral elements added with fertilizers are taken up by plants, the rest are typically trapped in the soil or leached to the aqueous environment, causing eutrophication. Thus, one of the most important current challenges of agriculture is to improve the sustainability of food production via an improved fertilizer efficiency. However, fertilizers have practically not improved for decades and this calls for an acute rethinking of fertilizer procedures.

We have proposed a novel approach that bypasses nutrient fixation and microbial immobilization in the soil. We take advantage of the most recent breakthroughs within bio-nanotechnology, which allow us to produce biocompatible fertilizers based on smart nanomaterials, tailored to more effectively deliver nutrients to agricultural plants, both when applied to the soil or via the foliage. To study uptake and distribution of nanoparticles in plants we use a range of different ICP-MS based technologies, including single particle-ICP-MS analysis and laser ablation-ICP-MS for bioimaging.

I will demonstrate various cases where we have used ICP-MS as a powerful workhorse to characterize how nanoparticles interact with plant tissue and show how it can be combined with other bioimaging techniques to study the fundamental biochemical processes controlling uptake and assimilation at the single cell level.

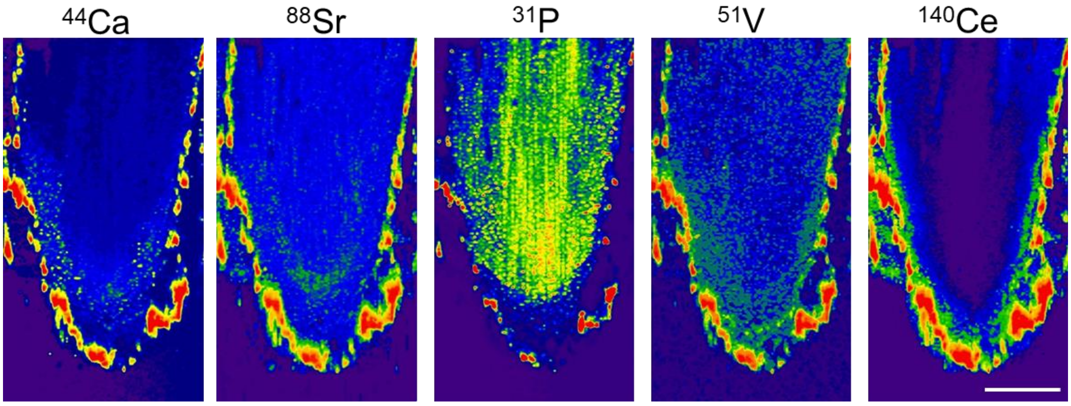

Figure 1. Longitudinal sections of barley root tips (1 mm) analyzed by LA-ICP-MS, using a 5 µm spot size. Szameitat et al. (2020). Environmental Sci. Nano. DOI: 10.1039/d0en00974a.

(O-16)

BIOIMAGING OF ZN AND CD IN LEAVES OF HYPERACCUMULATOR *ARABIDOPSIS HALLERI* USING LASER ABLATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY WITH REFERENCING STRATEGIES

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Laser ablation of whole leaves is affected by several factors, such as their physical density, tissue overlaps, tissue damage, differing topology or focus. Conventional methods of external calibration or standardization are unavailable due to missing certified reference materials. Usually, these issues can partially be accounted for via internal standardization. However, homogeneous application of such standards is not possible within leaves. In addition to that, interference of the standard with analytes cannot necessarily be ruled out.

Therefore, this work investigates internal standardization with innately abundant isotopes 13C, 25Mg, 31P, 44Ca and 85Rb contained within leaves. Freshly harvested leaves of heavy metal hyperaccumulator Arabidopsis halleri were glued onto a sample plate and analyzed via laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Analytes of interest are the environmental pollutants Zn and Cd. The success of internal standardization was tested by introducing common experimental issues of sample preparation and leaf analysis, such as loss of focus, tissue overlap and tissue damage. The resulting images are presented as so-called referenced images, where the intensity of each pixel of the analyte of interest is divided by the intensity of the corresponding pixel of an internal standard. The resulting images are compared to non-referenced images and are evaluated with respect to gain of information and correction of ablation-related errors.

This work shows that referencing with 25Mg, 31P, 44Ca or 85Rb was not beneficial to the representation of Zn or Cd distribution in the leaf, as their differing ion mobilities or their role in biological response mechanisms introduced unwanted artifacts in the resulting referenced images. With respect to all tested aspects, solely 13C is found to be best suited for referencing leaves. Here, the distributions of Zn and Cd were most optimally stabilized in referenced images of all samples.

This method was successfully applied to A. halleri leaves that grew on soils of differing heavy metal concentrations as well as on a leaf of A. thaliana. Referencing therefore enables a more direct comparison of different samples, even if conventional methods of quantification are unavailable.

(O-17)

ELEMENTAL BIOIMAGING FOR THE SIMULTANEOUS QUANTIFICATION OF CISPLATIN AND A GADOLINIUM-BASED CONTRAST AGENT IN LIVER TISSUE

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Liver cancer is the sixth most occurring cancer type worldwide. Symptoms and signs of liver cancer usually appear late in the course of the disease, which is often medicated by the antitumor agent cisplatin. Due to the late diagnosis, survival rates are poor and therefore, often palliative therapies are chosen. Hence, an early and reliable diagnosis of liver carcinomas and tumor stages plays an important role in suggesting an appropriate therapy and increasing survival rates. In this context, magnetic resonance imaging in combination with liver-specific contrast agents significantly improves the detection and characterization of liver lesions.

This study focuses on the simultaneous determination of cisplatin and the liver-specific gadolinium-based contrast agent gadoxetic acid in liver lesions. Rats with liver tumors were medicated with gadoxetic acid as well as cisplatin and sacrificed 15 minutes after injection. The resection of tumor tissue with surrounding liver tissue allows the direct comparison of gadolinium, platinum, and other endogenous elements in both tissue types. A 213 nm laser ablation (LA) system hyphenated to inductively coupled plasma-mass spectrometry (ICP-MS) revealed quantitative and spatially resolved element information in the tissue thin sections. Element distributions were correlated with different pathological tissue types, which were examined by hematoxylin and eosin staining. Furthermore, gadolinium and platinum were quantified in regions of interest, providing information on how the uptake of gadoxetic acid and cisplatin varies in different tumor regions and stages.

(O-18)

FLUORINE SPECIATION USING ICPMS: IS THAT NECESSARY AND USEFUL?

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Fluorine is an element which cannot been determined by standard ICPMS due to its high ionisation potential which renders the ionisation efficiency to form F^+ close to zero. The are possibility to use indirectly ICPMS for fluorine-specific detection and that is by introducing a barium solution simultaneously to the sample into the plasma so that BaF^+ is forming. We have shown that this can be used for fluoride detection (Jamari et al. 2017, 2018) and can be used for speciation of per and polyfluorinated alkylated substances (PFAS) (Jamari et al. 2019).

PFAS, a group of more than 4700 compounds is usually analysed by target analysis using LC-ESI-MS/MS. However only 30-40 are usually monitored. How many compounds do we miss? To answer the question a non-targeted approach using high resolution MS such as Orbitrap or qTOF-MS can be used. However, the data mining is also problematic. Here we could demonstrate that using ICPMS can be useful to detect a novel PFAS for which no standard exists (Heuckeroth et al. 2021).

The lecture will demonstrate that other methods such as CIC or HR CS MAS can be used for total analysis of fluorine using a fractionation scheme might as extractable organofluorine (EOF). The lecture will demonstrate that a fluorine- specific detector is necessary, since without such a tool, the extend of PFAS pollution in our waters cannot be assessed.

S. Heuckeroth, T.N. Nxumalo, A. Raab, J. Feldmann, Fluorine-specific detection using ICP-MS helps to identify PFAS degradation products in non-targeted analysis, **Analytical Chemistry** (2021) **93** (16), 6335-6341.

N.L.A. Jamari, J.F. Dohmann, A. Raab, E.M. Krupp, J. Feldmann, Novel non-targeted analysis of perfluorinated compounds using fluorine-specific detection regardless of their ionisability (HPLC-ICPMS/MS-ESI-MS). **Analytica Chimica Acta** (2019) **1053**, 22-31.

N.L.A. Jamari, A. Behrens, A. Raab, E.M. Krupp, J. Feldmann, Plasma processes to detect fluorine with ICPMS as M-F+: an argument for building a negative mode ICPMS/MS. **Journal of Analytical Atomic Spectrometry** (2018) **33**, 1304-1309.

N.L.A. Jamari, J.F. Dohmann, A. Raab, E.M. Krupp, J. Feldmann, Novel non-target analysis of fluorine compounds using ICPMS/MS and HPLC-ICPMS/MS, **Journal of Analytical Atomic Spectrometry** (2017) **32**, 942-950.

(O-19)

POTENTIAL TOXIC ELEMENTS AND ARSENIC SPECIES IN NEW AQUAFEED INGREDIENTS - ARE THERE CONCERNS IN TERMS OF FEED AND FOOD SAFETY?

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Fish feed was traditionally composed primarily of marine feed ingredients, i.e. fish oil and fish meal from pelagic fish, but these are today partly replaced by plant-based feed materials. With the European Green deal, there is a focus on more sustainable raw materials from low-trophic organisms, where e.g. algae and mussel are considered promising candidates. With new feed ingredients, there is a potential risk for introducing undesirable substances, including potentially toxic elements (PTEs), such as mercury (Hg), cadmium (Cd), lead (Pb) and arsenic (As). For some elements, such as As, it is also important to consider the chemical species present as the speciation affects the toxicity of the element, e.g. some species are classified as carcinogenic (inorganic As, iAs), others are considered non-toxic (arsenobetaine, AB), whereas the toxicity of several organic As species (e.g. arsenosugars, AsSug and arsenolipids, AsLipids) has not been established.

In this study, commercial fish feeds (n= 20) were analysed for their content of Hg, Cd, Pb, As and inorganic and organic As species, using inductively coupled plasma mass spectrometry (ICP-MS) and high pressure liquid chromatography (HPLC) coupled to ICP-MS, respectively. Feed ingredients, including fish meal and fish oil (n = 40), as well as novel feed ingredients (n = 38) from low-trophic level organisms, i.e. microalgae, shrimp meal, crab meal, insect meal and tunicates were analysed for the same analytes.

The commercial feeds contained PTEs below the EU maximum levels (MLs) for feed and feed ingredients (EU directive 2002/32). The concentrations of iAs were up to 0.20 mg/kg, accounting from 0 to 50% of total As. For most samples, AB was the major species present (20-80% of total As). Similarly, AB was also predominant in fish meal, and low levels of iAs were detected in all samples (<LOQ to 0.21 mg/kg). Of the novel feed ingredients, the levels of PTEs and As species varied among sample types. Microalgae contained low levels of PTEs, and AsSugars were the predominant form of As. For meals of crab, shrimp and tunicates, relatively high levels of Cd (0.01 to 2.6 mg/kg), As (0.25 to 47 mg/kg) and inorganic As (<LOQ to 1.8 mg/kg) were seen for some of the samples. Other feed ingredients contained AB as the major As species, and iAs was below 0.4 mg/kg.

This study shows that the levels of PTEs in fish feed and traditional feed ingredients are generally below EU MLs. However, for some of the new feed ingredients, elevated levels of Cd, As and iAs were detected. Some of the feed ingredients contained relatively high levels of AsSug and AsLipids, for which toxicity has not yet been established. This further emphasizes the importance of documenting the occurrence of As species present in feed and food, for future risk assessments.

(O-20)

SPECIATION ANALYSIS OF ARSENIC IN SEAFOOD AND SEAWEED AT THE U.S. FOOD AND DRUG ADMINISTRATION

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Seafood and seaweed are regarded as important parts of a healthy diet, as they contain various beneficial nutrients. On the other hand, these products are known to be significant sources of human exposure to dietary arsenic. [1] Most risk assessment practices associated with dietary arsenic are based on monitoring inorganic arsenic (iAs), which is a Class I carcinogen. Such an approach is generally adequate, as most products are known to accumulate arsenic in forms of defined properties. However, the approach may leave species of potential or unknown toxicities unidentified when applied to seafood and seaweed, where arsenic has a complex and variable distribution of species. Comprehensive speciation analysis which aims at capturing a complete picture of the arsenicals' distribution is recommended. Recently, studies were conducted at the U.S. Food and Drug Administration to determine the concentrations of arsenic species in seafoods and seaweeds. Samples of the top ten most consumed seafoods were collected from across the U.S. and other commonly consumed seaweeds were collected from supermarkets in Maryland. The samples were analyzed for sixteen water-soluble arsenic species as well as non-polar arsenic using a method recently developed [2] and single lab validated [3] by the U.S. Food and Drug Administration. In the presentation, the findings of the study will be discussed along with the development and validation of the method. Though not a statistically rigorous sampling, the study nevertheless represents the most comprehensive assessment to date of arsenic species in the U.S. diet from seafood and seaweed consumption.

[1] M. Molin *et al.*; *J Trace Elem Med Biol* 31 (2015) 249
[2] M. M. Wolle and S. D. Conklin; *Anal Bioanal Chem* 410 (2018) 5675
[3] M. M. Wolle and S. D. Conklin; *Anal Bioanal Chem* 410 (2018) 5689

(O-21)

ARSENIC SPECIATION IN MESOPELAGIC BIOMASS – AN INSIGHT INTO ARSENIC BEHAVIOR DURING AQUAFEED PROCESSING

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For a more sustainable use of marine resources, the European Commission recommends responsible harvest at low-trophic levels. The mesopelagic zone consists of low-trophic aquatic organisms estimated at 1 billion tons, which, when sustainably harnessed, has the potential to augment aquafeed ingredients. Within the European Union, maximum limits are established for undesirable substances in feed and feed ingredients (Directive 2002/32 EC and amendments). Arsenic (As) is an element which is prevalent in the marine environment, mainly in the form of the non-toxic arsenobetaine (AB) in marine animals. However, inorganic and some organic forms exhibit carcinogenic, neurotoxic, and cytotoxic potential. This complex nature of As highlights the importance of speciation data as basis for further risk assessment.

An analytical method for the determination of water-soluble As species based on anion- and cation-exchange HPLC-ICP-MS has been developed for marine matrices. The extraction step was improved using a fractional factorial design and HPLC-ICP-MS parameters were optimized. A single-laboratory validation was conducted using marine certified reference materials. The method was subsequently applied to five of the most abundant mesopelagic species in Norwegian fjords. To understand how As behaves during feed processing, As species were also investigated in mesopelagic biomass and resulting meal and oil products from a feed-processing study. Arsenolipids were estimated by extraction using methyl tert-butyl ether and methanol, then determining the total As in the extracts. Total As levels in the mesopelagic organisms ranged from 2.2 to 28 mg/kg ww. Arsenobetaine was the major As species in mesopelagic crustaceans and fish, representing 70% and 50% of total As, respectively. A strong correlation was also observed between total As and AB in these samples. Arsenolipids accounted for 25% to 45% of total As. For the feed processing simulation, AB was the primary As species in the biomass, stickwater, and mesopelagic meal. However, notable levels of arsenolipids were detected in the biomass, which were then transferred to the meal and up-concentrated in the oil. Inorganic arsenic and other organic forms, including simple methylated species, were present in trace amounts. This study presents valuable occurrence data of up to 12 As species in mesopelagic organisms. The results provide baseline information which can be helpful in food and feed safety assessments of mesopelagic biomass as future feed ingredients.

(O-22)

FAST AND AUTOMATED TOTAL ARSENIC AND ARSENIC SPECIATION BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Understanding the specific chemical species found in different samples is important to toxicological, clinical, environmental, food, pharmaceutical, and geochemistry. Arsenic is found in many forms in the natural environment, some of which are significantly more toxic than others. Therefore, fast and reliable analytical methods are required to determine which arsenic species are present. We present two methods for determining arsenic species in urine by LC-ICP-MS. The first method is a high-throughput method for separating 6 arsenic species (AsB, DMA, MMA, AsC, As(III), and As(V)) in under 2 minutes. The second method provides a separation of 7 arsenic species (AsB, TMAO, DMA, MMA, AsC, As(III), and As(V)) in under 5 minutes. The validation of both methods was carried out by analyzing proficiency testing (PT) samples from the Centre de Toxicologie du Québec (CTQ) and New York Department of Health (NYDOH). Recovery of the two methods falls between 94 and 107% and the limits of detection in a urine matrix ranged from 2.8-6.0 ng L^{-1} As and 4.1-9.1 ng L^{-1} As for the one- and two-column methods, respectively.

(O-23)

OCCUPATIONAL EXPOSURE TO ORGANOTIN SUBSTANCES: SPECIATION OF ORGANOTIN COMPOUNDS IN WORKPLACE AIR SAMPLES VIA HPLC-ICP-MS

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Occupational exposure limits (OELs) for metals most often refer to the total content of a metal in a certain particle fraction in workplace air. Since bioavailability and adverse effects do not only depend on particles penetration depth into the respiratory tract and content of a metal, but significantly on bonding form, speciation analysis is a current research area in occupational health and safety regulations.

Organotin compounds (OTCs) are widely regulated for their proven human and ecotoxicity. Due to their excellent physicochemical properties they still rank among the most used organometallic-compounds in various industrial sectors. At workplaces (e.g. plastics manufacturing) OTCs can be released as particles, vapors or mixed phases and be incorporated by inhalation or skin contact. In Germany occupational exposure limits are specified for 23 OTCs in Technical Rules for Hazardous Substances (TRGS). Specific measurement methods for monitoring workplace air exposure to these OTCs currently do not exist.

In the fields of environmental and product analysis gas- (GC) and liquid chromatography (HPLC) applications can be found for various matrices. While GC enables high peak capacity it lacks in robustness due to error-prone derivatization. HPLC in comparison requires minimal sample preparation and gives high sensitivity when hyphenated to ICP-MS but has shown limited peak capacity and resolution in previous works (max. 6 OTCs).

In this work we present the development of a simple and routine-compatible speciation method for eleven regulated OTCs via reversed phase HPLC-ICP-MS. The method allows a near baseline separation of Monomethyltin (MMT), Monobutyltin (MBT), Monooctyltin (MOT), Monophenyltin (MPhT), Dimethyltin (DMT), Dibutyltin (DBT), Diphenyltin (DPhT), Trimethyltin (TMT), Tributyltin (TBT), Triphenyltin (TPhT) and Tetramethyltin (TTMT) within 22 minutes by means of a C18 column and a ternary solvent and flow rate gradient using methanol (MeOH), acetonitrile (ACN) and ultrapure water + acetic acid + α-tropolone. Instrumental limits of quantification range between 0,5- and 2 µg (Sn)/L. Air Sampling, sample preparation and storage stability are object of current research.

(O-24)

IDENTIFICATION AND QUANTIFICATION OF METAL COMPLEXES BY ISOTOPE DILUTION HPLC - ICP MS / ESI MS

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Metal complexes play an important role in the functioning of various ecosystems. Bacteria and plants have developed several mechanisms to control and regulate metal uptake, transport, and storage. Identification of the species responsible for metal fixation is an important part of the research to answer the question of how individual genus cope with metal excess or deficiency in the environment. This study presents the development of a methodology for the identification and quantitative analysis of low molecular weight complexes of essential metals in plant fluids.

The proposed analytical approach is based on the addition of enriched isotope metal probe prior to coupling hydrophilic interaction chromatography (HILIC) and size exclusion chromatography (SEC) with mass spectrometry. The parallel elemental (ICP) and molecular (ESI) mass spectrometric detection allows the identification of the chemical species responsible for the translocation of metals based on the consistency of retention times between the two techniques and the unique isotope pattern. The prerequisite is the complete reaction of the added spike, which can be easily verified by HPLC-ICP MS. The additions of isotopically enriched metal ions solution result in the formation of the same (but labelled) complexes as those present in the original sample to establish a calibration curve serving for the quantification[1]. Particular attention was paid to the reaction environment of the formation of labelled complexes depending on the stability of the individual complexes of interest. In contrast with the classical post-column isotope spiking, the proposed method compensates for possible on-column dissociation of metal complexes allowing for quantitative speciation analysis.

[1] AlChoubassi, G., Aszyk, J., Pisarek, P., Bierla, K., Ouerdane, L., Szpunar, J., Lobinski, R., Advances in Mass Spectrometry for Iron Speciation in Plants, *TrAC Trends Anal. Chem.* **2018**, *104*, 77–86.

