European Symposium
on Analytical Spectrometry
24-28 June 2024
POLAND, WARSAW

# BOOK of ABSTRACTS

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# MONDAY 24 June 2024

9.00 – 10.30 The short courses organised by Pro-Environment Polska

10.30 – 10.45 COFFEE Break (in front of Aula A/B)

10.45 – 12.15 The short courses organised by Pro-Environment Polska

12.15 – 13.30 Refreshment (in front of Aula C and in the patio)

## SESSION 1 AULA A/B Chair: Ewa Bulska & Barbara Wagner

13.30 – 14.00 OPENING CEREMONY

14.00 – 15.00 PLENARY LECTURE / Fijałkowski PRIZE CEREMONY

Margaretha T.C. de Loos-Vollebregt: *How to deal with carbon-induced matrix effects in ICP-OES and ICP-MS: possibilities and limitations.*

15.00– 15.45 COFFEE BREAK (in front of Aula A/B)

## SESSION 2 AULA A/B Chair: Beata Godlewska-Żyłkiewicz & Zofia Kowalewska

15.45 – 16.20 INVITED LECTURE

Frank Vanhaecke: *Quantitative element mapping in biomatrices using laser ablation – ICP-mass spectrometry.*

16.20 – 16.55 INVITED LECTURE

Marketa Hola: *Laser Ablation for ICP-MS: Simple Routine or Big Challenge.*

16.55 – 17.15 Zuzana Gajdosechova

*Use of imaging and counting techniques for the identification and analysis of metal particles in unused legal and illegal cannabis vaping products.*

17.15 – 17.35 Ewelina Kowa

*Revealing the composition of coralline algae skeleton with LA-ICP-ToF-MS imaging.*

17.35 – 17.55 Tomáš Vaculovic

*Tools for determination of specific proteins by LA-ICP-MS.*

17.55 – 18.15 Jaromir Stráník

*Determination of SP LA ICP MS transport efficiency using photon upconverting nanoparticles.*

## GET TOGETHER (in front of Aula C and in the patio)

# TUESDAY 25 June 2024

## SESSION 3 AULA A/B Chair: Heidi Goenaga & Barbara Leśniewska

9.00 – 9.35 INVITED LECTURE

Joanna Szpunar: *Mass spectrometry approaches to the analysis of environmental nanopollutants.*

9.35 – 10.10 INVITED LECTURE

Victor G. Mihucz: *Towards a better understanding of indoor air pollution.*

10.10 – 10.30 Magdalena Muszyńska

Solutions for Single Cell, Single Particle, and Other Demanding Applications Through the Use of Multiquadrupole ICP-MS.

10.30 – 10.50 Guillermo Grindlay

Elemental analysis of environmental and food samples by means microwave-sustained inductively coupled atmospheric-pressure plasma optical emission spectrometry: matrix effects and calibration strategies.

10.50 -11.10 Bartłomiej Cieślik

Investigating Trace Element and Radioisotope Migration in Solid Waste from Sewage Sludge Incineration.

11.10 – 11.30 COFFEE BREAK (in front of Aula A/B)

## SESSION 4 AULA A/B Chair: Viktor Kanicky & Katarzyna Kińska

11.30 – 12.05 INVITED LECTURE

Thomas Prohaska: *Monitoring chemical processes in materials science – novel approaches for in situ measurements of elements and isotopes.*

12.05 – 12.40 INVITED LECTURE

Jörg Feldmann: *Potential risk from the decommissioning of oil and gas infrastructure to the marine environment: a multimethod study.*

12.40 – 13.00 Katarzyna Pawlak

Terpenoic acid oxidation by hydroxyl radical in the aqueous phase: kinetics and product study.

13.00 – 13.20 Barbara Leśniewska

Study of bioaccessible forms of Mn and Cu in rosemary (Rosmarinus officinalis L.) by SEC-ICP-MS and LC-MS/MS methods.

13.20 – 13.40 Tomas Matoušek

Seasonal changes of the chemical speciation of arsenic, antimony, germanium and tellurium in Czech freshwater reservoirs.

13.40 – 14.30 LUNCH (in front of Aula C and in the patio)

## SESSION 5 AULA A/B Chair: Thomas Prohaska & Anna Ruszczyńska

14.30 – 15.05 INVITED LECTURE
Heidi Goenaga-Infante: *The unlimited power of combined spICP-MS with AF4-ICP-MS/Light scattering: Providing new insights into the fractionation of engineered nanomaterials in consumer products.*

15.05 – 15.40 INVITED LECTURE
Yukihiro Ozaki: *Infrared, far-infrared, and Raman spectroscopy studies of minerals, rocks, and biogenic minerals.*

15.40 – 16.00 Justyna Kostrzewa
Advantages and disadvantages of different sample preparation methods for ferrosilicon magnesium alloy analysis using X-ray fluorescence spectrometry.

16.00 – 16.20 Kamil Polok
Exploring 2-propanol and its fluorinated derivatives using femtosecond optical Kerr effect spectroscopy and theoretical chemistry methods.