(O-25)

UTILIZATION OF ICP-MS TECHNIQUE FOR INVESTIGATION OF BOVINE LACTOFERRIN INTERACTIONS WITH METALS AND CHARACTERIZATION OF RESPECTIVE METAL-RICH PROTEIN COMPLEXES

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Nowadays researchers started to pay more attention to milk proteins as a source of new biologically active substances. Of all milk proteins, lactoferrin (LTF) belongs to one of the most valuable. LTF exhibits a wide spectrum of biological functions in the organism, i. e. takes part in iron homeostasis, immune response to infections and inflammation, cell proliferation and migration, has antimicrobial activity.

LTF is a iron-binding metalloprotein. Apart from iron, LTF can also bind zinc, manganese, aluminum, etc. Moreover, our studies have shown that lactoferrin can bind much more metal ions than can be structurally predicted [1]. Thus, the study aimed to investigate the process of the metal binding to protein as well as the physicochemical and biological properties of respective complexes. For this purpose, three different metals, that are of great importance in humans' life and medicine were chosen, namely Zn^{2+}, Fe^{3+}, and Ag^{+}. Zinc and iron complexes can be utilized as dietary supplements, while Ag-LTF can be utilized as an antibacterial agent in the treatment of chronic wounds.

The methodology of the studies comprises the batch sorption study where metal removal from the solution was measured by ICP-MS. The studies were also complemented by characterization of respective complexes with the utilization of electron microscopy, spectroscopic as well as separation techniques. Interestingly, the combination of capillary electrophoresis with on-line ICP-MS revealed that Zn^{2+} binding to lactoferrin is less strong in comparison to Fe^{3+} and Ag^{+}. When the Zn-bLTF complex was analyzed, the Zn^{2+} eluted from capillary later than protein. Finally, the ICP-MS was useful for the evaluation of Fe^{3+} bioavailability from Fe-LTF.

[1] *O. Pryshchepa, et al. Synthesis and physicochemical characterization of zinc-lactoferrin complexes, J. Dairy Sci. 105, https://doi.org/10.3168/jds.2021-20538*

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(O-26)

OF ULTRA-TRACE SPECIATION ANALYSIS OF CHROMIUM IN FOODSTUFFS BY SPECIES-SPECIFIC ISOTOPE DILUTION AND HPLC-ICP-MS

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It is largely accepted that a better understanding of the impact of food chemical contamination on human health is important taking into account that food represents one of the most important pathways of humans' exposure to chemical hazards. The determination of potentially toxic trace elements in foodstuffs is nowadays carried out almost exclusively by using inductively coupled plasma-mass spectrometry (ICP-MS). Nevertheless, for some elements such as chromium (Cr), the knowledge of their total content is not adequate to assess their actual impact on the human health via food consumption, due to the large difference in toxicity of their species. Actually, Cr^{6+} species has been classified for a long time as carcinogenic whereas Cr^{3+} was considered until recently as a beneficial micronutrient, mainly due to its property to promote insulin efficiency in diabetic patients. It is worth to note that there is a lack of information regarding chromium speciation in foodstuffs most probably because of the challenges in Cr chemical speciation analysis at ultra-trace levels in such matrices. Several studies have shown that the conventional approaches employed for Cr speciation analysis, including those based on HPLC-ICP-MS, are prone to the formation of analytical artefacts, e.g. formation of Cr^{6+}. Species specific-isotope dilution (SS-ID) in combination with HPLC-ICP-MS has proven to be the only analytical approach suitable for the speciation analysis of Cr^{3+} and Cr^{6+} in foodstuffs due to its capability to quantify both species and to the ability to simultaneously correct for their interconversion during the same analytical run.

The present work addresses the challenges of accurate simultaneous speciation analysis of trace and ultra-trace levels of Cr^{3+} and Cr^{6+} in various foodstuffs by using a primary method based on SS-ID and HPLC-ICP-MS. This approach was successfully applied a selection of foodstuffs (meat, dairy products, bread, cereals and rice) hence proving its full capacity to correct for species interconversion and accurately quantify Cr^{3+} and Cr^{6+} in a single analytical run. It is also worth to note that a controversy exists nowadays regarding the presence of Cr^{6+} in foods, especially in the largely consumed ones such as bread and rice. In this work, Cr^{6+} was not quantified in any of the studies samples; Cr^{3+} and total Cr levels were comparable hence demonstrating that Cr is found exclusively as Cr^{3+} species. In addition to the analytical challenges mentioned above, another bottleneck is related to the accurate food risk assessment taking into account that this task is mostly carried out for raw food. The impact of food consumption needs actually to be assessed for the prepared food because these processes may lead to changes in the speciation profile as well as lead to species loss compared to the raw sample. Therefore, the assessment of the impact of food cooking on the fate of Cr species is important for accurate risk assessment. In this context, this study aimed also at the assessment of the impact of various culinary processes on the fate of chromium species (Cr^{3+} and Cr^{6+}) in infant formula milk, semi-skimmed milk and bovine meat samples. The levels of Cr^{3+} and Cr^{6+} in raw and cooked samples were determined by SS-ID HPLC-ICP-MS. The results showed no oxidation of Cr^{3+} to Cr^{6+} during thermal cooking of milk and bovine meat samples. It is interesting to note that in all cases, Cr^{6+} was entirely reduced to Cr^{3+} during the analytical processes but the SS-ID approach was capable to correct the species interconversion concomitantly with their quantification. Therefore, without the capability of SS-ID, Cr^{6+} eventually incorporated into foodstuffs cannot be accurately assessed because of its very likely reduction to Cr^{3+} during the analysis.

(O-27)

RAPID SPECIATION ANALYSIS OF ANTHROPOGENIC GADOLINIUM IN SURFACE AND DRINKING WATERS

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Since its first commercialization in the 1980s, the substance class of gadolinium-based contrast agents (GBCAs) has evolved into one of the most successful metallodrugs. The paramagnetic substances are administered in approximately 40% of all magnetic resonance imaging (MRI) examinations to enhance MR signal and improve image contrast. After intravenous administration, the highly polar Gd complexes are excreted unmetabolized within a few hours. Due to their inert nature, they also pass through wastewater treatment plants almost quantitatively, leading to a worldwide release of up to 50 tons of anthropogenic Gd into the environment every year. As a result, anthropogenic Gd anomalies can be observed in rivers, lakes, coastal and even drinking waters, and due to its persistence, anthropogenic Gd can be used as a sensitive tracer for other polar microcontaminants and to monitor hydrological processes. However, the long-term behavior and ecotoxicological effects of GBCAs are largely unknown, and thus, powerful methods of speciation analysis are required to monitor their distribution and fate in aquatic systems.

This work presents the development and application of a fast ion-chromatographic (IC) method for monitoring GBCAs in environmental samples. A fully automated single platform system for total metal analysis and syringe-driven chromatography combined with inductively coupled plasma-mass spectrometry (ICP-MS) was employed. The developed IC-ICP-MS method enables a rapid separation and detection of the five most commonly administered contrast agents in the European Union in less than two minutes, which significantly improves analysis time in comparison to previously published methods. Different quantification approaches based on automated external calibration or isotope dilution analysis have been evaluated that offer similar and highly sensitive detection limits in the lowest ng/L range. Furthermore, different strategies of sample preparation were investigated for surface water samples. The automation approach and a simplified sample preparation workflow enable efficient high-throughput analysis of even larger numbers of samples, as demonstrated by the large-scale GBCA monitoring of several tap water samples, which have been collected in the 30 largest cities in the German state of North Rhine-Westphalia.

(O-28)

A METROLOGICAL JOURNEY INTO THE HIGH ACCURACY DETERMINATION OF TOTAL ARSENIC IN BIOLOGICAL MATERIALS BY ICP-MS

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High accuracy procedures providing traceability to the SI system for the determination of arsenic in biological materials including food products have been developed over several years at the National Measurement Laboratory of LGC utilising ICP-MS. The core metrology capability has been used for assigning reference values to CRMs and for providing reference values to PT schemes. Demonstration of the capability is provided by the outcome of participation in a number of high-level international metrology studies including P39.1 salmon (2005), K49 bovine liver (2007), K89 herbal medicine (2013), and K158 rice flour (2022). In each study, careful consideration of the analytical method was made to ensure high accuracy and to minimise the measurement uncertainty.

There are a number of known analytical challenges associated with the determination of total arsenic and each study material brought their own. They range from the difficulty of mineralising arsenobetaine (the major As species in fish) (1) to the impact that the oxidation state or species can cause to the ICP-MS response.(2) However, the most significant problem associated with total As quantitation is the charge transfer effect which enhances the As signal response caused by residual carbon in the samples from the digestion process. This has been demonstrated to lead to positively biased results.

The presentation will discuss how the analytical challenges were overcome for each study and show how uncertainty estimates were established. It will also demonstrate how the NMI competence has improved over the years for the analytical methods used to provide services to our key customers (CRM producers, PT organisers). In particular, the benefits of ICP-MS technology improvement will be demonstrated through performance of participation in a recent international intercomparison for As and As species in rice. For this purpose, methodology based on the use of ICP-MS/MS with oxygen reaction mode and exact single matching calibration and its performance to achieve a relative expanded uncertainty (k=2) of less than 3% in a complex food matrix at <0.2 mg/kg will be described.

References:

1. John Entwisle, Ruth Hearn. (2006) Spectrochimica Acta Part B. **61**, 438-443.
2. Tomohiro Narukawa, Koichi Chiba, Takayoshi Kuroiwa and Kazumi Inagaki. (2010) *J. Anal. At. Spectrom.* **25**, 1682-1687.

(O-29)

USING ICP-TOFMS TO SIGNIFICANTLY REDUCE MEASUREMENT UNCERTAINTY FOR PD, PT AND RH IN AUTOCATALYSTS

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Platinum-group elements, especially Pd, Pt and Rh, are used globally as autocatalysts to reduce the impact of exhaust emissions. Due to the extremely high cost of these metals, loading of the catalyst must be tightly controlled by the manufacturer. To support this, SI-traceable methods and certified reference materials (CRMs) are required to ensure accuracy to the highest degree as well as very reduced measurement uncertainties, e.g. below 1% (U, k=2). Internal standardisation (IS) and/or isotope-ratioing techniques such as isotope dilution (ID) or exact single matched (ESM) standard calibration ICP-MS (for monoisotopic elements) have been demonstrated to fulfil these criteria. The largest contribution to the combined measurement uncertainty when analysis is performed by isotope-ratioing methods derives from the uncertainty of the measured isotope ratio (IR). ICP-Time-of-Flight (TOF) MS has been demonstrated to improve the isotope ratio precision for a range of elements in comparison to ICP-quadrupole (Q) MS due to quasi-simultaneous determination of all the isotopes of interest providing that these isotopes are free of interferences (Emteborg et al, 2000).

Autocatalysts are complex materials containing high levels of matrix elements such as Zr and Hf that can lead to significant spectral interferences affecting determination of Pd and Pt by ICP-MS. Using ICP-TOFMS (icpTOF 2R, TOFWERK AG) with He collision gas and a desolvation inlet interface, spectral interferences that affect Pd and Pt isotopes were successfully removed. Using such approach with isotope dilution methodology for Pd and Pt (e.g by measuring ^{104}Pd/^{105}Pd and ^{196}Pt/^{195}Pt) and ESM standard-sample-standard bracketing calibration for Rh (with Ru as an IS), recoveries of 99-100% for Rh, Pt and Pd in NIST SRM 2557 (Used Auto Catalyst, Monolith) and 96-103% for Pd and Pt in ERM-EB503a (Unused Automobile Catalyst) and ERM-EB504a (Used Automobile Catalyst) were achieved. Expanded relative measurement uncertainties (k=2) obtained with the developed ICP-TOFMS based methodology (0.7% for Pt, 0.8% for Pd and 0.9% for Rh) were improved in comparison with those obtained using ICP-QMS and the same quantification approaches (2.9% for Pt, 3.3% for Pd and 1.1% for Rh).

Emteborg H, Tian X, Ostermann M, Berglund M & Adams FC (2000) *J. Anal. At. Spectrom.* **15**, 239–246.

(O-30)

MULTI-ENERGY CALIBRATION AS A POTENTIAL TOOL FOR REGULATORY ANALYSIS OF NUTRIENT ELEMENTS IN FOODS BY ICP-OES

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Nutrient element analysis of foods is an important regulatory mission of the FDA, and ICP-OES is an efficient elemental analysis technique for foods. Multi-energy calibration (MEC) is a new matrix-matched calibration approach. [1] Different from traditional external calibration strategies, MEC determines analyte concentration according to relationships across multiple lines and uses two solutions per sample. In this work, we evaluate MEC applied to ICP-OES with the immediate goals of determining (1) the working range for MEC for Ca, Cu, Fe, K, Mg, Mn, Na, P, S, and Zn, (2) the effectiveness of a strategy based on Cook's distance to identify and remove lines biased from spectral interference, and (3) if there is a difference between MEC and a simple one-point standard addition calibration.

Ten reference materials were microwave digested and used to evaluate MEC performance in food matrices. MEC solutions one and two, were prepared with 50 % sample and 50 % standard, and 50 % sample and 50 % blank solution, respectively. Relevant instrumental parameters include an integration time of 15 s, axial viewing of the plasma, and interference removal using fitted background correction. Signals from up to ten lines for each element were recorded. Due to a limited number of lines available, signals from only eight, nine, and six lines were recorded for K, Na, and S, respectively.

Accurate results are observed for MEC with and without filtering lines based on Cook's distance (**Fig. 1a**). The working range for MEC is defined from the slope of the MEC plot, and the best results are observed for slopes less than 0.9 (**Fig. 1b**), confirming previous reports on other elements. [2] MEC is an accurate method for nutrient element analysis, and MEC results agree with one-point standard additions with an average percent difference of 3.17%. MEC offers the added benefit of spectral interference identification from MEC plots and an internal QC check of a MEC slope less than 0.9 providing a higher confidence in the result for nutrient element analysis.

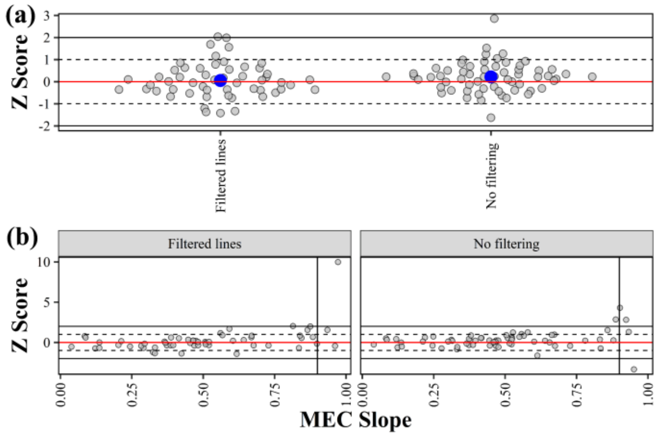

Fig. 1. Dry-mass results from the analysis of ten different reference materials (n = 53). **(a)** Z scores by spectral line selection. Results shown for MEC slopes of 0.9 and below. Blue dots represent the mean for each group; **(b)** Z scores according to MEC slope and spectral line selection.

[1]. A. Virgilio et al., *Anal. Chim. Acta*, 982 (2017), 31-36

[2]. A. Virgilio et al., *J. Anal. At. Spectrom.*, 35 (2020), 1614-1620

(O-31)

RAPID AND ACCURATE DETERMINATION OF URANIUM AND NEODYMIUM CONCENTRATIONS IN ENVIRONMENTAL AND URINE SAMPLES USING STANDARD ADDITION HPIC-SF-ICP-MS

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Determining the isotopic and elemental concentration / mass fraction of uranium in urine samples is important for early dose assessment following a nuclear emergency [1]. Moreover, the interest in determining the concentration / mass fraction of rare earth elements, such as neodymium, in environmental soil samples has been increasing due to the ecological and human health risk of rare earth elements [2]. The analysis of uranium in environmental samples requires labour-intensive sample preparation prior to long measurement time when using alpha spectrometry. Alternatively, inductively coupled plasma-mass spectrometry (ICP-MS) can be used after minimal sample preparation to determine the concentration of uranium as well as that of neodymium in environmental samples, in addition to offering a higher sample throughput compared to alpha spectrometry. However, ICP-MS suffers from interferences of ions having the same mass-to-charge ratio, such as 238Pu+ and 238U+, and 142Ce+ and 142Nd+. These interferences can be eliminated by using high-pressure ion chromatography (HPIC), which can be coupled online to ICP-MS. Furthermore, standard addition calibration offers an advantage over using external calibration for the ICP-MS analysis thanks to the elimination of matrix effects. On the other hand, one should take into account the higher detection limits when using HPIC coupled to ICP-MS compared to using alpha spectrometry.

In this talk, the potential of using HPIC coupled to sector field (SF)-ICP-MS for the separation and accurate quantification (by standard addition calibration) of uranium and neodymium concentrations / mass fractions in three types of matrices, water, soil and urine, will be presented. The applicability of the previously published HPIC separation method [3] to environmental samples was investigated. The HPIC method consists of using a mixed bed ion exchange guard column (CG5, 4.6 x 50 mm) and column (CS5, 4.6 x 250 mm) as stationary phase. An isocratic flowrate of 1 M nitric acid followed by 0.1 M oxalic acid (at pH 4.5) was used as mobile phase in each injection. Samples were spiked with plutonium and americium in order to verify their elution using this HPIC method and thus to prove the separation of plutonium and uranium nuclides as well as that of plutonium and americium nuclides in environmental samples. Standard addition calibration was used with both online HPIC-SF-ICP-MS and offline SF-ICP-MS (on uranium and neodymium fractions collected after elution from the HPIC column) to quantify uranium (in water, soil and urine matrices) and neodymium (in water and soil matrices). The concentrations / mass fractions of uranium and neodymium obtained by both online and offline analyses were found to be in agreement with each other (100 % ± 5 %) as well as with their reference values (certified values or alpha spectrometry results). Overall uncertainty budgets corresponding to the concentrations / mass fractions of uranium and neodymium obtained using standard addition calibration were determined by using the bottom-up approach following the Eurachem / CITAC guide CG4 rules. The relative expanded uncertainties obtained using online HPIC-SF-ICP-MS were between 4 % and 5 %, and those obtained using offline SF-ICP-MS were between 2.7 % and 4 %.

[1] Y. Shi, X. Dai, R. Collins and S. Kramer-Tremblay, “Emergency uranium bioassay method in urine by ICP-MS - CW-508790-CONF-009,” IAEA, 2010.

[2] I. Gunther-Leopold, B. Wernli, Z. Kopajtic and D. Gunther, “Measurement of isotope ratios on transient signals by MC-ICP–MS,” Analytical and Bioanalytical Chemistry, 378 (2004) 241-249.

[3] N. N. Wanna, K. Van Hoecke, A. Dobney, M. Vasile and F. Vanhaecke, “Determination of the lanthanides, uranium and plutonium by means of on-line high-pressure ion chromatography coupled with sector field inductively coupled plasma-mass spectrometry to characterize nuclear samples,” Journal of Chromatography A, 1617 (2020) 460839.

(O-32)

DISTRIBUTION OF INORGANIC NANOPARTICLES IN A NORWEGIAN FJORD

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The marine environment is the principal sink for natural, incidental and engineered nanoparticles (NPs). Due to the analytical challenges of detecting and quantifying nanoparticles in seawater, the data on distributions of NPs the marine environment is limited to qualitative studies or by ensemble measurements subject to various analytical artifacts. Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a technique allowing precise determination of individual inorganic NPs at concentrations in the nanograms per liter range, yet thus far only few studies have been done on select elements in surface sea water. Here, a multi-element screening method using SP-ICP-MS was developed and applied using a trace element sampling procedure using acidification and a neutral sampling protocol developed for NP specific purposes. Employing this method, a first survey of the horizontal and vertical distributions of inorganic nanoparticles and trace elements was performed in a pristine Norwegian fjord prospect for submarine tailings deposition. Statistical control of false positive detections while minimizing the size detection limit was ensured using a novel raw signal processing. To confirm the results of the single particle measurements, and for qualitative information regarding particle morphology and composition, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) was used. Following SP-ICP-MS screening for particles of 16 elements, particulate Al, Fe, Mn, Pb, Si and Ti were found and determined to number concentrations in the range 4×10^6 to 10^8 particles per liter. A strong depth dependence was observed for both trace elements and particles, concentrations increasing with depth. The particulate fraction was for all elements found to compromise only a few mass percent of the total metals, at concentrations mostly in the hundreds of ng/L range versus µg/L for total metals. The sampling protocol was found to have a strong influence on the particles consisting of Fe, Mn, Pb and Ti, whereas no significant influence was found for Si and Al containing particles. Our results provide a baseline for the fjord and new data on environmental levels of both total metals and metal containing nanoparticles including the vertical and horizontal distribution of natural nanoparticles.

(O-33)

ON THE FIRST DECADE OF TRIPLE QUADRUPOLE ICP-MS: ADDRESSING CHALLENGING APPLICATIONS USING ICP-MS/MS

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At the 2012 Winter Plasma Conference in Tucson, Arizona, a new ICP-MS was announced, based on a novel tandem mass spectrometer configuration (MS/MS). It was soon evident that the new ICP-MS/MS technique offered a solution to many of the spectral interferences that had hampered ICP-MS measurements since the technique was introduced in the 1980s.

Single quadrupole ICP-MS instruments equipped with a collision/reaction cell (CRC) use helium (He) collision mode to control common polyatomic ion overlaps in typical sample types. He mode gives much better accuracy and consistency that is possible with non-cell instruments. But some applications – particularly those involving ultralow level determinations or analysis of non-typical analytes or sample types – could still suffer errors due to spectral interferences that were not successfully resolved using He mode. Reaction gas methods on ICP-MS/MS offer a solution to these interferences, using the first mass filter to control the ions that can enter the CRC and take part in the reactions. Reactive cell gas modes can resolve polyatomic ion overlaps that are too intense for He mode, while also providing a solution to spectral overlaps from isobaric and doubly charged ion interferences. We will present data using application examples to illustrate each of these types of interferences.

MS/MS is fundamental to reliable interference control using reactive cell gases. But the double mass selection of MS/MS also dramatically improves the separation of adjacent mass or “peak tail” overlaps. The quadrupoles used in commercial single quadrupole ICP-MS instruments can reject adjacent masses very efficiently. For every 10 million counts per second (cps) at a given mass, only 1 cps “leaks” through the quadrupole to be detected at the wrong mass (+1 u or -1 u). This translates into an abundance sensitivity (AS) specification of 10^{-7}. This means peak tail overlaps are not usually a concern in typical ICP-MS applications.

However, in some cases, a trace analyte needs to be measured adjacent to a major element, and some of these cases can suffer from peak tail overlaps. Examples include the measurement of trace boron in organic solvents, trace manganese in iron-rich samples, and trace neptunium 237 in a uranium matrix. ICP-MS/MS uses 2 high performance mass filters, each rejecting all but 1 of every 10 million incident ions from the neighbouring mass, so the peak rejection efficiency is multiplied to give an overall theoretical AS of 10^{-14}. This is more than sufficient to allow the trace elements mentioned above to be analyzed with no measurable contribution from the neighbouring major element peak.

The control of reactive cell gas modes and double mass selection supported by ICP-MS/MS, have transformed ICP-MS performance for advanced applications and challenging spectral overlaps.

(O-34)

DETECTION OF NANOPARTICLES AND MICROPLASTICS IN ENVIRONMENTAL SAMPLES WITH ATOMIC AND MOLECULAR MASS SPECTROMETRY

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In this presentation, recent advances in plasma spectrochemistry for the detection of nanoparticles and microplastics will be reviewed and some contributions from our laboratory to this field will be presented.

In the first part, recent developments in inductively coupled plasma mass spectrometry (ICP-MS) instrumentation for nanomaterials characterization in complex mixtures will be reviewed. The current state-of-the-art in single-particle (sp) ICP-MS instrumentation for the detection and characterization of single nanoparticles (NP) 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 nanoparticle 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.

In the second part of the presentation, we turn to a cooler plasma source, which proved useful in ambient desorption/ionization mass spectrometry (ADI-MS). Specifically, the use of molecular mass spectrometry with a home-built flowing atmospheric-pressure afterglow (FAPA) source (which was first developed in the Hieftje laboratory [1-2]) for the direct analysis of microplastics will be discussed. Microplastics (MPs) are typically characterized by Raman spectroscopy and pyrolysis/thermal desorption coupled to gas chromatography, respectively. In this work, the FAPA source is coupled to a high-resolution mass spectrometer (HR-MS) and used to probe selected microplastics directly on a sample target without a preceding separation step. Characteristic mass spectra from polystyrene (PS), polypropylene (PP), polyethylene (PE), and polycarbonate (PC) MPs were obtained and multivariate statistical data analysis tools were used to process the raw data. FAPA-HRMS analysis in combination with principal component analysis is considered an interesting tool for microplastics analysis.

[1] F.J. Andrade, J.T. Shelley, W.C. Wetzel, M.R. Webb, G. Gamez, S.J. Ray, G.M. Hieftje, Anal. Chem., 80, 2646-2653 (2008).
[2] F.J. Andrade, J.T. Shelley, W.C. Wetzel, M.R. Webb, G. Gamez, S.J. Ray, G.M. Hieftje, Anal. Chem., 80, 2654-2663 (2008).

(O-35)

INFLUENCE OF SAMPLE HANDLING ON THE QUALITY OF SINGLE CELL ICP-MS DATA

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In recent years, single cell ICP-MS (sc-ICP-MS) has evolved as a promising technique to obtain biodistribution data of endogenous as well as ingested elemental contents in biological cells. Here, instead of applying digestion and homogenisation protocols prior to ICP-MS analysis, cell suspensions are introduced directly into the plasma. The atomization and ionization process of intact cells leads to the formation of distinct ion clouds, which can be separated from background signals when using appropriate experimental conditions. In contrast to the classical approach, where cell homogeneity is assumed, sc-ICP-MS data provides the elemental content of large numbers of individual cells, making the data more statistically viable. Obviously, maintaining cell integrity until the plasma is reached is crucial. Therefore, the objective of this work is to examine the influence of cell handling techniques, such as aldehyde fixation and choice of working buffers, and different measuring parameters on the quality of sc-ICP-MS data of two different cell types.

For this purpose, both mammalian NR8383 cells (alveolar macrophage, *Sprague Dawley* rats) and algae (*Cyanidioschyzon merolae*) were fixed with varying concentrations of formaldehyde and glutaraldehyde prior to sc-ICP-MS analysis. A high-efficiency total consumption sample introduction system was operated at different gas flow values to achieve optimal experimental conditions. Biodistributions of endogenous manganese and magnesium were obtained and compared for all different approaches. Additionally, exact cell concentrations of every sample were determined using flow cytometry to calculate precise transport efficiency data. Especially for *C. merolae*, the use of different working buffers led to a significant increase in detected cell events. For NR8383, transport efficiency could be improved using formaldehyde fixation, while the determined intracellular concentration of manganese remained in good agreement with native cells. The results indicate that sample handling as well as experimental conditions have a large impact on the overall quality of sc-ICP-MS data.

(O-36)

ENDOGENOUS METAL ANALYSIS IN LABELED SINGLE CELLS USING TIME OF FLIGHT ICP-MS FOR THE ELUCIDATION OF A CELLS METALOME ON A PER CELL LEVEL

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Mass cytometry is a valuable tool for investigating protein expression by individual cells within heterogeneous cellular suspensions. With this approach, heavy metal isotope conjugated probes – typically antibodies – label multiple cellular proteins, and TOF-ICP-MS is then used to simultaneously detect these probes on single cells. Analysis of the resulting data allows population heterogeneity to be determined at the individual cell level.

In many applications it is crucial to not only detect the metal labels, which allow the differentiation of cells, but also endogenous elements. When combining the information from all elements, the metalome can be examined on individual cell level. Herein, data recorded on a Vitesse TOF-ICP-MS is shown. The high acquisition speeds allow for precise cell identification and integration in the NuQuant software, while the full elemental capabilities enable the detailed examination of the metalome of single cells. Data reduction methods were possible using both Python scripts within NuQuant as well as output in Flow Cytometry Standard (FCS) format, which is compatible with commonly used flow cytometry data analysis pipelines.

(O-37)

AUTOMATED SINGLE CELL ICP-MS FOR THE QUANTIFICATION OF TRACE METALS IN BEER SAMPLES

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Trace elements play an essential role in the biologic activity of every living cell. Researchers have been studying cellular trace metal uptake and distribution for decades. However, these studies usually employ an acid digest to determine the average bulk concentration for a given cell population. More recently, the detection power of fast scanning inductively coupled plasma-mass spectrometry (ICP-MS) instruments enabled the quantification of trace elements in single cells by a methodology called single cell ICP-MS (scICP-MS). Similar to flow cytometry, this approach uses a microliter low flow sample introduction system allowing it to operate with very low sample volumes and cell concentrations.

While the mass flow sensitive detection principle of ICP-MS provides a straightforward and direct qualitative comparison of different cell populations, quantification can be more laborious. Because the metal content of each cell cannot be lowered by dilution, an external calibration may require standards with concentrations of up to several hundred µg/L for certain elements. Furthermore, both the particle size and the particle frequency calibration method for scICP-MS depend on the precise knowledge of the liquid sample flow rate usually in the range of 10 µL/min. These conditions need a sample introduction system of low dead volume, precise flow control and low carry-over materials to fulfill the requirements.

In this work, an automated sample introduction platform was used to analyze trace elements in yeast cells extracted from commercial bottled beer. Across different brands and products, unique variations of the trace metal composition were observed. Cellular concentrations of endogenous elements including Fe, Cu, Mn, Zn and Mg were determined. Qualitative data on the non-metal elements P, C and S were also recorded using a triple quadrupole instrument in oxygen mode. On top of that, samples from before, during and after the brewing process were collected in collaboration with a local brewery emphasizing automated scICP-MS as a process-accompanying analytical tool for biotechnological applications. In order to keep the cell suspensions stable, the platform's loading syringe was used for mixing prior to analysis. Finally, quantification via the particle size calibration method required the development of a procedure to stabilize ionic standards with the complexing agent EDTA in order to match the neutral pH matrix of the cell suspensions.

(O-38)

MDG-ICP-MS - A VERSATILE TOOL FOR QUANTIFICATION IN THE FIELD OF SINGLE PARTICLE ICP-MS USING ISOTOPIC DILUTION

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In recent years, the release of nanoparticles into the environment has increased significantly, not least due to their rapidly growing market share. Due to the strongly differing properties of nanoparticles compared to bulk materials, the detection and evaluation of nanoparticles in the environment is an important issue for environmental analytics.

An established method for the detection of type and size of nanoparticles is single particle ICP-MS. Here, they are introduced as a suspension into the plasma of the mass spectrometer and the particles are recorded as "events". In addition to the influence of the matrix, which can lead to ion suppression and thus to underestimation in addition to superposition of the event signal, calibration with ionic standards is also non-trivial. Here, the transport efficiency plays a major role, as it has an influence on the signal intensity for ionic standards as well as on the frequency of detected events for particles.

To circumvent these two challenges an isotope dilution (ID) method comprising a microdroplet generator (MDG) as the introduction system coupled on-line with an ICP-ToF-MS was used in this work. For ID, ICP-ToF-MS has the advantage that isotopic patterns can be measured in individual particles.

Using platinum nanoparticles as proof-of-concept application, it was shown that it is possible to correctly determine the size of the particles on basis of the known volume of the droplets generated by the MDG applying isotope dilution. With this method, the determination of the transport efficiency as well as external calibration becomes redundant. This makes the developed method very fast and robust and due to the ICP-ToF-MS applicable to a plethora of nanoparticles.

(O-39)

LA-ICP-MS AND PROTEINS: UTILIZATION OF NANOPARTICLE-BASED BIORECOGNITION ELEMENTS

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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 are not suitable for this puprpose. Hence, the biorecognition tools for their determination by LA-ICP-MS are being developed. One of them is the labeling of antibodies by nanoparticles and the second one is based on utilization of molecularly imprinted polymers. Examples of their utilization in combination with LA-ICP-MS will be presented.

(O-40)

SINGLE PARTICLE ICP-OES ANALYSIS OF BATTERY MATERIALS DETERMINING PARTICLE INACTIVATION AND ITS CONSEQUENCES FOR THE BATTERY

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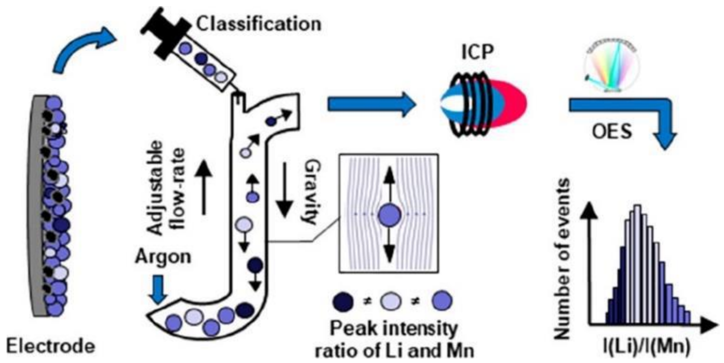

Lithium ion batteries, like any other battery technology, tend to lose capacity with continued charging and discharging. One of the effects contributing to the decline in capacity is the inactivation of positive electrode particles. The electrodes typically consist of polydisperse active material particles, a conductive agent and a binder. By charging and discharging of the battery the active material particles are lithiated and delithiated. If a particle becomes inactive, e.g. by losing the electronical contact or by the formation of ion blocking surface films, it stops following the lithiation and delithiation of the rest of the electrode. Analyses of the degree of lithiation (DOL) of single particles therefore provide valuable information on the capacity loss attributed to inactive particles.[1,2]

Since TOF-SIMS and synchrotron-based techniques which are usually used to determine the lithium content of single electrode particles only analyze small areas of the electrodes and are not well suited for measuring large numbers of samples, a method has been developed applying common ICP-OES instrumentation. For the determination of the DOL of single particles, the most important advantage of many ICP-OES instruments is the simultaneous detection of several analytes. In case of common positive electrode materials such as Li(NixMnyCoz)O2 (x+y+z=1) the ratio of e.g. Li to Mn signal intensities can be used to determine the DOL. As an aqueous sample introduction cannot be used because these materials would undergo Li+/H+ exchange reactions, a sample introduction using argon gas that furthermore enables a classification of particle sizes was developed.

This presentation will focus on the method development and application of single particle ICP-OES for battery materials. It will be shown how this method helps to elucidate the mechanisms of capacity fading, and the advantages and disadvantages of ICP-OES will be compared with those of alternative methods for this application.

[1] T. N. Kroger, S. Wiemers-Meyer, P. Harte, M. Winter, S. Nowak, *Analytical Chemistry* **2021**, *93*, 7532-7539.

[2] T.-N. Kröger, P. Harte, S. Klein, T. Beuse, M. Börner, M. Winter, S. Nowak, S. Wiemers-Meyer, *J. Power Sources* **2022**, *527*, 231204.

(O-41)

CAPABILITIES OF FAST SINGLE PARTICLE ICP-MS WITH NANOSECOND TIME RESOLUTION AS A NEW TOOL FOR NANOMATERIAL ANALYSIS

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Over the last decade, single particle inductively-coupled plasma mass spectrometry (spICPMS) has emerged as a powerful method for nanomaterial analysis. Initially, the technique utilized millisecond time resolution in a transient measurement of a colloid dispersion to enable the detection of individual particles. Recently, microsecond time resolution helped to improve the particle size detection limit of spICPMS by reducing the continuous background signal, addressed issues of split-particle events and particle coincidence, and also provided insights into the temporal profile of individual ion clouds. [1]

In this proof-of-principle study, we present our contribution to spICPMS developments with a novel in-house built data acquisition system with nanosecond time resolution (nsDAQ) and a matching data processing approach. The new system can continuously sample the secondary electron multiplier (SEM) detector signal and enables the detection of gold nanoparticles (AuNP) as small as 7 nm with a commercial single quadrupole ICPMS instrument.

The nsDAQ records the SEM signal in intervals of approximately 4 ns. A tailored method was developed to process this type of transient data, which is based on determining the temporal distance between detector events, which is denoted as event gap (EG). During the measurement of a continuous background signal, the EG has a relatively constant and high level, because the analyte ions are distributed homogeneously and have a low density in the plasma. In contrast, the ion density increases rapidly over a short time frame as soon as a small analyte particle is vaporized and ionized in the plasma and, subsequently, the resulting ions hit the detector. Consequently, the EG value decreases significantly during such a particle event in comparison to the background signal.

The scope of the current study is to evaluate the capabilities of the nsDAQ for fast nanoparticle characterization including particle size and particle number concentration calibration.

[1] I. Strenge, C. Engelhard, *J. Anal. At. Spectrom.* **31**, 135 (2016), DOI: 10.1039/C5JA00177C.

(O-42)

MULTI-ISOTOPE APPROACH WITHIN ENVIRONMENTAL FORENSICS

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Environmental Forensics is a scientific methodology developed for identifying sources, the timing of release, and transport pathways for potentially hazardous environmental contaminants. The field has gained significant attention in the last few decades as the need to identify contaminant sources and dispersal pathways in our environment continues to grow. Such understanding is essential to mitigate the potentially harmful effects on ecosystems and on human health as well as to optimize remediation strategies. Over the last few decades, isotope ratio analysis has become an important tool within the Environmental Forensics' toolbox. Improved analytical capability offered by the advent and continued developments of MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometry) instrumentation and analyte purification techniques have introduced non-traditional isotopes, such as Cd, Cu, and Zn, into the field of Environmental Forensics. As isotopic fractionation may occur in many industrial processes with incomplete mass transfer, isotope systems with different degrees of fractionation can be used as powerful tracing tools and such tracer studies using isotope ratio measurements are increasingly adopting multi-elemental approaches to fingerprint pollution sources. Expanding the number of elements utilized in isotope tracing empowers our abilities to decipher the source(s) and the extent of environmental exposure from contamination events However, the applicability of such multi-elemental methods may be limited by the uncertainties of interpreting the isotope ratio data.

This presentation will focus on Environmental Forensics investigations where isotopic information of several elements (Cd, Cu, Pb, U and Zn) was used in source identifications demonstrating both potential and limitations of the approach.

(O-43)

COMMON USE OF LA-ICP-MS IN EARTH SCIENCE & NEW APPROACHES WITH LASER ABLATION, ICP-MS, ICP-OES, SEM, EMPA AND OPTICAL MICROSCOPY

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been used for more than 30 years to measure elemental compositions of natural and synthesized materials*. In Earth sciences the use of LA-ICP-MS allows spatially resolved quantitative measurements of major, minor and trace element abundances as well as isotopic ratios from minerals and rocks with an equal or better precision than several other in situ techniques, and more rapidly than solution chemistry procedures. Common use of LA-ICP-MS in Earth sciences focus on analysing the composition of natural and experimental geological materials using bulk silicate glasses, pressed powder tablets, fused aliquots, in situ analysis of separate minerals, xenocrysts, fluid and melt inclusions, and to provide multidimensional chemical maps of complex (multiphase) materials. LA-ICP-MS has proven to be an extremely important analytical tool within the Earth and Environmental sciences, and some frequently used LA-ICPMS applications are outlined.

New developments in both instrumentation and methodology have offered the ability to quick and cost-effectively extract *in situ* dates and tracer information at a variety of scales from nm to cm, in 2- and 3-dimensions, providing a considerable analytical flexibility compared to other micro-analytical techniques*. At GEUS this application versatility of the LA-ICP-MS technique are further explored by connecting the analyses obtained by LA-ICP-MS with analyses performed by other analytical tools such as scanning electron microscopy (SEM), electron microprobe analyser (EMPA), optical microscopy and fluid and melt inclusion microthermometry. An approach for measurement on the exact same point location involving the above-mentioned instrumental equipment is developed to be able to acquire corresponding data sets for all analyses from the very same location (i.e. within a few µm).

Ongoing research combining this point-to-point coordination approach with a split-stream laser ablation analytical methodology including ICP-OES, quadrupole ICP-MS and SF-ICP-MS instruments further enable us to obtain comprehensive sets of corresponding data that can include isotopic ratios and dates, all important major, minor and trace components, the abundance of impurities, fluid or melt components, textural information, and being able to relate this all to various kinds of images obtained by these instruments for a more profound interpretation. This approach offers improved spatial control of the analyses obtained by different analytical tools compared to what is common at present. Examples with corresponding analyses acquired from selected minerals, rocks, stone axes, and biological material are presented.

** Sylvester PJ, Jackson SE (Eds.) 2016: Studying the Earth with LA-ICP-MS. Elements.*

(O-44)

ANALYSIS OF PERMANENT GASES AND LIGHT HYDROCARBONS EVOLVING DURING OPERATION OF LITHIUM ION BATTERIES WITH A BARRIER DISCHARGE IONIZATION DETECTOR

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To understand the overall processes behind the decomposition of state-of-the-art organic liquid electrolytes in lithium ion batteries (LIBs) it is necessary to investigate and quantify the permanent gases and light hydrocarbons evolving during electrolyte decomposition. As a suitable tool for measurements of these components, GC equipped with various detector systems such as thermal conductivity detector (GC-TCD), flame ionization detector (GC-FID) and mass spectrometer (GC-MS) were applied so far. One of the main focuses of these studies was on reaction pathways leading to decomposition products of the electrolyte. A relatively new detector system invented by Shinada et al. is the barrier discharge ionization detector (BID). In this detector system, the samples are ionized by a vacuum ultraviolet (VUV) radiation which is created by a cold plasma resulting from an electrical discharge.