16.20 – 16.40 Carlos Gómez Pertusa
Standardization of microwave-assisted extraction procedures for characterizing metallic nanoparticles by means single particle ICP-MS.

16.40 – 16.50 GROUP PHOTO

## 16.50 – 18.00 COFFEE & POSTER SESSION (in front of Aula A/B:

## POSTERS P1-P30

# WEDNESDAY 26 June 2024

## SESSION 6 AULA A/B Chair: Joanna Szpunar & Andrzej Gawor

9.00 – 9.35 INVITED LECTURE
Érico M. M. Flores: *Current Status and Challenges in Sample Preparation for Atomic Spectrometry.*

9.35 – 10.10 INVITED LECTURE
Jirí Dedina: *Exploring potential of hydride generation atomic fluorescence spectrometry for ultratrace elemental analysis.*

10.10 – 10.30 Pawel Pohl
The determination of Ge by hydride generation–atmospheric pressure glow discharge optical emission spectrometry (HG–APGD OES).

10.30 – 10.50 Jan Kratzer

Atmospheric plasma discharges as hydride atomizers for trace element analysis: their development, applications and mechanistic studies.

10.50 – 11.10 Shim-Pol

11.10 – 11.30 COFFEE BREAK (in front of Aula A/B)

## SESSION 7 AULA A/B Chair: Iwona Szynkowska & Jan Kratzer

11.30 – 12.05 INVITED LECTURE

Ryszard Łobiński: *Atomic vs. molecular mass spectrometry in speciation analysis.*

12.05 – 12.40 INVITED LECTURE

Martín Resano: *Advances in single event-ICP-MS.*

12.40 – 13.00 Beata Godlewska-Żyłkiewicz

Studies of uptake and translocation of metal nanoparticles in edible plants using single-particle ICP-MS/MS method.

13.00 – 13.20 Ketolly Natanne da Silva Leal

Performance of single-cell ICP-MS/MS for investigating HSA-induced alterations in zinc uptake in paraformaldehyde-fixed HUVECs.

13.20 – 13.40 Nuria Guijarro-Ramírez

Speciation of ionic selenium and biogenic SeNPs by means of spICP-MS after an ion exchange resin treatment.

13.40-14.00 Magdalena Matczuk

Is CE-ICP-MS/MS a proper tool for examining the encapsulation of active compounds in liposomes?

14.00 – 14.50 LUNCH (in front of Aula C and in the patio)

## SESSION 8 AULA A/B Chair: Ryszard Łobiński & Monika Sadowska

14.50 – 15.25 INVITED LECTURE

Marco Aurélio Zezzi Arruda: *Multimodal platform towards non-target speciomics: from known to new molecules.*

15.25 – 15.45 Wojciech Hyk

Estimation of measurement uncertainty and optimization of algorithms for signal processing in the Single Particle -ICP-MS technique.

15.45 – 16.05 David Milde

Measurement uncertainty of complex measurements from correlated performance data: Determination of total Cr in yeast.

16.05 – 16.25 Vera Scharek

Speciation Analysis of Organo-Tin in Environmental Samples via Electrothermal Vaporization/Inductively Coupled Plasma-Mass Spectrometry.

## SESSION 9 AULA C Chair: Beata Krasnodębska-Ostręga & Andrii Tupys

15.25 – 15.45 Krzysztof Gręda
Dispersive micro-solid phase extraction for the determination of Cd by slurry sampling microplasma optical emission spectrometry.

15.45 – 16.05 Oskar Ronda
The influence of mineralization conditions on the recovery of metals from sewage sludge ash: implication for analytical and technological applications.

16.05 – 16.25 Stanislav Musil
Recent advances in photochemical vapor generation with a focus on the less abundant elements.

## 16.25 – 17.35 COFFEE & POSTER SESSION (in front of Aula A/B)

POSTERS P31-P60

## start: 19:30 GALA DINNER

# THURSDAY 27 June 2024

## SESSION 9 AULA A/B Chair: Jörg Feldmann & Bartłomiej Cieślik

9.35 – 10.10 INVITED LECTURE

Márcia Foster Mesko: *Overcoming Sample Preparation Challenges for Halogen Determination by Mass Spectrometry Techniques*

10.10 – 10.30 Zofia Kowalewska
Graphite furnace and fluorine determination.

10.30 – 10.50 Viktoria Müller
Fluorine mass balance analysis in wild boar organs from the Bohemian Forest National Park.

10.50 -11.10 COFFEE BREAK (in front of Aula A/B)

## SESSION 10 AULA A/B Chair: Katarzyna Wróbel & Zuzanna Gajdosechova

11.10 – 11.45 INVITED LECTURE

Gerhard Schlemmer: *Graphite and Carbon: Once Panacea, Redundant Today?*

11.45 – 12.05 Aleksandra Sentkowska
Does green mean better? A critical look at the green synthesis of selenium nanoparticles.