In this work a convenient way of sampling gas from pouch cells without any previous preparation of the cell as well as a comprehensive gas chromatographic (GC) investigation of the gas phase is shown. A barrier discharge ionization detector (BID) was utilized for gas quantification and a multi component gas standard in combination with a gas mixing device was implemented to prepare calibration standards for validation. [1]

[1] M. Leißing, M. Winter, S. Wiemers-Meyer, S. Nowak, Journal of Chromatography A, 1622 (2020) 461122.

(O-45)

ICP-MS/MS ANALYSIS OF TECHNOLOGICALLY CRITICAL ELEMENTS IN PRINTED CIRCUITBOARD WASTE

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Printed circuit board (PCB) waste is a potential source of many valuable metals that are technologically critical because of their economic importance in essential technologies and their supply risk. Only a fraction of PCB waste is recycled at present. Fit-for-purpose analytical methods are needed for this complex and challenging sample matrix to evaluate the waste materials recycling potential.

The presentation deals with the development of microwave-assisted acid digestion methods of PCB waste and the development of a triple quadrupole ICP-MS method for several technologically critical elements (In, Nd, Pr, Dy, Gd, La, Au, Pt, Pd, Rh). Challenges and observations during the method development are presented as well as background to the work conducted.

(O-46)

MATERIALS MAPPING, WHAT LASER INDUCED BREAKDOWN SPECTROSCOPY CAN AFFORD IN ORDER TO HELP US?

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Catalysts used in various processes can be altered by several phenomena, degrading their properties and efficiency. Therefore, accurate studies of elemental repartitions on catalysts are of primary importance to improve refining modelling and allow more realistic predictions and understanding of processes. However, carbon and metals analysis on catalysts encounter challenging issues as they imply frequently heterogeneous repartition while the most widespread chemical characterization for catalysts are bulk analysis. The procedure to analyze such catalyst is mainly based on X Rays Fluorescence or Inductively Coupled Plasma for the global concentration of poisons, but also microprobe imaging when elemental mapping is required. Anyhow, mapping of carbon presence is not feasible with microprobe due to limited sensitivity with light elements.

In this context, Laser Induced Breakdown Spectroscopy (LIBS) might be able to provide individual information on each grain of the catalyst, but also multi-element mapping of the cross section of a catalyst in order to detect and quantify elements that are not clearly evidenced using conventional techniques[1]. Such procedures were developed and are optimised in our institute. Mapping of trace elements and carbon were observed over catalyst sections sampled at different time of an industrial refining process[2]. This imaging method was also applied to wet catalyst grains impregnated with a nickel nitrate solution and the diffusion of certain metals was observed and compared with more conventional techniques such as Raman and Magnetic Resonance Imaging[3]. The proposed approach allows to shorten drastically the analysis time, allowing nearly in situ monitoring of the maturation process. These results emphasize LIBS imaging potential as a very helpful characterization technique for catalysts characterization.

More recent examples of LIBS application on plastics of different composition (PET, PP and PE) containing various number of inorganic additives were developed, few results will be shown to emphasize promising perspectives of such an efficient tool over different matrix.

1. Jolivet L., Leprince M.. Moncayo S., Sorbier L., Lienemann C.-P., Motto-Ros V. Review of the recent advances and applications of LIBS-based imaging, Spectro Chimica Acta Part B., 151, (2019), 41-53, https://doi.org/10.1016/j.sab.2018.11.008
2. Jolivet L, Motto-Ros V., Sorbier L, Sozinho T., Lienemann C.-P., Quantitative imaging of carbon in heterogeneous refining catalysts, J. Anal. At. Spectrom, 35, (2020), 896-903, https://doi.org/10.1039/c9ja00434c
3. Jolivet L,, Catita L., Delpoux O., Lienemann C.-P., Sorbier L, Motto-Ros V., Direct multi-elemental imaging of freshly impregnated catalyst by Laser-Induced Breakdown Spectroscopy, J. Catalysis, 401, (2021), 183-7, https://doi.org/10.1016/j.jcat.2021.07.010

(O-47)

EVALUATION METHODS FOR LIBS DATA IN INDUSTRIAL ON-LINE APPLICATIONS

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Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique capable of fast analysis of both solids and liquids of various types. Two important characteristics of LIBS are: 1) in many applications no sample preparation is needed; 2) it is contact-free and there can be a considerable distance between the instrumentation and the sample. Combined, these characteristics make LIBS fit for use in industrial on-line applications.
There are two major types of industrial on-line LIBS applications: 1) sorting of a flow of material in a limited number of classes (e.g. metal or plastic scrap); 2) fast quantitative analysis of material in a process flow.

Sorting of materials can often be accomplished with a single laser pulse, or a very short burst of pulses from a high frequency laser. Using a fast sorting algorithm up to 100 pieces/second can be processed. A few types of sorting algorithms will be discussed, both in terms of accuracy and speed.

Needless to say, a fully quantitative analysis is more challenging than sorting. Usually, at least a few hundred laser pulses are needed for a statistically robust result. For inhomogeneous materials, a mechanism to sample data over a larger area is also needed. In this work, the focus is on quantitative analysis of slags. Two different approaches will be presented and discussed: 1) a conventional univariate method normally used in metallurgical analysis; 2) a method based on multivariate analysis (MVA).

(O-48)

LA-ICP-MS IMAGING METHOD: CAN MAKE A GEOLOGIST HAPPY?

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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 including applications in geological science. 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.

Each LA-ICP-MS instrumentation has its limits for the imaging method - they can be in the laser system (scan speed and movement accuracy, repetition rate, wavelength, pulse length…) or in ICP-MS (acquisition speed, accuracy, sensitivity…). The limits of the used instrumentation indicate the possibilities of the application for imaging (ultra-trace imaging, high-resolution imaging, high-speed imaging, imaging for geochronology…). Satisfaction with the results of the analyses is therefore related to ideas of a geologist and the possibilities of available instrumentation. This work will show how it is possible to use the most common LA-ICP-MS instrumentation with nanosecond laser ablation system and quadrupole ICP-MS to achieve the best possible results for imaging in geology. Can this instrumentation be sufficient? And can make a geologist happy?

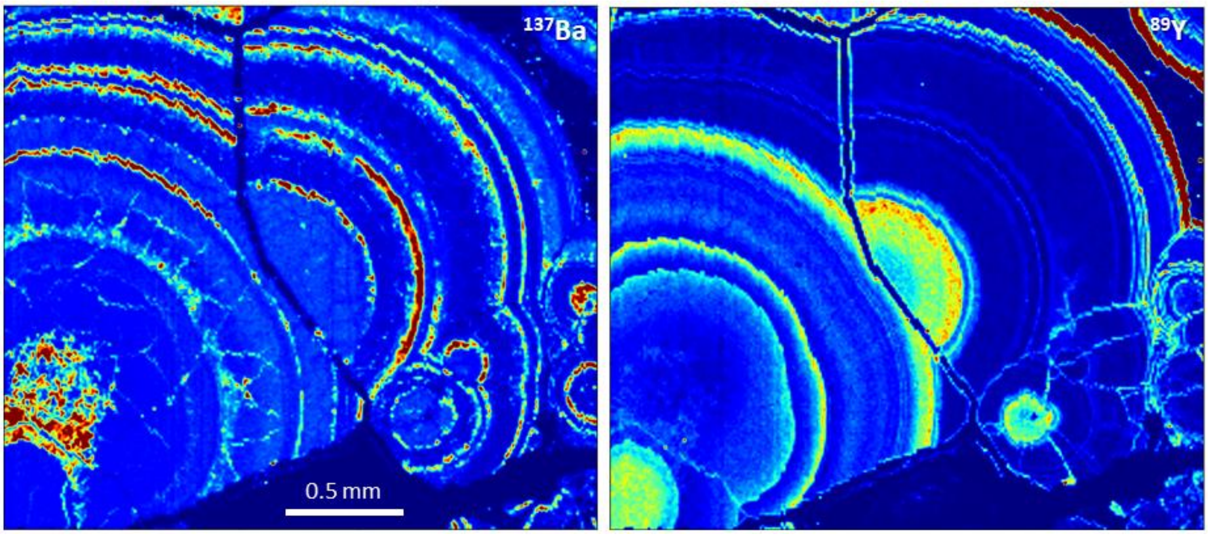

Figure 1. Distribution of Ba and Y in uraninite obtained by LA-ICP-MS. Normalised intensities in cps, blue colour as minimum, red as maximum.

(O-49)

APPLICATION OF ANALYTICAL TECHNIQUES FOR THE CHARACTERIZATION OF BATTERY MATERIALS

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In the drive towards reducing dependence on burning fossil fuels for energy generation, several technologies have become established as front runners in the race to reduce carbon emissions and improve air quality. One of the most significant is lithium ion battery technology and a rapid ramp up in production of these batteries is currently underway globally. As a result, a corresponding increase in analytical testing of the battery component materials has arisen. Techniques such as elemental analysis are vital for both research and quality control analysis of cathode, electrolyte and anode materials. This presentation will give a complete overview on integrated analytical solutions available for the battery sector.

(O-50)

DO WE STILL HAVE TO WORRY ABOUT INTERFERNCES IN ICP-MS?

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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 presentation we will focus 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.

(O-51)

SEAWEED FOR FOOD AND FEED APPLICATIONS – NEED FOR ELEMENTAL ANALYSIS

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Seaweed is the common term for marine macroalgae plants, which may be divided into green, red and brown algae types. There is a growing interest in increasing the exploitation of marine macroalgae for commercial purposes including their uses in relation to food and feed production and thereby contribute to the green transition.

Many seaweeds have the potential to accumulate various trace elements and contain consequently relatively high levels of both essential and potentially toxic elements (PTEs). There is consequently a need to document the levels of potential toxic elements in seaweeds and to ensure that the use/consumption of the seaweeds is safe. In this context, a better understanding of how biological and environmental factors, like seaweed type, location, sampling season etc affects the levels of trace elements is called upon, in order to be able to select seaweeds with optimum characteristics for commercial use. Additionally, further knowledge and understanding of the effect of post-harvest processing on the levels of elements in the biomass is called upon.

The lecture will present the outcome of recent research projects related to seaweed use in food and feed applications conducted at the National Food Institute with a focus on the analytical procedures used for the determination of trace element (species) and the subsequent evaluation of the obtained data in relation to the assessment of food and feed quality and safety.

(O-52)

ICP MS DETERMINATION OF METALS IN SODIUM HYPOCHLORITE SOLUTIONS USED FOR DESINFECTION OF DINKING WATERS

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One of the possible sources of metals in drinking water are the reagents used in the water treatment processes. One of these reagents with particular relevance is sodium hypochlorite since it is used directly into drinking water with the purpose of disinfection. In order to control the content of metals in sodium hypochlorite and guarantee the quality of drinking water supplied, an ICP MS method was developed in EPAL laboratory for the determination of Nickel, Chromium, Antimony, Lead, Arsenic, Selenium, Cadmium and mercury simultaneously. The concentrations of these metals allow to classify commercial solutions of sodium hypochlorite accordingly to EN 901, from Class 1 (highest quality) to Class II (lowest quality).

The EPAL S.A. is the major water supplier company in Portugal, responsible for production and distribution of drinking water to about 2,5 million inhabitants in Lisbon and in other 25 Town Halls nearby the city of Lisbon.

Analyses of metals by ICP MS in sodium hypochlorite poses some analytical problems in ICP MS such as spectral interferences and matrix effects due to high contents of sodium, chloride and basic media. In this work it is presented a methodology to study the preparation of sample, instrumental parameters approach, the internal standards to be use and minimization of interferences. The limits of detection were estimated for each metal, varying from 0,19 mg/kg active Cl_2 (for Cd, As and Hg), 0,37 mg/kg active Cl_2 (for Ni, Pb, Sb and Cr) and 0,74 mg/kg active Cl_2 for Se. Precision was lower than 9% (highest for As) and accuracy lower than 4% (also highest for As).

The method was successfully applied to real samples and it is implemented in a routine basis. From the samples analyzed until February of 2022, contents of metals fulfil the requirements of Class 1 defined in EN 901.

(O-53)

UTILIZATION OF 3D PRINTED METAL SCAVENGERS FOR PRECIOUS METAL RECOVERY AND FOR PRE-CONCENTRATION AND SPECIATION OF MERCURY

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3D printed scavengers have been shown to be highly efficient tools in recovery of precious metals from acidic solutions, as well as in preconcentration and speciation of mercury from natural waters. The simple, effective, and highly selective Nylon-12 based 3D printed scavenger filters were used for the recovery of gold directly from an *aqua regia* extract of waste printed circuit boards (PCBs). Using the easy to handle and reusable 3D printed meshes or columns, gold can be selectively and effectively captured in continuous flow processes by passing the gold containing solution through the 3D printed filter.

The recovery of platinum and palladium were performed using the 3D printed filter containing type-1 anion exchange resin and polypropylene as the printing material. The 3D printed filters with type-1 anion exchange resin were able to capture Pd and Pt with high efficiency and selectivity from a complex solution of metal ions that contained up to 100 times higher concentrations of other metals like copper. By using the Pd/Pt filter together with nylon based Au filter, the most precious metals i.e. Au, Pd and Pt could be recovered from the electronic waste leachate in a single flow-through process. One of the main advantages of the 3D printed filters is that all recovered metals can be easily extracted from filters as separate fractions by using aqueous solutions of 0.1 M thiourea, 0.5 M thiourea and 6 M nitric acid for Pd, Pt and Au, respectively. The determination of precious metal concentrations was performed with the Perkin Elmer Optima 8300 flat plate plasma using a cyclonic spray chamber equipped with a GemCone nebulizer. The robust plasma conditions were used throughout and were reached using the plasma gas flow rate of 8 L min^{-1}, nebulizer gas flow rate of 0.6 L min^{-1} and power of 1500 W.

The pre-concentration of mercury was performed with the 3D printed filter using thiol as a scavenging group. The quantitative pre-concentration of mercury was obtained for HCl acidified natural waters followed with the recovery using a mixture of thiourea and HCl. As low detection limit as 0.4 ng L^{-1} was reached with the Perkin Elmer NexION 350D instrument.

(O-54)

TECHNOLOGY-CRITICAL ELEMENTS (TCE) IN SOILS IN AREAS AROUND WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE) RECYCLING PLANT

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Soil contamination originating from anthropogenic industrial activities is a global concern, adversely impacting health of living organisms and affecting natural ecosystems. The development of electrical and electronic industry, rapid consumption and "ageing" of the equipment entail the necessity of regular replacement, which increases the amount of electrical and electronic waste (called just e-waste or WEEE). E-waste is a specific type of waste, that is a source of potentially toxic elements including TCE (Technology Critical Elements). Worn e-waste after getting into the environment become a potential source of TCE. The research concerned the influence of the WEEE processing plant on the content and mobility of selected critical elements in soils in the surrounding areas. In the work, sequential chemical extraction was used to determine the mobility of Te, Tl and Ge in the areas under pressure of the WEEE processing plant.

Soil samples were collected from topsoil (0-5 cm) and subsoil (<15 cm) in industrial area influenced by WEEE plant in Kraków City, Poland. Magnetic susceptibility measurements of topsoil (κ) were carried out in order to preliminarily estimate soil condition. Concentrations of elements were determined with Inductive Coupled Plasma-Mass Spectrometry (ICP-MS) after microwave digestion. Results revealed that almost all studied elements were in higher amount in the topsoil suggesting the anthropogenic pollution as a source of their content in soil. This preliminary study focuses on the following TCEs: Te, Ge and Tl, whose environmental impact is poorly understood. Additionally, content of more common PTE (As, Cd, Cu, Pb, Sb, Zn) was determined in order to discover some relationships between these both groups.

Our research results have evidenced an increase in the TCE content in soils in the close vicinity of the WEEE processing plant, significantly exceeding the geochemical background value. The relationships between changes in magnetic susceptibility, the concentration of selected TCEs, and the dominant wind direction in this area were found. Tellurium was bound mainly with sulphides and silicates. Germanium and thallium were strongly demobilized in the residual fraction of the studied soils.

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(O-55)

DETERMINATION OF CADMIUM AND OTHER ELEMENTAL CONTAMINANTS IN COCOA/CHOCOLATE PRODUCTS AND THEIR PACKAGING BY ICP-MS

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Cadmium (Cd) is a trace metal without essential biological functions that is toxic to plants, animals and humans. Due to an increasing concern regarding safe levels of Cd in cocoa, the European Union (EU) laid down maximum levels (ML) for Cd in different cocoa products categories from a legislation formulated in 2014 and taken into force in 2019 (EC Regulation No 1881/2006 and amendments).

Various cocoa/chocolate products (n=61) from the EU market, corresponding to the four categories (cocoa powder, chocolate with < 30% of dry cocoa solids, chocolate with 30% < > 50% of dry cocoa solids and chocolate with ≥ 50% dry cocoa solids) defined by the European Commission were analysed by ICP-MS for their content of 14 elements : As, Al, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sr and Zn. A correlation between the measured elements and the cocoa origin was made in order to assess the level/element, which were linked to a specified geographical origin. Moreover, the different cocoa/chocolate packaging (e.g. cardboard, aluminium foil, and white plastic) were analysed to assess a potential contamination to the food product from the packaging material. Certified materials: SRM 2384 Baking chocolate, ERM BD512 (Dark chocolate), ERM EC680m and ERM EC681m (low density polyethylene) were used to confirm the quality of the analysis.

The results of this work showed that approx. 10 % of the samples were not compliant with the EU legislation. Most of them were cocoa powders (ML = 0.60 mg/kg wet weight) and the results illustrated that cocoa from South and Central America contained higher levels of Cd than samples originating from Africa. The results highlighted that the levels of most of the elements were linked to the cocoa content in the product. Regarding the packaging, the results showed that aluminium was the main element for most of them following by iron (except for plastic packaging). A relatively high concentration of Ti (817 and 993 mg/kg) was detected in white plastic and may be due to the use of titanium dioxide as a white pigment. No correlation between the elemental concentrations in the cocoa/chocolate samples and the concentrations in the packaging was identified.

13 Short Course Abstracts

(A-1)
SOURCES OF CONTAMINATION AND REMEDIAL STRATEGIES

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In theory, state of the art inductively coupled plasma mass spectrometry (ICP-MS) instrumentation possesses the prerequisite sensitivity to carry out multi-elemental trace analyses at sub-ng l^{-1} to sub-pg l^{-1} levels in solution. In practice, constraints mainly imposed by various sources of contamination in the laboratory and the instrument itself, as well as the need to dilute sample solutions prior to analysis ultimately limit the detection capabilities. Here we review these sources of contamination and wherever possible propose remedial strategies that we have found efficacious for ameliorating their impact on the results of multi-elemental trace analyses by ICP-MS.

(A-2)
ELIMINATE SAMPLE DIGESTION

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Paradigm changes take time as society adopts innovation; it’s hard to give up habits until there are compelling value propositions for change. Photographic film has been replaced by digital images, typewrites replaced by computers, etc. But these changes did not happen overnight, they take decades. For centuries, chemists have established a culture of digesting samples with strong acids to measure elemental and isotopic composition. However, there is a 21st century approach to sample analysis – use a focused laser beam to remove a few micrograms or less of the sample for direct spectroscopic characterization. We know the process today as laser ablation. Laser ablation science began around the same time as the invention of the laser in the early 1960’s and has progressed into a commercial technology – six decades of innovation. The value propositions are compelling – no acid digestion, rapid analysis, increased sample throughput, safe and Green, laboratory and field use, and inline advanced manufacturing.

This workshop will delve into the history and science of laser ablation for chemical analysis, with an overview of the technology, instrumentation and applications.

(A-3)

ARSENIC SPECIATION, HOW TO DO IT FOR RICE AND SEAFOOD: ROUTINE AND AFFORDABLE OPTIONS

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The short course will cover the dos and don’ts of arsenic speciation for different environmental and biological samples. HPLC-ICPMS has been routine for arsenic speciation in rice. But here also other method which does not use HPLC can be used for this speciation such as discriminative hydride generation coupled to ICPMS for inorganic arsenic in rice. This can also be replaced by AFS or even a field deployable method (Gutzeit method) can be used to determine inorganic arsenic in the field.

Arsenic speciation and especially the identification of inorganic arsenic in marine samples is challenges. Here the course will give examples what to avoid and what needs to be covered.

(A-4)

USE OF THE ORBITRAP AS AN ANALYZER FOR ISOTOPE RATIO MASS SPECTROMETRY

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Perhaps the greatest of advance in the area of biological molecule mass spectrometry has been the advent of the orbitrap mass analyzer. The orbitrap provides the ultimate in obtainable mass resolution, with commercial off-the-shelf (COTS) systems providing $m/\Delta m = 70{,}000 – 1{,}000{,}000$. While a scarcely studied aspect of the instruments, the fact that ion packets are captured and processed in a simultaneous fashion should also provide greater measurement precision for isotope ratio (IR) analysis. The laboratory of Marcus et al. have coupled the liquid sampling-atmospheric pressure glow discharge (LS-APGD) microplasma to a variety of orbitrap platforms, concentrating of methods development of uranium IR measurements. These efforts have been paralleled by efforts by the group of Shelley using a solution cathode glow discharge (SCGD) Eiler who has concentrated on IR measurements for GC/MS analysis of small organic molecules. (There are efforts in coupling ICP sources to orbitraps, but nothing has been presented in the open literature.) We present here the rationale and experimental variables which have been evaluated towards obtaining high precision IR measurements. Specific examples will concentrate on the uranium isotopic system, which itself is challenging due to the wide dynamic range. Interlaboratory comparisons involving TIMS and SF-ICP-MS will be presented. Use of novel data acquisition systems and alternative processing methods will be presented as paths forward to obtaining high resolution, high precision IR analysis.

(A-5)

NANOMATERIALS CHARACTERIZATION BY ICP-MS IN SINGLE PARTICLE MODE AND RELATED TECHNIQUES

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Single particle inductively coupled plasma mass spectrometry (spICP-MS) is becoming an important tool for the characterization of nanoparticles (NPs). The technique utilizes a standard ICP-MS setup and makes use of time-resolved detection to probe NPs that are introduced in diluted suspensions (ideally) one by one. The signal abundance is proportional to the mass of a NP after careful calibration of the system. NP size can then be calculated from the NP mass if an element-specific density and particle geometry are assumed. The frequency of the detected signal pulses can be related to the particle number concentration (PNC) in the suspension. Overall, spICP-MS allows obtaining the average size, size distribution, and PNC of NPs after only a few minutes of measurement.

In this short course, fundamental principles of spICP-MS and selected applications will be discussed. This course will begin with a tutorial on spICP-MS basics including sampling, sample preparation, microsecond time-resolved detection, and data processing. A particular emphasis will be placed on measurement artifacts that can arise during data acquisition, which – if unnoticed or uncorrected – may lead to errors in results and particle size histograms. In the second part, selected applications will be highlighted including the detection of NPs in complex matrices and environmental samples.

This course is intended for those with a background in ICP-MS but beginners are also very welcome to attend.

(B-1)

MODERN PLASMA-BASED DESORPTION/IONIZATION: FROM MOLECULAR ANALYSIS TO CHEMICAL SYNTHESIS

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Electrical plasmas and mass spectrometry (MS) have gone hand-in-hand since J.J. Thomson used a reduced-pressure glow discharge as the first ionization approach in the discovery/development of mass spectrometry. Historically, plasma ion sources were used for these experiments because they were one of the few known sources of gas-phase ions at the time and they were relatively simple to setup and operate. However, developments in plasma ionization have continued to inform and motivate advances in other areas of MS long after the work of Thomson and Aston. More recently, atmospheric-pressure (AP) plasmas have been explored for a variety of purposes including direct mass-spectrometric analyses, molecular and elemental ionization, surface modification, chemical synthesis, and environmental remediation. Atmospheric-pressure discharges are unique in that they simultaneously produce highly energetic species as well as lower energy chemical reagents. Furthermore, it has been shown that plasma conditions (e.g., power, gas composition, etc.) can be slightly altered to favor one condition, even on the timescale of analysis. This short course will cover emerging trends in AP plasma source usage in chemical and analytical sciences, with an emphasis on methods that utilize MS.

(B-2)

GLOW DISCHARGE: THE MOST VERSATILE SOURCE

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In this short course, an overview will be provided about the characteristics, instrumentation, and applications of glow discharges (GD) in both optical and mass spectrometry. Included will be GDs sustained in various gases, over a range of pressures, by supplies at either DC or radiofrequencies and in the presence and absence of magnetic fields. Diagnostics of GDs will be considered briefly, and use of GDs for both depth and lateral resolution will be covered. Recent work with solution electrodes and in a flowing-afterglow mode will be briefly examined.

(B-3)

SURFACE ANALYSIS OF LITHIUM ION BATTERIES – CHALLENGES AND OPPORTUNITIES

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Lithium-ion batteries are widely used in modern consumer electronics and are increasingly Being successfully introduced into the market only 25 years ago, lithium ion batteries are already state-of-the-art power sources for portable electronic devices and the most promising candidate for energy storage in large-size batteries. A major challenge is the degradation of the cell constituents, which is called aging and which minimizes both storage lifetime (calendar life) and operation lifetime (cycle life). Due to the numerous aging effects, both in the individual constituents and their interactions with each other, a myriad of instruments and methods are reported in literature for the investigation of these effects.[1, 2]

Until today, numerous attempts on characterization of these reactions and on elucidation of the aging mechanisms were performed. However, there is only a limited number of approaches trying to clarify the mechanisms. To the present day, fundamental understanding of the aging mechanisms is not achieved.

This short course will focus on the surface analysis of ICP-based methods in the field of lithium ion battery research. A brief overview and comparison with other techniques will be presented as well as recent method development and application to the current challenges.

[1] S. Nowak, M. Winter, Accounts of Chemical Research, 51 (2018) 265-272.
[2] S. Nowak, M. Winter, Journal of Analytical Atomic Spectrometry, 32 (2017) 1833-1847.

(B-4)

LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY AS A TOOL FOR BIOIMAGING

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The course will introduce into the methodology of bioimaging by laser ablation inductively coupled plasma mass spectrometry. The major topics to be discussed are:

a) Instrumentation used for LA-ICP-MS and its possibilities
b) Methods of sample preparation and its influence on image quality
c) Optimization of LA parameters for obtaining optimal spatial resolution
d) Calibration methods for quantitative analysis
e) Single particle analysis for LA-ICP-MS
f) Data analysis and visualization

(B-5)

FROM ICP-QUADS TO TOF & SINGLE PARTICLES TO CELLS – THEORY, APPLICATIONS, FUTURE POSSIBILITIES

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I) From bulk to single particle-ICP-MS

- Theory of single particle-ICP-MS
    - ICP-MS parameters (dwell time)
    - sample introduction (Transport efficiency, nebulizers & spray chambers, microdroplet generators)
    - challenges in ionic background removal & data evaluation
    - mass analyzers (ICP-QMS -> ICP-QQQ-MS -> ICP-ToF-MS)
    - application examples

II) From single particle to single cell-ICP-MS

- Theory of single cell-ICP-MS
    - sample preparation strategies
    - application examples (environment, medicinal, clinical)

III) Future perspectives

- Challenges and future fields of application

(C-1)
LIQUID-ELECTRODE DISCHARGES

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In the last two decades, liquid electrode discharges have become alternative excitation/ionization sources for analytical spectrometry, either used in combination with Optical Emission Spectroscopy or Mass Spectrometry detection. Their versatility and simplicity in the instrumentation required to operate them offer alternative approaches, not achievable with more traditional sources, including in-situ measurements or continuous on-line monitoring. Moreover, they present a good environment to study complex plasma-liquid interactions, which has recently attracted the plasma-physics community. This attraction has been fostered by the diverse applications of plasma-liquid sources appeared in the last decade, including microbial deactivation, nanoparticle synthesis or contaminant degradation, along with their better-known use in analytical chemistry.

This course will provide an overview of these group of plasma sources used for analytical applications, comparing their plasma characteristics with others more routinely used. A special emphasis will be given to the Solution-Cathode/Anode Glow Discharge. Its particular characteristic to transfer the liquid constituents directly from the interaction between the plasma and the solution will be examined from the last reported information. The interesting and promising utility of liquid electrode discharges will be shown providing examples of their application in diverse fields.

(C-2)

SIMS AND RELATED TECHNIQUES FOR ELEMENTAL AND ISOTOPIC IMAGING AT NANOMETER SCALE

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In this short course, element specific imaging techniques with a focus on secondary ion mass spectrometry (SIMS) will be presented. The principles of SIMS including ion sources and the ionization process will be covered as well as the difference between dynamic and static SIMS techniques. This course discusses also briefly related X-ray based techniques such as electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS, TEM-EDS). In a second part nanoscale secondary ion mass spectrometry (NanoSIMS) will be the main subject for chemical and isotopic imaging at the nanometer scale: principle, ion sources, ion transmission, lateral resolution, mass resolution, and useful yield. This course includes furthermore challenges for sample preparation especially for biological material as well as solutions for correlative imaging with related techniques. Finally, challenges and limitations of image date treatment will be discussed and application examples from our laboratory will be presented.

(C-3)

AN INTRODUCTION TO ISOTOPIC ANALYSIS USING SINGLE- AND MULTI-COLLECTOR ICP-MS

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In contrast to most other techniques for trace element determination, ICP-mass spectrometry (ICP-MS) also provides information on the isotopic composition of the targeted elements [1]. Most ICP-MS users take advantage of this capability, e.g., when evaluating the potential occurrence of spectral overlap by comparing the isotopic pattern observed for an element to the corresponding theoretical one or by relying on mathematical correction to overcome spectral overlap. However, this feature also opens the way to various other types of applications.

The capability to measure induced changes in the isotopic composition of a target element, e.g., offers the possibility to use isotope dilution as a highly robust and reliable quantification approach, while a similar approach can also be used in the context of tracer experiments, e.g., for studying the uptake of essential mineral elements from food.

Elements with one or more radiogenic isotopes (e.g., Sr and Pb) show a quite pronounced natural variation in their isotopic composition and their isotopic analysis can be deployed in the context of, e.g., dating of geological materials and provenance determination of, among other, raw materials used in the manufacturing of archaeological artifacts, agricultural products of plant and animal origin, and human remains.

While for the applications above (at least the easier ones), single-collector ICP-MS may suffice, for revealing and quantifying natural variation in an element's isotopic composition caused by isotope fractionation, multi-collector ICP-MS is needed (except in the case of the lightest elements). Such MC-ICP-MS isotopic analysis has proven useful in a wide variety of research domains, including archaeometry, geo- and cosmochemistry, environmental studies and the biomedical sciences.

Tips & tricks concerning the measurement of isotope ratios will be provided, the capabilities and limitations of various types of instrumentation will be discussed and the utility of isotopic analysis will be documented by using application examples from the author's lab or reported in the literature.

1. Use of single-collector and multi-collector ICP – mass spectrometry for isotopic analysis – A tutorial review, F. Vanhaecke, L. Balcaen and D. Malinovsky, Journal of Analytical Atomic Spectrometry, 24, 863-886, 2009. DOI: 10.1039/B903887F.

(C-4)

CALIBRATION STRATEGIES FOR QUANTITATIVE BIOIMAGING BY LA-ICP-MS

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Calibration in LA-ICP-MS still represents an Achilles' heel of the technique, lacking appropriate certified reference materials and commercially available calibration standards, especially in the field of life sciences (i.e. biological samples). The complexity and heterogeneity of biological tissue makes it difficult to precisely mimic the sample matrix and to develop appropriate calibration strategies that provide the desired accuracy, precision and robustness. Therefore, most laboratories have developed matrix-matched calibration strategies that are based on well-described in-house procedures [1]. Recent bioimaging studies focused on the development of quantification strategies that included tissue-type section standards, gelatin-based sections/droplet approaches, micro-droplets or isotope dilution strategies [2-4].

This short course will provide a comprehensive overview about the state-of-the-art of quantification concepts and internal standardization strategies available for the quantitative multi-element analysis of biological samples by LA-ICP-MS. Recent progress in the development of novel calibration strategies will be highlighted and related challenges, limitations and appropriate validation concepts will be critically discussed. Moreover, practical examples for the multi-element quantification of biological samples, including different tissue types and single cells using LA-ICP-(TOF)MS analysis, will be given.

References

[1] Limbeck, A.; Galler, P.; Bonta, M.; Bauer, G.; Nischkauer, W.; Vanhaecke, F., *Anal. Bioanal. Chem.* 2015, *407* (22), 6593-6617.

[2] Šala, M.; Šelih, V. S.; van Elteren, J. T., *Analyst* 2017, *142* (18), 3356-3359.

[3] Schweikert, A.; Theiner, S.; Wernitznig, D.; Schoeberl, A.; Schaier, M.; Neumayer, S.; Keppler, B. K.; Koellensperger, G., *Anal. Bioanal. Chem.* 2022, 414, 485-495.

[4] Douglas, D. N.; O'Reilly, J.; O'Connor, C.; Sharp, B. L.; Goenaga-Infante, H., *J. Anal. At. Spectrom.* 2016, *31* (1), 270-279.

(C-5)

THE RIGHT SAMPLE PREPARATION TECHNIQUE FOR YOUR ELEMENTAL ANALYSIS: WHICH ARE THE KEY FACTORS?

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The aim of the course will provide more knowledge in sample preparation. Sample preparation step is a crucial part in environmental, food samples etc., which will influence the reliability and accuracy of the analytical results.

The following questions will be addressed:

- Which are the causes of common errors in chemical analysis?
- Why microwave closed-vessel digestion?
- Which are the key parameters in sample preparation?
- Why the temperature is important in the digestion process?
- Which are the guidelines to dissolve organic matrices?
- Which are the guidelines to dissolve inorganic matrices?

(D-1)
MAKE YOUR LECTURE COUNT!

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In “The Making of a Scientist” (1953), Anne Roe said, “Nothing in science has any value to society if it is not communicated…”. Among the ways by which this communication is achieved, the scientific lecture is one of the most important. Yet, too many of us squander opportunities to communicate in this way by crafting and delivering lectures that are not as effective as they might be.

In this short course, based on a long-running series of seminars at Indiana University, suggestions will be offered on how to prepare for, present, and benefit from scientific lectures, be they in a classroom environment, technical conference, local seminar, job interview, or short course.

(D-2)

PRACTICAL APPROACHES TO USE REACTION GASES IN ICP-MS TRIPLE QUADRUPOLE

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This short course will show how to proceed in method development working on an ICP-MS triple quadrupole. The course is aimed at users of ICP-QQQ who would like to get more knowledge about the reactions in the reaction cell and how to change these reactions. The following questions will be addressed:

- Does the interference or the analyte have an exothermic or endothermic reaction with the added gas?
- How does the collision energy affect the reactions in the cell?
- Why is the ionization energy important?
- Which gases are suitable for the different analytes and mass interferences? What are the products?
- Regarding manually optimizing of the cell parameters, which parameters are important? How do these affect the reaction efficiency?

These questions will be answered with examples on polyatomic-, doubly charged-, and isobar mass interferences.

14 Poster Abstracts

(P-1)

CADMIUM LEVELS IN WHELKS FROM DANISH WATERS – INFLUENCE OF SIZE, SAMPLING LOCATION AND SEASON

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Cadmium (Cd) is a trace metal without essential biological functions that is toxic to plants, animals and humans. Whelks (*Buccinum undatum*) are edible marine molluscs that are consumed in Europe and in Asia, and the coast of Denmark is home to several colonies that have the potential for an industrial fishing production of whelks. However as it has been shown for other marine animals, whelk may accumulate potentially toxic elements among which Cd that is of principal concern for human health.

10 kilogram of whelks from ten different coastal locations in Denmark were fished at the four different seasons during 2020 and 2021. Each sample consisted of 20 whelks. After measurements, the soft parts were taken out of their shell, then freeze-dried and homogenised prior to analysis by ICP-MS. The levels of Cd were determined in the whole animal, in the muscle (edible part) and in the digestive track. The amount of the different elements were measured depending on the geographical origin of the samples, the season during which they were fished but also depending on the size of the animals.

The first results showed little variation of the Cd concentration with the size of the animal. On the other hand the Cd concentration proved to be very location dependant. Furthermore, on top of this geographical variation a seasonal variation was also observed. This may be linked to the yearly physiological cycle of the whelks. Cd concentration was higher in the summer compared to the other seasons and this will have to be taken into account if the Danish fishing industry wants to move forward and fish whelks commercially.

(P-2)

AN AUTOMATED SINGLE ALGAE-ICP-TOF-MS APPROACH FOR THE QUANTIFICATION OF METAL UPTAKE IN DIATOMS

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Diatoms are located at the bottom of the food chain. Thus, toxicological relevant metals taken up by diatoms can possibly accumulate within the food web and cause harmful effects. Diatoms are a common test system in ecotoxicology. Toxicological effects weaken the growth of algae which is by default investigated by means of fluorescence detection - diminished fluorescence compared to a non-exposed control group indicates an effect. On basis of the expose concentration as well as obtained fluorescence data potential threshold exceedance in e.g. surface waters is assessed.

However, this approach does not allow for the determination of “real” accumulated metal concentration in diatoms. Common approaches are based on microwave assisted digestion and elemental analysis via e.g. ICP-MS, ICP-OES or AAS. But, with regard to low absolute metal-content in algae this strategy is only feasible in case of availability of a high biomass.

To tackle this problem, alternative, complementary approaches are highly needed. Within the last years, sp-ICP-MS for nanoparticle as well as single cell analysis turned out as a powerful technique to analyze metal contents as well as size distributions on broad size range (nano- to low micrometer scale). But, common ICP-MS systems do not allow for multi-element detection within single particle/cell events. Thus, simultaneous MS detection devices are needed - just recently, ICP-ToF-MS experienced a revival.

Within our previous work, we developed an automated sample introduction system based on a HPLC system on-line with single particle-ICP-MS, which allowed for ionic background separation and single algae analysis. However, for unambiguous tracing several fingerprint elements and multielement analysis in single algae (diatoms) is needed. Thus, we coupled our previous setup on-line to ICP-ToF-MS. Test diatom species were exposed to test substances (Zn) as well as nanoparticles (FeNPs).

The developed setup allowed for a fast, automated and multielement analysis in single diatoms. Furthermore, we combined our approach with multivariate data assessment - multielement detection of characteristic fingerprint elements allowed for an unambiguous diatom tracing. Clustering of diatoms according to metal exposure concentration levels was enabled. Our approach is a new potential tool in ecotoxicological testing.

(P-3)

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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Bioimaging is a valuable tool to gain insight into the elemental composition of biological thin sections. Using the newest laser ablation techniques single bursts of data can be generated in a matter of a few milliseconds. This requires the fast detection to enable the fastest and most accurate possible recording of images. Since the analysis of as many elements as possible is typically required a TOF-ICP-MS becomes an important part of a modern LA-ICP-MS system for bioimaging.

The power of the Vitesse to record transient full mass spectra in sub-millisecond dwell times enables the full potential of the laser ablation systems creating large images at high resolutions in a matter of a few hours or even minutes. Furthermore, the full elemental detection enables the analysis of endogenous elements as well as higher mass isotopes often used as markers to further understand the metalomics and metabolomics in living organisms.

Data will be presented showing the latest images of biological materials highlighting the speed, resolution and sensitive detection of many elements. Spot sizes down to one micrometre were able to be used while still being able to ablate multiple square centimetres due to the modern ablation systems and fast acquisitions times. This allows an in-depth examination of endogenous elements for detailed analysis of the metabolome of biological samples on a cellular level.

Data reduction can be achieved during acquisition for the live viewing of images using powerful python scripts in the NuQuant software. More detailed analysis in other third-party software packages is also easily possible though flexible export formats which will also be shown.

(P-4)

THE USE OF TIME OF FLIGHT ICP-MS AND VERY FAST WASHOUT LASER ABLATION SYSTEMS TO ACCURATELY IMAGE MAJOR AND MINOR ISOTOPES AS WELL AS ELEMENTAL RATIOS IN GEOLOGICAL SAMPLES

Lukas Schlatt

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The ability for multi-elemental analysis in solid samples using rapid and direct methods is a key point in the development of analytical science. Over the years, in situ techniques based on Laser Ablation and Inductive Coupled Plasma Mass Spectrometry (LA-ICP-MS) have been widely used rapidly evolving into well-established, mature powerful tools for direct, high sensitivity and precision, and high lateral resolution analysis in numerous fields such as geology, biology, metallurgy, environmental sciences, etc. Significant research and advances continue to thrive to achieve the fastest, most accurate and efficient analysis.

The fast acquisition speeds of the full elemental mass spectrum make a TOF-ICP-MS the most appropriate instrument for the fast examination of high-resolution elemental maps using the newest laser ablation systems. The often mentioned downside of a TOF-ICP-MS is it’s limited dynamic range, especially if all examined isotopes have to be examined. The Vitesse allows for beam attenuation, enabling a novel technique to create images showing elements between 100% and sub-ppm levels in one image. Examples of this technique will be shown and normalization techniques discussed.

Furthermore, the Vitesse can be tuned for the optimal detection of isotope ratios. Examples showing the differentiation of lead uranium ratios in Zicons at low micrometer resolutions will be shown. Combining the various acquisition methods in an automated fashion allows for the detailed examination of various samples in a short time with minimal input from the user. It will also be demonstrated how the finalized data can be shown live or exported to import into other software packages.

(P-5)

ACCURATE IDENTIFICATION, EXAMINATION AND DIFFERENTIATION OF MULTIELEMENT NANOPARTICLES USING TIME OF FLIGHT ICP-MS AND SUB-MILISECOND SPECTRAL ACQUISITION TIMES

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The use of nanoparticulate materials has been increasing with large amounts being released into the environment each year. Therefore, sensitive methods are needed to detect these particles. While the size detection limit has been decreasing over the years with more sensitive detection methods becoming available, completely new instrumentation to scanning mass spectrometers is necessary to examine the composition of individual particles.

The Vitesse TOF-ICP-MS can measure the full mass spectrum continuously at acquisition speeds down to 80 µs. Together with powerful peak integration and identification methodologies, the data from individual nanoparticles can be identified and reduced efficiently and easily. In addition to the capability to record multiple full mass spectra for every particle, examinations of nanoparticles with a reduced mass range can be recorded to gain a higher sensitivity for a smaller number of observed isotopes. This allows for the reduction of size detection limits and more detailed examination of elemental ratios in single nanoparticles.

Data is shown, which differentiates a mix of various particles into clusters. This way a mixture containing various similar as well as different particles can be differentiated quickly and easily. Furthermore, the advantage of reduced mass range examinations is shown and discussed.

(P-6)

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.

(P-7)

ANALYSIS OF TOXIC AND NUTRITIONAL ELEMENTS IN BABY FOODS BY ICP-MS

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Commercial baby foods are the main source of nutrients and energy for many children around the globe, and therefore, the quality and safety of baby foods is extremely important during these crucial development stages. Arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) are toxic elements. The Food and Drug Administration (FDA) and the World Health Organization have declared them to be harmful to human health, particularly to babies and children who are undergoing neurological development. These elements can be taken up by the ingredient crops, such as rice, fruits, vegetables and meats, from the air, water and soil during growth, and/or introduced as contaminants during processing and storage.

In March of 2021, the US House of Representatives introduced the bill " Baby Food Safety Act of 2021" (1) to regulate the presence of toxic elements in infant and toddler food products. The maximum levels of the toxic elements are: inorganic arsenic (10 ppb, 15 ppb for cereal), lead (5 ppb, 10 ppb for cereal), cadmium (5 ppb, 10 ppb for cereal), and mercury (2 ppb). Following this act, the U.S. FDA published a 'Closer to Zero' plan, which outlines steps that the agency will take over the next three years (and beyond) to reduce the toxic elements in foods eaten by babies and young children to as low levels as possible.

ICP-MS is a powerful elemental analysis technique with multi-element detection capabilities, low detection limits, high speed of analysis and wide linear dynamic range, making it the clear choice for total elemental analysis for baby food products.
As with all analytical techniques, it is affected by plasma and matrix-based polyatomic and doubly charged ion interferences. PerkinElmer's NexION ICP-MS is equipped with Universal Cell Technology (UCT) that can operate in Collision mode with Kinetic Energy Discrimination (KED) and Reaction mode with Dynamic Bandpass Tuning (DBT) and Standard mode to mitigate/remove the interferences effectively with versatility.

This work describes a procedure for the analysis of toxic elements: Cd, Hg, Pb, and As, and other trace elements: Cr, Mn, Fe, Ni, Cu, Zn, Mo, and Tl, in baby foods (pureed and cereal) following US FDA EAM 4.7 using the Titan™ MPS microwave digestion system for sample digestion and the NexION ICP-MS 2000 for sample analysis.

(P-8)

QUANTITATIVE DETERMINATION OF LITHIUM PLATING ON GRAPHITE ANODE SURFACES UTILIZING GC-BID

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Lithium ion batteries (LIBs) are considered to be one of the most important storage devices for electric energy, especially with regard to automotive applications. To ensure safety of the cells, investigations on aging processes, especially the deposition of metallic lithium on the anode surface (lithium plating), are of great interest.

In state-of-the-art LIB graphite is used as anode material due to its high cycling stability and low costs. As cathode material usually lithium transition metal oxides are used. One of the most important ageing effects is lithium plating which is a process that occurs especially during charging at low temperatures, high C-rates, high states-of-charge (SOC) or due to manufacturing defects resulting in an acceleration of cell aging. Lithium plating can occur as a reversible or irreversible deposition of metallic lithium. On the one hand, reversibly plated lithium is stripped during the discharge step and is available again in the next charging step. On the other hand, the irreversibly plated lithium results in the loss of active lithium which causes capacity fading. Besides that, the plated lithium can form dendrites which can penetrate the separator and cause a short circuit. In the worst case, this can lead to self-heating of the cell, which can further result in a thermal runaway. To better understand these safety risks quantitative and qualitative investigations of lithium plating behaviour are of great interest.

In the study presented on this poster, irreversible deposited lithium on graphite electrodes in graphite||$\text{Li}[\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}]\text{O}_2$ (NMC 622) cells will be quantified by gas chromatography coupled with a barrier discharge ionisation detector (BID). For this purpose, the reaction of metallic lithium with water to hydrogen is used to derive the amount of deposited lithium from the hydrogen content in the gas phase.[1], [2] Therefore, a comparison of the causes of lithium deposition with the quantitative amount of deposited lithium is possible. In addition, the capacity loss can be compared with the inactive lithium content. This allows the determination of the proportion of capacity loss caused by lithium deposition. In order to additionally enable a spatially resolved quantification of the lithium distribution, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is used. A major advantage of the LA-ICP-MS method is that minimal sample preparation is necessary. This means that the anode can be analysed directly after disassembling the cell. To obtain a quantitative analysis, matrix-matched standards were produced to which lithium carbonate was added as a lithium source. This allows quantitative investigations of the homogeneity of the deposited lithium.
By using both methods mentioned above, both the quantitative determination of plated lithium and the investigation of the lithium distribution on the anode surface is possible.

[1] C. Fang, J. Li et al., Nature, **2019**, 572, *511-515*
[2] Y. C. Hsieh, M. Leißing et al., Cell Reports Phys. Sci., **2020**, 1, *100139*

(P-9)

ASSESSING LITHIUM MIGRATION IN LITHIUM ION BATTERIES AT DIFFERENT STATES OF CHARGE BY COMBINING ISOTOPE DILUTION ANALYSIS WITH PLASMA-BASED TECHNIQUES

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Efficient energy storage devices play a vital part in creating a sustainable energy future by relying on renewable energy sources and appropriately dealing with their natural fluctuations. Lithium Ion Batteries (LIBs) are the current State-of-the-Art energy storage technology and a promising tool in securing a sustainable energy infrastructure.[1] Current LIBs mostly consist of a graphitic negative electrode and a Lithium transition metal oxide ($\mathrm{Li}M\mathrm{O}_2$: M = Ni_x, Co_y, Mn_z (x+y+z=1)) positive electrode.[2]

One significant drawback of LIBs is the degradation of cell components during usage. This phenomenon is called aging and leads to performance loss over time.[3] A major aging mechanism is the loss of active Lithium and thus the loss of cell capacity. During the first cycle of a cell, degradation of electrolyte, conducting salt and electrode material occurs to form the Solid Electrolyte Interphase (SEI). The formation of the SEI is partially responsible for the loss of active Li.

While fundamental aging mechanisms have been examined in the past, details on Li migration and the origin of Li loss still need to be investigated in detail. Generally, Li in a LIB can be divided into Li originating from the positive electrode, also called cathodic Li, and Li originating from the conducting salt in the electrolyte, also called electrolytic Li. Two techniques to analyze the Li content in electrodes are the Glow Discharge-Sector Field-Mass Spectrometry (GD-SF-MS) for depth-resolved Li profiles and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for bulk analysis of electrodes. Further, Isotope Dilution Analysis (IDA) can be used to determine the origin of Li fractions in the electrodes.

This work focuses on investigating the Li migration mechanisms in the cell by combining IDA with GD-SF-MS in a novel State of Charge (SoC) approach. General Li distribution in cells with natural Li isotope abundances was additionally investigated by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Full cells were built with graphitic negative electrodes and ^{6}Li-enriched or standard positive electrodes respectively. Both electrodes from each cell were investigated at various SoCs, meaning the cells were charged to specific cut-off voltages during the first formation cycle. Electrodes from cells with ^{6}Li-enriched positive electrodes were analyzed via GD-SF-MS and electrodes from cells with natural Li abundances were analyzed via ICP-OES.

[1] X. Li, L. Yao, D. Hui; J. of Modern Power Systems and Clean Energy **2016**, *4*, 593-603.
[2] S. Dühnen et al.; small methods **2020**, *4*, 2000039.
[3] J. Vetter et al.; Journal of Power Sources **2005**, *147*, 269-281.

(P-10)

INVESTIGATION OF THE C-RATE DEPENDENT GASSING DURING FORMATION OF LITHIUM-ION BATTERIES UTILIZING GAS CHROMATOGRAPHY - BARRIER DISCHARGE IONIZATION DETECTOR

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Counteracting climate change is the task of our time. Lithium-ion batteries (LIBs) as an energy storage medium for electromobility and stationary applications are intended to help reduce the massive use of fossil fuels.[1]
State-of-the-art LIBs consist of a negative carbonaceous anode, a positive lithium transition metal oxide cathode and a liquid electrolyte. The electrolyte is a mixture of carbonate-based organic solvents, in which the conducting salt is dissolved. During the first charge and discharge cycle(s), known as formation of the battery cell, an electrolyte decomposition takes place mainly due to reduction reactions at the anode side. During this step, a protective layer - so called solid electrolyte interphase (SEI) - is formed. The SEI is essential for the battery as it protects the electrolyte from further decomposition on the anode surface.[2]

However, formation of battery cells is a time consuming (days to weeks) and therefore costly step, especially with regard to the industrial production of LIBs. The formation of a proper SEI is usually correlated with low C-rates (0.05 C - 0.2 C) to form a homogeneously distributed layer on the graphite particles.[3] By-products of the SEI building due to electrolyte decomposition are different permanent gases and light hydrocarbons which can be analyzed by gas chromatography (GC).[4,5] The latest detector for GC is a plasma based, barrier discharge ionization detector (BID) which offers better sensitivities than conventionally used detectors, especially for critical gases such as hydrogen.[6]

In this study, we investigate the influence of faster formation procedure on the gassing resulting from electrolyte decomposition in LiNi0.6Mn0.2CO0.2O2||graphite LIBs using GC-BID. The influence of C-rates between 0.05 C to 2 C on the gas volume and the quantitative composition in cells is investigated, considering also the advantages of the BID[7].

References

[1] M. Mittelviefhaus, G. Pareschi, J. Allan, G. Georges, K. Boulouchos, *Applied Energy* **2021**, *301*, 117445.
[2] M. Winter, *Zeitschrift für Physikalische Chemie* **2009**, *223*, 1395–1406.
[3] D. L. Wood, J. Li, C. Daniel, *Journal of Power Sources* **2015**, *275*, 234–242.
[4] S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, D. L. Wood, *Carbon* **2016**, *105*, 52–76.
[5] Y. P. Stenzel, F. Horsthemke, M. Winter, S. Nowak, *Separations* **2019**, *6*, 26.
[6] M. Leißing, M. Winter, S. Wiemers-Meyer, S. Nowak, *Journal of chromatography A* **2020**, *1622*, 461122.
[7] M. Leißing, F. Horsthemke, S. Wiemers-Meyer, M. Winter, P. Niehoff, S. Nowak, *Batteries & Supercaps* **2021**, *4*, 1344–1350.

(P-11)

THE INFLUENCE OF ADDITIVES ON PRIMARY SEI-DEVELOPMENT ON LITHIUM METAL – AN ACCUMULATION STUDY

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The research-objective of this work is a deeper understanding of the reactions of the solid electrolyte interphase (SEI) protecting the surface of lithium metal anodes which are used as higher capacity materials in lithium-based batteries. As the primary SEI is formed initially during the first contact between the anode with the electrolyte it is therefore present in all lithium metal batteries being assembled. Extensive investigations on the SEI composition and reactions were enabled by a newly developed sample-preparation method which will be the main focus of this poster together with the applied gas chromatographic methods.

As the SEI is a very thin layer on the anode, one must deal with low amounts of the compounds of interest, especially when it comes to the initially developed layers. Therefore, a new method for accumulating these compounds in the sample container was developed to assure deeper insights into the ongoing reactions and the resulting compounds using analytical methods such as plasma-based quantitative gas chromatography with barrier discharge ionization detector (GC-BID) [1] and gas chromatography with thermal conductivity detector (GC-TCD) [1]. Further, various qualitative methods based on mass spectrometry and nuclear magnetic resonance spectrometry were utilized for structure elucidation. The electrolytes used for the experiments were carbonate-based with lithium hexafluorophosphate ($LiPF_6$) as conducting salt and were prepared whether without any additives or with different amounts of vinylene carbonate (VC) or fluoroethylene carbonate (FEC).

The first results of the accumulation method of SEI-derived compounds in general demonstrate the proof of principle of this method. Further, different sample types assure the correctness of the method together with the expected signals in the GC-BID measurements. The results of the GC-BID and GC-TCD measurements together with GC-MS reference data allow the identification and semi-quantification of gases that form as side products of the SEI-formation. An experiment to check for the changes over time were obtained by using different treatment-durations to demonstrate the formation of the different gases and their total percentage of the overall formed gases. In addition, the application of VC and FEC in different amounts reveal their influence on the development of the primary SEI on lithium metal, resulting in higher contents and changed ratios of measured gases.

In summary. the new preparation method allows the accumulation of all components of the SEI-formation, overcoming the problem of detectability and quantification via GC-BID, GC-TCD and other methods. This poster will mainly focus on gaseous products and will only give a short outlook on the results of the liquid, electrolyte phase.

References:

[1] F. Horsthemke et. al; RSC Advances, 2017, 7, 46989-46998.

(P-12)

SPATIALLY RESOLVED *POST-MORTEM* ANALYSIS OF LITHIUM DISTRIBUTION AND TRANSITION METAL DEPOSITIONS ON CYCLED ELECTRODES *VIA* LASER ABLATION-ICP-OES / -MS METHODS

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Modern LIBs are usually made of graphite anodes and mostly layered Lithium transition metal oxide ($LiMO_2$) cathodes. State of the art LIBs consists of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM 811) or $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM 622) cathode materials. NCM exhibits several desirable properties such as high capacity, low toxicity, low cost and low thermal runaway when charged. Deposition of Manganese has been shown to lead to cracking and contamination of the solid electrolyte interphase (SEI) and hence to sustained lithium loss.

As part of aging studies of modern Lithium Ion Batteries (LIBs), we use Laser Ablation Inductively Coupled Plasma Optical Emission Spectrometry (LA ICP-OES) and -Mass Spectrometry (LA ICP-MS) at the MEET Battery Research Center. With this method it is possible to examine the surface of the electrode postmortem and depict it in a visual representation. Changes in the distribution of Lithium or transition metal deposition in the LIB can have a tremendous impact on cell cycling and calendar life.

Electrochemical stress when using LIBs, as well as external influences and surface properties lead to locally non-homogeneous aging of the electrodes, meaning that bulk analysis is not suitable for investigating loss of performance or an early end of life of LIBs. For current and future LIBs, understanding these phenomena is a crucial factor.

Therefore, LA ICP-OES / -MS methods were developed to investigate the phenomena. Electrodes were examined with a 193 nm ArF excimer and a 213 nm Nd:YAG laser, respectively.
Due to the lack of commercially available reference materials, matrix-matched solid standard materials with a known analyte content were developed. The investigations were carried out by ablating electrodes of coin cells and pouch-bag type. Afterwards the depositions of Lithium and transition metals (Ni, Co, Mn) were visualized.

(P-13)

INVESTIGATION OF THE MESOSCALE STATE-OF-CHARGE DISTRIBUTION IN LITHIUM ION BATTERY CATHODE MATERIALS BY MEANS OF SINGLE-PARTICLE INDUCTIVELY COUPLED PLASMA-BASED ANALYTICAL TECHNIQUES

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The mesoscale, i.e., the inter- and intraparticle levels of the electrode, is considered to be an area of utmost importance because the macroscopic behavior of the lithium ion batteries (LIBs) results from its microscopic structure and chemical properties. The charging and discharging process of a LIB is based on the (de)lithiation of the active particles. The distribution of the respective state-of-charge (SOC) at the particle level is an important indicator for the homogeneity of the (de)lithiation reactions at the mesoscale and thus for the utilization of the available capacity of the LIB. However, many reasons exist why the (de)lithiation of individual particles is prevented due to the interruption of the electronic and/or ionic contact. The contact loss manifests itself in the immobilization of active lithium in isolated particles. As a result, the lithium content of the isolated particles varies from that of the intact particles.

The presented work provides mesoscopic insights into the SOC distribution of cathode materials containing layered transition metal oxides by means of classification-single-particle inductively coupled plasma optical emission spectroscopy (CL-SP-ICP-OES). The application of CL-SP-ICP-OES enables the rapid screening of the mesoscale SOC distribution between different particles through measurements directly based on the lithium content of individual cathode active material particles achieving a statistically viable elucidation. By determining the intensity ratio of Li and e.g. Mn (I(Li)/I(Mn)), isolated particles can consequently be identified and counted by means of CL-SP-ICP-OES. CL-SP-ICP-OES demonstrates the potential for important advances in the future using widely available ICP-OES equipment for routine analysis of the SOC distribution in material research.

Furthermore, promising first results on the application of laser ablation-ICP-time-of-flight-mass spectrometry (LA-ICP-TOF-MS) for the investigation of cathode materials based on layered transition metal oxide are presented.

(P-14)

ANALYSIS OF HETEROGENEOUS WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT SAMPLES BY ICP-OES

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The global shortage of raw materials is pushing the technology industry in a new direction, in which end-of-life (EOL) products i.e. secondary waste streams are considered an increasingly important source of raw materials for new products. One potential source is waste electrical and electronic equipment (WEEE), which contains valuable and noble metals as well as critical raw materials (CRMs) identified by the European Commission. CRMs such as rare earth elements (REEs), gallium and indium, currently have very limited circular economy. In Europe, total metal demand covered by recycling is 8 % for heavy rare earth metals, 3 % for light rare earth metals and 0 % for gallium and indium. The potential for loss due to non-recycling and non-utilization of secondary raw materials is thus very high. Successful utilization of complex and mixed streams of undetermined composition will require efficient and innovative recovery technologies as well as reliable elemental analysis. For the analysis of heterogeneous WEEE samples, especially for relatively scarce gallium and indium, a suitable solution has been sought from inductively coupled plasma optical spectrometry, ICP-OES. The studied WEEE fraction of selected computer components has been shown to be very diverse in its elemental distribution, including e.g. higher concentrations of iron, copper, tin, nickel, titanium, barium, silicon and aluminum. Due to the challenging sample background, interference from iron, titanium and chromium has been observed at the measurement wavelengths of gallium and indium. These spectral interferences have been successfully corrected by matrix matching for iron and chromium, and furthermore by multicomponent spectral fitting (MSF) for titanium, to produce a high quality analytical result.

(P-14)

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(P-16)
ANALYTICAL PLASMA CHEMISTRY IN A MINI-PILOT SCALE HYDROMETALLURGICAL LABORATORY

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A new hydrometallurgical laboratory has been founded in the University of Jyväskylä (JYU), Department of chemistry last year. The laboratory operates in a larger scale than a conventional scientific laboratory, in the so-called mini-pilot or bench scale, having reactor unit volumes of approximately 5-10 liters. The laboratory is part of an upcoming Center of Expertise for Circular Economy (CECE) infrastructure serving both academic and industrial collaboration needs and is furnished with semi-modular state-of-the art equipment. These include, but are not limited to various pumps, filter press units, lamella separators, mixer-settlers, an electrolysis cell, and a cutting mill. In its first year, research in the laboratory has revolved around a commercial joint venture involving local Finnish enterprises (ALVA, Elker, Tapojärvi) and JYU. A pre-commercial pilot plant has been planned from the ground up to meet the demands of waste electric and electronic equipment (WEEE) recycling and valuable metal recovery from printed circuit boards (PCB), a ludicrous and fast growing secondary raw material. The venture is currently in its business model and feasibility assessment step, since a proven process concept to extract pure metals (Cu, Au, Ag, Pd) from PCB has been successfully designed and tested in the mini-pilot scale. Experimental studies have been widely changing from one process step to another, but one specific need of elemental analysis, especially metal analysis from aqueous samples, has carried through the entire project. Metal analysis involving inductively coupled plasma - optical emission spectrometry (ICP-OES) has been the workhorse of our hydrometallurgical laboratory. Despite the complex nature of PCB, elemental determinations from different process steps have been done with high throughput and sufficient accuracy, including Cu and impurity element survey in an acid leaching process followed by electrowinning, Au content determination in liquid-liquid extraction and subsequent reduction steps, and heavy metal content assessment in waste streams

(P-17)

OPTIMIZATION OF ANALYTICAL METHOD FOR SELENIUM SPECIATION IN FISH FEED AND FEED INGREDIENTS USING A CHEMOMETRIC APPROACH

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Selenium (Se) is an essential element for humans and animals, including Atlantic salmon (*Salmo salar*). One of the main sources of Se and other elements for farmed salmon is the diet. In feed ingredients, Se will be naturally present, but supplementation of Se in feed has been considered necessary to maintain normal functions in fish. In fish feed, Se can be supplemented in forms of inorganic Se (e.g. selenite) and as organic Se (e.g. selenomethionine (SeMet) or SeMet produced by Se-enriched yeast. Maximum limits for Se as a feed additive for animals have been established by the European Commission and is set to 0.5 mg Se/kg. For SeMet and SeMet produced by the Se-enriched yeast (*Saccharomyces cerevisiae*), the limit is 0.2 mg Se/kg. Due to the difference in legislations for the supplementation of Se species, there is a need for development of analytical methods that can discriminate between different Se species.

In this study, method development was performed to optimize the extraction of Se species in fish feed and feed ingredients, and further analysis of extracts for organic SeMet using High Performance Liquid Chromatography (HPLC) coupled to Inductive Coupled Plasma Mass Spectrometry (ICP-MS). Optimization was performed using chemometric tools. Different factors were tested using experimental designs: i) extraction solutions at pH 7 (ammonium phosphate or a mixed buffer solution), ii) an enzymatic pre-extraction step (with or without papain) and iii) enzymes for main extraction (protease type XIV, protamex, α-amylase or cellulase). Principal component analysis (PCA) was performed on the SeMet recovery as a response for the certified reference materials ERM BC210a (wheat flour) and SELM-1 (selenized yeast).

The results show that the most optimal method for increasing the SeMet recovery was to combine protease and cellulase (1:1 ratio) for enzymatic digestion, with ammonium phosphate as a buffer, and without a pre-extraction step. The optimized method was applied to experimental feed, commercial fish feed and feed ingredients (i.e. plant meal, fish meal and insect meal). The method was evaluated to be more accurate for the determination of higher concentrations of SeMet in feed but did not show sufficient recovery for SeMet in feed and feed ingredients at lower concentrations. Other Se peaks were observed in the chromatograms for selected feeds and fish meal, with unknown chemical structures. Although the results show that further method optimization would be needed for a full recovery of all Se species in fish feed, the use of statistical and chemometric approaches was considered beneficial for the method development for Se speciation in this study.

(P-18)

INVESTIGATION ON THE BIOACCUMULATION AND TRANSLOCATION OF RARE EARTH ELEMENTS IN THE SOIL-RICE SYSTEM

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Rare earth elements (REEs) play a key role in the world economy and in new technologies manufacturing. Their extraction has increased in recent years as well as their diffusion and availability in the environment and they can now be considered as emerging pollutants. Moreover, since they are not ubiquitous elements, REE have recently proven to be geographical markers for food authentication and traceability [1]. Therefore, many efforts have been and should be made to investigate their translocation, bioaccumulation, and toxicity [2]. Given the importance in human nutrition, rice was chosen as case study to investigate the factors which could affect the amount and the distribution of REE during their translocation from soil to rice grains. Hence, an ICP-MS method was developed and thoroughly validated for the REE determination, whereas chemometric tools were applied to discriminate which internal (subspecies, and genotypes) or external (geographical origin, seasonality, and irrigation methods) factors were mostly predominant on the final elemental signature. A particular attention has been paid on the nature of the irrigation method because of its effect on soil conditions and element availability [3]. Intermittent irrigation methods have been here considered besides the continuous flooding one, which is employed worldwide for rice grown. Among them, sprinkler irrigation ensures, achieving the same yield of that obtained using the traditional ones, considerable water savings [4] and an excellent food safety because it avoids the accumulation of toxic metals and metalloids [5].

References

1. G. P. Danezis et al. Current Opinion in Food Science, 2016, 10, 22–31, https://doi.org/10.1016/j.cofs.2016.07.003
2. G. Pagano et al. Ecotoxicology and Environmental Safety, 2015, 115, 40–48, https://doi.org/10.1016/j.ecoenv.2015.01.030
3. A. Spanu et al. Science of The Total Environment, 2020, 748, 142484, https://doi.org/10.1016/j.scitotenv.2020.142484
4. A. Spanu et al. Italian Journal of Agronomy, 2009, 4 (2), 47–58, https://doi.org/10.4081/ija.2009.2.47
5. A. Spanu et al. Chemosphere, 2021, 277, 130351, https://doi.org/10.1016/j.chemosphere.2021.130351

(P-19)

NANOGRAM LEVEL ANALYSIS OF MERCURY IN HUMIC-RICH NATURAL WATERS BY ICP-MS

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Mercury (Hg) is one of the most toxic elements which is released into the environment from both anthropogenic and natural sources. Due to the extreme toxicity of Hg, it is essential to develop accurate and precise analytical methods for the determination of Hg and its species.

Natural waters contain only some tens of ng $L^{-1}$of Hg, and the ultra-trace concentration level poses analytical challenges. The determination of Hg by ICP-MS has generally been considered challenging mainly due to the memory effect. However, at the nanogram level, poor spike recoveries were found to be more problematic than the memory effect. The developed direct ICP-MS method overcomes previously observed problems by adding 0.12% thiourea and 3% HCl to all samples and standards, whereby Hg is released from the matrix and stabilized in solution. The method detection limit (MDL) for this direct ICP-MS method is 2 ng L^{-1}. If even lower detection limits are required, water samples can be preconcentrated by using the developed 3D printed metal scavenger technique. This method achieves the MDL as low as 0.037 ng L^{-1}

(P-20)

DETERMINATION OF XANTHATES IN AQUEOUS SOLUTIONS BY HPLC-ICP-MS/MS

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The rising concern over the environmental impact of xanthates especially in the arctic region has increased the need to study these traditional flotation chemicals in more detail. Xanthates ($ROCS_2^-$) are organosulfur compounds which are easily degraded in aqueous solutions. Xanthates and their degradation products are toxic especially to the aquatic environment. Their greatest environmental impact is related to the formation of carbon disulfide (CS_2) and heavy metal complexes.

Due to the unstable nature and multiple reaction mechanisms of xanthates, their reliable quantitation is difficult. Spectrophotometric and titrimetric methods are traditionally used for monitoring xanthate concentrations in the flotation processes, but they are non-selective, and the detection limits of these methods are typically high. Selective methods are needed to study the reactions of xanthates more reliably.

The aim of our study was to develop new methods for the selective determination of low xanthate concentrations by reversed-phase high performance liquid chromatography – inductively coupled plasma tandem mass spectrometry (RP-HPLC-ICP-MS/MS). Two pretreatment methods for xanthates were studied: In the first method xanthates were oxidized to dixanthogen using triiodide. In the second method, transition metals (Cd, Co, Cu, Ni, Zn) were used to form metal-xanthate complexes.

In this work, HPLC-ICP-MS/MS technique was used for the separation and detection of different xanthate derived species. HPLC allows selective determination of different xanthates and their separation from sample matrix. Xanthates were detected by ICP-MS/MS based on their sulfur content. The instrument was operated in MS/MS mode using O_2 as reaction gas. This allows the detection of $^{32}S^+$ as $^{32}S^{16}O^+$ resolving the significant overlap of $^{16}O_2^+$ with $^{32}S^+$. In the case of metal-xanthate complexes, the detection based on the corresponding metal was studied to improve the sensitivity of the measurement compared to sulfur.

(P-21)

METHOD DEVELOPMENT AND OPTIMISATION FOR THE ELEMENTAL ANALYSIS OF ACETIC ACID LEACHATES OF NEODYMIUM MAGNETS

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Potential supply issues and uncertainty loom over the rare earth element (REE) market, which has aroused great interest in exploitation of secondary raw materials, such as spent neodymium (NdFeB) magnets. The permanent magnet alloy is rich in REEs (Nd, Pr, Dy, Tb), which are of critical importance in various high-tech applications, making their recycling desirable. Hydrometallurgical methods are among the more common approaches, and inductively coupled plasma-optical emission spectroscopy (ICP-OES) is one of the primary tools for their monitoring. This presentation demonstrates the process of developing and optimising a method for the elemental analysis of NdFeB leachates using ICP-OES. Parameters affecting plasma and measurement conditions include RF power, plasma gas, nebuliser gas, auxiliary gas and sample flow rates. Goal of the optimisation process was to achieve maximum robustness of the plasma (expressed as the Mg II/Mg I ratio) and maximum analyte emission intensity.

Furthermore, hard disk drive magnet samples dissolved in dilute acetic acid were analysed in the determined optimal ICP-OES conditions, and the obtained results compared with those obtained from ICP-MS.

(P-22)

ALUMINIUM MEASURMENTS 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, in general, 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 for the determination of aluminium by Inductive 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 participant’s results for the aluminium 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 aluminium 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 have significant effect on the recovery. In contrary, 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 a maximum digestion temperature of 240 and 280 ˚C. Regarding the duration of the digestion, there were no significant impact on the Al recovery measured between 20 and 50 min. The reagents used had a significant effect on the recovery and the use of nitric acid with ultrapure water gave 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 (respectively 200 ˚C and 20 min) from the recommendation in the EN. These findings provides 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.

(P-23)

CLASSIFICATION OF FERMENTED BEAN PASTE PRODUCTS USING PLASMA-BASED ELEMENTAL ANALYSIS TECHNIQUES

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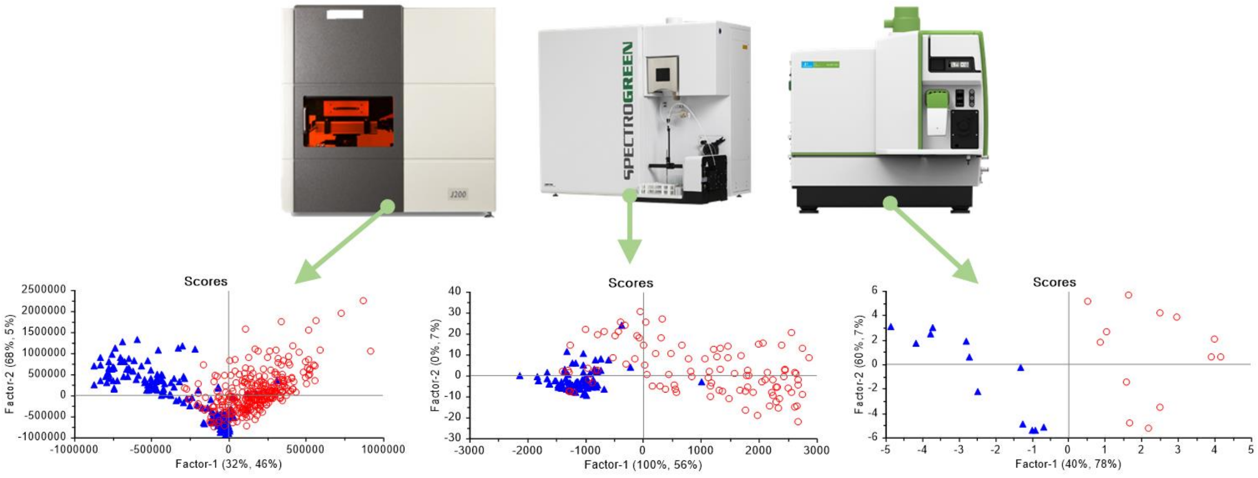
Fermented bean paste is one of the popular food sauces typically made of soybeans native to East Asia. It is called *Doenjang* in Korea, *Miso* in Japan, and *Huangjiang* (or Dajiang) in China, respectively. Flavours and tastes of the fermented bean pastes vary with production methods in which different ingredients are used. The main ingredients are soybean, salt, wheat flour, rice, etc. In this work, the elemental analysis techniques of laser-induced breakdown spectroscopy (LIBS), inductively-coupled plasma optical emission spectroscopy (ICP-OES), and inductively-coupled plasma mass spectrometry (ICP-MS) was employed to distinguish the fermented bean pastes produced in South Korea and those in China from each other. 101 products from South Korea and 66 ones from China were purchased in the Korean markets. From the LIBS analysis, atomic and ionic emission lines of Na, Cl, Mg, Ca, K, P, C, and H were identified. Among them, the emission lines of Mg and C were found to have most of the power distinguishing fermented bean pastes produced in South Korea and China. From the ICP-OES analysis, the concentrations of Al, Ba, Sr, Cu, Fe, Mn, Zn, Ca, and Mg could be determined. Discrimination power of the ICP-OES analysis were found to be dominated by Mg and Sr. The provenances, South Korea and China, were modelled by partial least squares-discriminant analysis (PLS-DA) based on LIBS (C and Mg) and ICP-OES (Mg and Sr). The LIBS and ICP-OES models could classified the products according to their provenances with the accuracy of 90.3% and 91.2%, respectively. For the products that could not be correctly classified, ICP-MS analysis was performed to determine the concentrations of Ni, Mn, and Co, and these elements were found to provide additional independent discrimination power from those of LIBS and ICP-OES. Considering two-step PLS-DA classification process based on ICP-OES and ICP-MS, the overall classification accuracy can reach up to 98.6%. Our results suggest that the plasma-based elemental analysis techniques can be used as highly reliable methodologies for screening fermented bean paste products with fake origin labels.



PLS-DA score plot from LIBS PLS-DA score plot from ICP-OES PLS-DA score plot from ICP-MS

(P-24)

TWO-STEP PARTIAL LEAST SQUARES-DISCRIMINANT ANALYSIS TO OVERCOME THE LIMIT OF GLOBAL MODELING APPROACH: APPLICATION TO CLASSIFICATION OF EDIBLE SALT PRODUCTS USING LASER-INDUCED BREAKDOWN SPECTRROSCOPY

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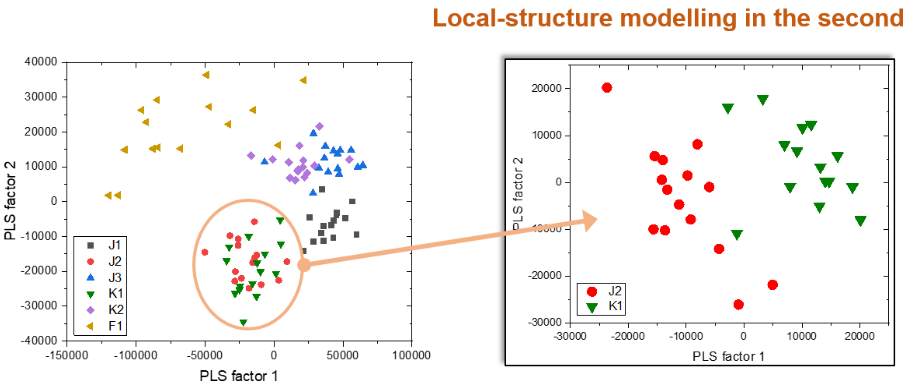
Laser-induced breakdown spectroscopy (LIBS) is one of the elemental analysis techniques based on optical emission spectroscopy. In spite of its lower analytical performance than those of conventional techniques such as inductively-coupled plasma optical emission spectroscopy, inductively-coupled plasma mass spectrometry, and atomic absorption spectroscopy, it is widely employed for material classification because of the capability of rapidly recording optical emission spectra covering wavelengths from ultraviolet to near-infrared. The LIBS spectra reflect composition of the elements contained in the sample at the percent-to-ppm level, and thus can be used as chemical fingerprints. LIBS spectra have been processed to model sample classes by a few classical multivariate analysis methods. Partial least squares-discriminant analysis (PLS-DA) is one of the classical multivariate statistics employed to model LIBS data structure. PLS-DA effectively extracts latent variables that explain the class differences. However, due to the global modelling nature of PLS-DA, i.e. fitting the whole data structure at a time, it risks losing the features describing local data structure that is useful for distinguishing particular classes.

In this work, we devised a two-step PLS-DA model for accurate classification of six edible salt products. Among the samples, two particular ones were found to be responsible for decrease in the classification accuracy by an ordinary PLS-DA model. Although the ordinary PLS-DA fit the whole LIBS data structure at a time, in the two-step modelling approach, the minute local structure corresponding to the difference between the two classes being confused with each other stayed un-modelled in the first step by treating the two classes as the same class. Then, the local structure was modelled separately in the second step. The classification accuracy of the ordinary and two-step models was evaluated by leave-one-out cross-validation, and the two-step model outperformed the ordinary one by correcting the misclassification of the confused class by the ordinary model. This improvement was explained by defining a normalized class distance, that is the distance between the centres of masses of the two sets of scores along the corresponding latent variable axis normalized by the geometric mean of the standard deviations of the two sets of scores. In the two-step model, the normalized class distance between the two classes confused with each other by the ordinary model was found to greatly elongated along the major latent variable axis. Our results provide an insight into PLS-DA modelling approach and how to improve the model performance considering the given data structure.



(P-25)

A NOVEL ICP-MS METHOD FOR SENSITIVE, ACCURATE AND HIGH-THROUGHPUT ANALYSIS OF BABY FOOD

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Food and food supplements contain essential nutrients and need to be tested for potentially toxic contaminants. For large scale testing, single quadrupole ICP-MS instruments are commonly applied, as triple quadrupole ICP-MS systems are often viewed as not fit for purpose due to potential constraints in sample throughput when using a variety of reactive gases. However, the use of oxygen only as the only reactive gas for a full multi-elemental analysis is a way to combine superior interference removal with short sample turnover times.

In this presentation, a variety of real baby food samples and appropriate certified reference materials have been measured using a novel method for triple quadrupole ICP-MS. The sample turnover time was reduced further by using a valve system to accelerate the sample uptake and wash out process. This method allowed to characterize the high amounts of different nutritional elements and potential small traces of toxic elements within different baby foods. Triple quadrupole ICP-MS technology enables achieving a high dynamic range, high sensitivity, as well as accurate and interference-free quantification of all target elements especially those of most concern, such as arsenic, cadmium or mercury. Long sequences of uninterrupted analysis over >10 hours demonstrated the methods robustness and once again highlight the ability to meet the requirements of high throughput laboratories.

The novel analysis mode proposed in this study using triple quadrupole ICP-MS combines the best of both worlds, the speed of analysis of a single quadrupole ICP-MS system with the added interference removal capabilities of a triple quadrupole ICP-MS.

(P-26)

SENSITIVE DETERMINATION OF IMPURITIES IN LITHIUM BATTERIES USING THE THERMO SCIENTIFIC ICAP PRO XP ICP-OES

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In the drive towards reducing dependence on burning fossil fuels for energy generation, several technologies have become established as front runners in the race to reduce carbon emissions and improve air quality. One of the most significant is lithium ion battery technology and a rapid ramp up in production of these batteries is currently underway globally. With this significant increase in production has come a corresponding increase in analytical testing of the battery component materials. As elemental impurities in battery materials affect charging / discharging and lifetime performance, elemental impurity analysis in cathode and electrolyte materials is an essential part of battery testing. In addition, to ensure consistent cathode performance for each battery cell, accurate and precise measurement of cathode matrix elements (e.g. Li, Co, Fe, Mn and P) for QA/QC in production is also required.

To meet these trace and major element analysis needs both ICP-OES and ICP-MS can be used, but the high sample matrix concentration and generally less demanding detection limit requirements for cathode and electrolyte material testing mean that ICP-OES is often suitable. In this presentation, the performance of a recently launched ICP-OES instrument, the Thermo Scientific™ iCAP™ PRO Series ICP-OES, for battery material analysis will be discussed. In particular, results will be presented for impurity and matrix element quantification in ternary cathode materials and elemental impurity analysis of graphite samples for battery anodes.

(P-27)

DEVELOPMENT OF GERMANIUM SPECIATION STUDY USING IC-ICP-MS TECHNIQUE IN SOIL SAMPLES

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Germanium is one of the Technology Critical Element (TCE) in European Union and has been widely used in electronic and industrial products - semiconductor detectors, optical and telecommunication industries, wind turbines, electric vehicles, photovoltaic, energy-efficient lighting. Expanding access of cutting-edge technologies lead to release more and more amounts of TCE to the environment. The transfer of these substances makes it necessary to get to know their mobility, reactivity, and chemical transformations in the surrounding world, which are critically dependent on their chemical form (speciation). The total concentrations of TCE elements are at trace level, which make their speciation analysis challenging. The determination of Ge was conducted using ICP-MS technique in DRC-e mode to remove polyatomic plasma and matrix-based interferences. The flow rate of the reaction gas and value of rejection parameter (Rpq) were the key parameters of the DRC operation. The optimized CH_4 flow rate was selected at 0.4 mL min^{-1} and when the Rpq value was 0.65, the signal of ^{74}Ge tended to be stable. Standard solutions with Ge concentrations from 0.5 to 10 µg L^{-1} were analyzed to construct a calibration curve with a correlation coefficient of 0.9998.
The optimization and validation of a methodology for determining and extracting inorganic Ge(IV) and methylated derivatives: monomethylgermanium (MMGe), dimethylgermanium (DMGe) in easily-leached fractions of soil by Ion Chromatography-Inductively Coupled Plasma-Mass Spectrometry (IC-ICP-MS) were studied. To separate analytes, a speciation apparatus set was applied. It consisted of an HPLC chromatograph (PerkinElmer) equipped with Series 200LC Peltier oven, Series 200LC autosampler and Series 200LC gradient pump. HPLC kit was hyphenated with ICP-MS spectrometer. Ions were successfully separated in 12 minutes on a Dionex IonPac AS9-HC column with ammonium nitrate and potassium sodium tartarate as an elution phase.

Soil samples were collected from areas subjected to the influence of an electrowaste processing and sorting plant. In most cases, the soils contained a Ge(IV) form.
The effect of extraction time on the degree of tellurium leaching after 1, 2, 3, and 4 h was investigated. The extraction efficiency of soils for the germanium species content by shaking was insufficient and it was chosen to use ultrasound to improve the degree of germanium extraction from the soil. The results showed that the best extraction efficiency was obtained by using 100 mM NH_4NO_3 with 1 mM potassium sodium tartrate as an extractant that washes out germanium from soils within 4 hours.

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(P-28)

IMPROVED ENVIRONMENTAL IMPACT ASSESSMENT OF HIGH SALINITY PRODUCED WATER

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When crude oil is produced large amounts of water are produced along with the organic petroleum material. This co-produced water (PW) is highly saline and contaminated from contact with crude oil in the formation and the production additives, thus it is heterogeneous and remarkably complex. Considering that this water is being discharged to the sea at most current offshore production sites, reaching the ambition of zero harmful discharge requires stringent produced water management and improved monitoring and toxicology evaluation.

This work aims at an initial characterization for improved environmental impact assessment of water production in connection with offshore oil, facing the analytical challenges given by a hypersaline and carbon-rich water sample.
This work presents a workflow for complex aqueous samples from oil wells starting with total alkalinity (TA) analysis of samples purified with respect to organic content and on the analysis of major inorganic anions and specific volatile and semi-volatile organic acids content using liquid ion chromatography (HPIC).

The determination of trace elements (As Cr, Cd, Co, Cu, As, Sb) in produced water has also been targeted using ICP-OES for analyzing non-digested, hot plate digested and microwave digested samples and comparing the results. Matrix matching for blanks, calibration standards and quality checks have been implemented to improve plasma stability, measurements reproducibility and raw data reliability. The same trace elements have been targeted in suspended particulate matter (SPM) of PW via cellulose 0,45 µm filters and using acidic digestion. In addition, due to the complexity of the matrix, for various trace elements, SPE pre-concentration techniques have been also applied and verified in order to minimize the matrix influence on analytical detection. Further characterizations on suspended particulate matter in PW samples have subsequently been carried out through scanning electron microscopy. This presentation includes the initial results of this analysis of actual Danish North Sea produced water as well as discharge point water samples.

(P-29)

DIGESTATE FROM ANAEROBIC DIGESTION AND POWER PLANT FLY ASH AS A CIRCULAR ECONOMY FERTILIZER: EVALUATION OF HEAVY METAL CONCENTRATIONS

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Due to global human population growth and the current political climate, the interest in alternative circular economy fertilizers is rising. Phosphorus and nitrogen are both vital macronutrients for plant growth. Phosphorus is a critical non-renewable nutrient, and its known reserves are currently depleting, whereas nitrogen is conventionally produced from fossil fuels via the Haber-Bosch process creating greenhouse gases. Using local waste and by-product streams as new recycled raw material for fertilizers or soil improvers could ease the environmental impact of conventional macronutrient production. Digestate from anaerobic digestion and power plant fly ash are potential circular economy fertilizers that are also currently separately in use. Combined and with the required pre-treatment they could provide a coherent NPK-fertilizer.

Power plant fly ash is often enriched with harmful heavy metals. In high quantities, certain heavy metals prohibit germination or accumulate in the plant. A heavy metal assessment is necessary to ensure safe use of the digestate and fly ash blend.

ICP-OES and ICP-MS measurements were carried out to determine the heavy metal concentration in different digestate and power plant fly ash blends. The heavy metal concentrations in different blends were compared to current legislative limits. The optimal blend considering macronutrients and legislatively limited heavy metals was determined.

(P-30)

COMPARISSON OF DIFFERENT PLASMA VIEWS FOR THE ANALYSIS OF COMPLEX SAMPLES

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The different views of the plasma and the torch orientation play an important role for the analytical capabilities of the instrument and the performance in difficult matrices and complex samples

ICP-OES instruments with axial plasma observation are still the instruments of choice for trace analytical work.

Viewing the plasma radially provides generally lower sensitivity, but matrix effects are greatly reduced. Therefore, the radial observation technique is typically chosen in the case of samples with high TSD (total dissolved solids) concentrations, for the routine analysis of organic solutions or where high stability and precision is required.

The possibility to view the plasma both axial and radial at the same instrument (dual view) seems to solve all disadvantages, but those techniques are a compromise since only one light path is direct.

The MultiView technology combines the benefits of the axial and radial view in one instrument.

Using a Dual Side-on interface is a new approach which provides the possibility of improvement of the radial plasma.

In this study the different plasma views will be critically compared for the analysis of more complex matrices, like volatile organics, high salt samples, Li-Ion battery materials etc. Sensitivity, linearity, robustness and stability will be reported.

The use of the different views with hyphenated techniques will be discussed as well.

(P-31)

FEED-TO-FISH TRANSFER OF ARSENIC AND ARSENIC SPECIES IN ATLANTIC SALMON FED ON DIETS CONTAINING NORWEGIAN FARMED BLUE MUSSEL AND KELP

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Norwegian aquaculture aims to significantly reduce the environmental and climate footprints of feed production. Consequently, low trophic marine resources such as blue mussels and kelp farmed locally are potential candidates to be used as ingredients in salmon feed. In this context, mapping of risks associated with the use of novel feed ingredients, as well as understanding the transfer of undesirables from feed-to-fish, is of high importance. Moreover, there is a current discussion on establishing maximum limits for inorganic arsenic in different foodstuffs in the European Union. Thus, it is important to obtain data on concentrations of arsenic and arsenic species in farmed salmon when being fed novel low trophic marine feed resources such as blue mussel and kelp.

The objectives of this work were: (i) to describe concentrations of total arsenic and its different chemical species present in novel salmon feeds containing blue mussel and kelp, and (ii) to evaluate whether the feed-to-fish transfer depends on the arsenic species. Atlantic salmon were fed experimental diets for 70 days. Four diets were prepared containing up to 4% fermented kelp, and four diets were prepared using up to 11% blue mussel silage or 12 % blue mussel meal. Concentrations of arsenic and arsenic species in feeds, faeces, liver and fillet of Atlantic salmon were determined by inductively coupled plasma mass spectrometry (ICP-MS) and high-performance liquid chromatography coupled to ICP-MS (HPLC-ICP-MS), respectively. The apparent availability (%) was determined using a ratio between the concentration of arsenic in diet and in faeces and the concentration of an inert marker (i.e. yttrium oxide) in diet and faeces. The retention (%) is expressed as the ratio of the difference between the final and initial arsenic concentrations in liver/fillet, and the concentration of arsenic in diet and feed intake.

The use of kelp or blue mussel-based feed ingredients increased the levels of total arsenic but maximum limits as defined in Directive 2002/32 EC and amendments were not exceed. The concentrations found in the experimental feeds ranged from 3.4 mg/kg to 4.6 mg/kg. Arsenobetaine, inorganic arsenic and one arsenosugar (AsSug328) were the most abundant arsenic species in the feeds. Arsenic speciation in the feed varied based on the ingredient, with arsenobetaine dominating in blue mussel-based feeds, while arsenosugars were abundant in kelp-included feed. The apparent availability of total arsenic ranged from 67% to 83%, but retention in fillet only ranged from 2% to 22% and in liver from 0.3% to 0.6%. For inorganic arsenic, the apparent availability ranged from 54% to 69%, but inorganic arsenic was not retained in fillet nor liver as no detectable levels were found. Despite relatively high apparent availability of total arsenic and inorganic arsenic, the retained concentrations of arsenic did not reflect the same trend.

This study shows that speciation analysis provides valuable information of the feed-to-fish transfer of arsenic.

(P-32)
STUDYING THE MECHANISM OF SILVER IONS BINDING TO CASEIN

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The present work includes kinetic and isotherm studies of silver binding on casein, which was carried out using batch sorption approach. Immobilization of silver ions to protein was conducted at slightly alkaline conditions (pH 8) and measurements were performed by ICP-MS. Sample preparation in ammonia solution facilitated the silver ions binding with the negatively charged surface of protein. Furthermore, silver ammonia complex is considered more stable than silver aqua complex. More detailed analysis of metal binding mechanism was also provided by spectroscopic, spectrometric, microscopic and separation techniques. The results indicated the formation of silver nanoparticles. Interestingly, the nanoparticles are formed inside the casein micelles. Silver nanoparticles shows higher antibacterial properties, thus synthesized naonocomposite has potential as novel antibacterial agent for healing of chronic wounds.

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(P-33)

SPECIATION OF ELEVEN ORGANOTIN COMPOUNDS VIA HPLC-ICP-MS USING THE COMPLEXING AGENT A-TROPOLONE

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Organotin compounds (OTCs) rank among the most used organometallic compounds and have been utilized in various industrial sectors for several decades. They are known for their severe effects on human and ecosystem health and are therefore widely regulated in their use. The degree of toxicity of OTCs varies considerably depending on the number and type of organic substituents. As a result, the speciation of different OTCs is of great interest in the fields of consumer protection, environmental and occupational health.

In terms of available analytical methods mostly gas or liquid chromatography coupled to ICP-MS are employed. While GC methods offer a higher peak resolution of more compounds, HPLC methods excel due to minimal sample preparation without the need of an error-prone derivatization. Previously published HPLC-ICP-MS methods describe a separation of maximum six compounds using a simple binary gradient.

Tropolone is an organic compound combining, aromatic, ketonic, hydroxylic functionalities. It is soluble in both water, organic solvents and due to its electronic structure, it forms very stable mono and bidentate complexes with various mono-, bi- and trivalent metal cations. This makes it a suitable complexing agent for liquid chromatography in metal speciation.

This poster shows the influence of varying α-tropolone concentrations on OTC separation in a ternary eluent and flow rate gradient consisting of methanol (MeOH), acetonitrile (ACN) and acetic acid (6 % v/v) in ultrapure water. The newly developed HPLC-ICP-MS method achieves a separation of the eleven OTCs Monomethyltin (MMT), Monobutyltin (MBT), Monooctyltin (MOT), Monophenyltin (MPhT), Dimethyltin (DMT), Dibutyltin (DBT), Diphenyltin (DPhT), Trimethyltin (TMT), Tributyltin (TBT), Triphenyltin (TPhT) and Tetramethyltin (TTMT) within 22 minutes using a C18 reversed phase column.

(P-34)

ANALYSIS OF ARSENIC AT ULTRA TRACE LEVEL IN HYDROCHLORIC ACID USING INNOVATIVE ICP-MS TECHNOLOGIES

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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 that the ICP-MS technique has ever faced is the measurement of Arsenic 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. 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 study provides a simple but yet effective method to measure ultra traces of arsenic in hydrochloric acid using a combination of innovative ICP-MS technologies.

(P-35)

A METHOD TO DETERMINE NUTRIENT AND OTHER ELEMENTS IN FOODS USING CLOSED VESSEL MICROWAVE ASSISTED DIGESTION AND INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY: SINGLE LAB VALIDATION

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The U.S. Food and Drug Administration currently uses AOAC 984.27 to measure nutrient elements in foods. This legacy method, however, was validated for a limited matrix scope using a single standard calibration. In the current work, we present the development and validation of an updated method that measures 23 elements (As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Sr, Tl, V, Zn) in foods using microwave assisted digestion followed by inductively coupled plasma optical emission spectrometry (ICP-OES). Special attention was placed on ten nutrient elements, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, and Zn, during method development and validation. The method harmonizes sample preparation with FDA method EAM 4.7, the FDA's toxic elements in foods method, and includes internal standardization, sufficient quality controls, and a calibration curve spanning multiple orders of magnitude. Sources of signal bias such as spectral interference on Na 589.592 nm from Ba will be discussed in detail.

Method validation was performed according to current FDA guidelines for a Level Two single lab validation whereby fortified analytical portions were prepared and analyzed at the 50, 100, and 250 % level. More than 20 foods spanning the AOAC food triangle were analyzed for validation in addition to several reference materials. Considering results above the LOQ, satisfactory agreement between measured and certified values is observed from the analysis of a suite of reference materials (**Fig. 1**). Similarly, except for explainable outliers (e.g., improper spiking concentration, contamination, unmitigated spectral interference), the method performs satisfactorily when analyzing fortified analytical portions (**Fig. 2**).

Given these results, the method will be evaluated with a Level Three multi-lab validation study to further verify its applicability to determine nutrient and other elements in foods.

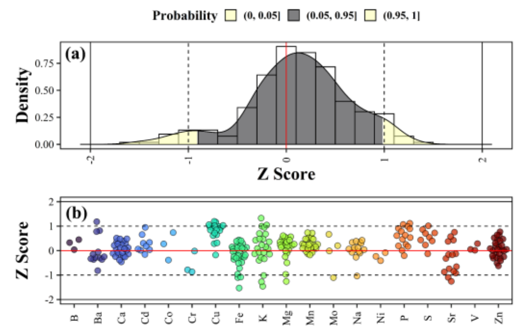

Fig. 1. Dry-mass results (n = 265) from the analysis of ten different reference materials. Sample portions were digested and analyzed in triplicate on three separate days. **(a)** the distribution of all Z scores; **(b)** Z scores by element.

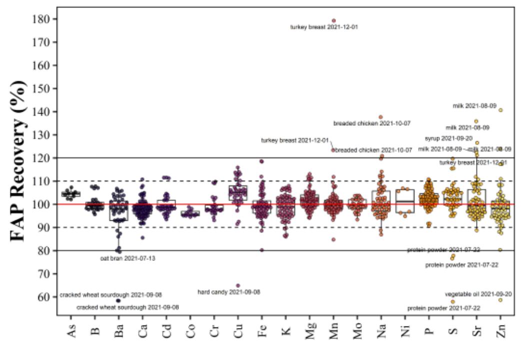

Fig. 2. Recoveries from analyzing fortified analytical portions (i.e. spikes).

(P-36)

INVESTIGATION OF GRAPHITE-BASED ANODES FOR LIB USING GD-OES – IMPACT OF PLASMA PARAMETERS AND ELECTRODE PROPERTIES

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Glow-discharge optical emission spectroscopy (GD-OES) is a powerful technique for layered elemental analysis of solid materials. Since mainly massive metal materials have been investigated in the past decades, the imperative need of new analytical methods for energy storage materials, such as lithium-ion battery (LIB) electrodes, has opened a new application field. GD-OES has recently been used for the characterization of aging mechanisms at graphite anode surfaces,[1] the detection of silicon in Si/C composite anodes,[2] as well as the elucidation of Li distribution in $LiFePO_4$ and graphite electrodes[3] as examples of the widespread application potential of this technique in the field of LIB research.

GD-OES depth profiles can only deliver valid elemental compositions if the sputtering process is homogeneous, resulting in a flat shaped crater released in the material. Since the porous solid structure of LIB electrodes differs significantly from massive metal structures, new methods and techniques need to be developed for highly resolved analysis.

The sputtering homogeneity strongly depends on plasma parameters such as applied voltage, pressure, as well as pulse frequency and plasma on-time in case of pulsed measurements. Additionally, the highest possible sputtering rate is desired to work most effectively and save plasma gas. Thus, a comprehensive investigation of these parameters with their impact to the sputtering rate and the resulting crater shape in porous graphite anodes was realised. It is further shown that electrode properties such as density, porosity, size and shape of the graphite particles influence the sputtering process significantly. Based on these results, the wide-ranging applicability of GD-OES methods for LIB electrodes with specific solid structure properties is discussed.

[1] N. Ghanbari et al., *J. Phys. Chem. C*, **120**, 22225 (2016)
[2] K. Richter et al., *J. Electrochem. Soc*, **165**, A3602 (2018)
[3] H. Takahara et al., *J. Electrochem. Soc.*, **160**, A272 (2013)

(P-37)

TOTAL MERCURY IN SNOW COLLECTED ON JAN MAYEN

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To study long range transport and local pollution sources at Jan Mayen, snow samples collected in July – August 2021 will be analyzed for content of organic pollutants, major ions, metals, and microplastic; different parameters which in combination may prove valuable in source apportionment.[1] Mercury in the artic is recognized as a threat to wildlife and human populations. Mercury originates from multiple sources, both anthropogenic (e.g., combustion of fossil fuel and biomass), and natural sources such as geogenic activity (e.g., volcanic activity). Characterization of particles found in the surface snow as well as multi element analysis could be effective tools in understanding where mercury might originate from.

The samples were divided into three categories based on their sampling site: transect, snow pit, and other samples taken around the island. Surface snow samples were collected in a transect from the top of the volcano, Beerenberg (2277 m), and continuing about every 100-elevation meter down towards the sea to an altitude of 139 meter. Additionally, a snow pit of one meter from surface to the glacier ice was dug at 1300 meters above sea level. In the snow pit, samples were collected by inserting 5-mL polypropylene tubes into the snow at 5-cm intervals. To stabilize mercury, all samples were added hydrochloric and nitric acid.

The samples were analyzed for mercury using an Agilent 8800 Trippel Quadrupole inductively coupled plasma mass spectrometer (QQQ-ICP-MS). To separate mercury from the sample matrix, a cold-vapor separation unit was used in tandem with the ICP-MS. This technique improved the method sensitivity. No-gas-mode was used as only Hg(0) would enter the ICP-MS. Three different isotopes were analyzed (200, 201, and 202), and 202 amu was selected among those.

The detection limit was 0.27 ng/L, and the quantification limit was 0.90 ng/L. Concentration of Hg in snow ranged between 2.1 ng/L and 72 ng/L from 0-600 meters above sea level. The highest concentration (72 ng/L) was noticed at 306 meters. The surface snow samples taken above 600 meters ranged from 2.1 ng/L to 6.0 ng/L. The amount of visible particles in the snow samples varied a lot. As very first result of the single particle analysis, silicates and fly ash particles were observed using a variable-pressure scanning electron microscope (VP-SEM, SU6600 Hitachi) with an energy dispersive X-ray detector (Bruker Nano GmbH, Berlin, Germany). Further analysis of single particles, elements and major ions may aid the understanding of the origin of the mercury in the snow samples collected around Jan Mayen.

The sampling campaign at Jan Mayen was a part of a project funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation): *Iceland as a model for high-latitude dust sources – a combined experimental and modeling approach for characterization of dust emission and transport processes (HiLDA*

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15 Author Index