12.05 – 12.25 Agata Błaziak
Insight into the formation and evolution of secondary organic aerosol (SOA) in the forest atmosphere.

12.25 – 12.45 Paweł Hać

Determination of potentially toxic elements in tobacco products in the perspective of consumer exposure.

12.45 – 13.05 Elham Kamgar

Analytical approaches to the comprehensive characterization of the mineral content and elemental speciation in Shilajit, a traditional Asian medicine.

## SESSION 10 AULA C Chair: Márcia Foster Mesko & Joanna Kowalska

11.45 – 12.05 Karina Kocot

Application of graphene oxide foams in preconcentration of ultratrace amounts of metal ions via X-ray fluorescence spectrometry.

12.05 – 12.25 Olha Korkuna

Spectrophotometric study of oxytetracycline derivatives and their use in analysis.

12.25 – 12.45 Bastian Wiggershaus

Micro-Discharge Optical Emission Spectroscopy – On-site analysis of lithium process samples by generating micro-plasmas.

12.45 – 13.05 Katarzyna Pawlak

Simultaneous determination of selected metals in Dried Blood Spot (DBS) by EDX.

13.05 – 13.55 LUNCH (in front of Aula A/B)

## SESSION 11 AULA A/B Chair: Ewa Bulska & Barbara Wagner

13.55 – 14.15 Simone Braeuer

Challenges of integrating metallome analysis in exposomics workflows.

14.15 – 14.35 Olga Stężycka

Application of mass spectrometry to analyze interactions between flavonoids and G-tetrad.

14.35 – 14.55 Alan Alexander González Ibarra

Isotopic Tracing in Amino Acid Biosynthesis: Insights from Galleria mellonella and MEF Cells.

14.55 – 15.15 Monika Adamowska

Comparison of XRF and ICP-OES measurements and investigation of selected metal cations removal from aquaeous solutions using poly(sodium acrylate).

## 15.15 – 15.50 CLOSING CEREMONY

PLENARY LECTURE

Katarzyna Wróbel: *Unconventional quantification methods in microwave induced plasma – atomic emission spectrometry (MP-AES).*

## 15.50 – 16.00 BEST POSTER AWARD CEREMONY

## 16.00 – 18.00 "GOODBYE COFFEE" (in front of Aula A/B)

## FRIDAY 28 June 2024

9.00 – 12.00 ESAS 2024 – Rising Chemists: Poster Session of Young Scientists of Faculty of Chemistry University of Warsaw

12.00 BEST FRIDAY POSTER SESSION AWARD CEREMONY

European Symposium
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# INVITED LECTURES

# Dr Jerzy Fijałkowski Award
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# Dr Jerzy Fijałkowski Award
of the Committee of Analytical Chemistry
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is given to

Professor

**Margaretha de Loos Vollebregt**

for her extraordinary achievements
in the field of atomic and mass spectrometry

Białystok/Warszawa
Poland, 24th June 2024

# Margaretha T.C. de Loos-Vollebregt

Education: Graduated from Delft University of Technology (1976).
PhD Thesis (1980): Zeeman atomic absorption spectroscopy (supervisor Prof. Dr. L. de Galan).
Position until 2009: associate professor at the faculty of Applied Sciences, Delft University of Technology, Netherlands.

Research interests: Analytical atomic spectroscopy, especially atomic absorption spectrometry, ICP optical emission and mass spectrometry.

2009 – 2016: guest scientist faculty of Applied Sciences, Delft University of Technology, Netherlands.
2009 – present: guest professor Atomic and Mass Spectrometry in the Department of Chemistry at Ghent University, Belgium.
2001 – present: Editor Spectrochimica Acta Part B: Atomic Spectroscopy
2006 – present: Editorial advisory board member Analytica Chimica Acta
2003 – present: Technical assessor Dutch Accreditation Council
2009 – present: Teacher atomic spectroscopy for analytical chemists in industry, University of professional education (Avans+)
1998 – 2001: Reviews editor Spectrochimica Acta Part B: Atomic Spectroscopy
1991 – 2016: Advisory board Journal of Analytical Atomic Spectrometry
1992 – 1997: Editorial advisory board member Spectrochimica Acta Part B
Publications: about 80 research articles and review articles published in international peer reviewed scientific journals.
Presentations: about 130 lectures presented at international conferences, including several invited and keynote lectures.

On the 24th of June, Professor Margaretha will give a plenary lecture on
How to deal with carbon-induced matrix effects in ICP-OES and ICP-MS: possibilities and limitations.

# Quantitative element mapping in biomatrices using LA-ICP-MS

**F. Vanhaecke[1], I. Basabe Mendizabal[1], A. Lores-Padin[1], T. Van Helden[1], K. Mervič[2], M. Šala[2], J.T. van Elteren[2], I. Nemet[3], S. Rončević[3], T. Van Acker[1]**

1) *Atomic and Mass Spectrometry – A&MS research unit, Department of Chemistry, Ghent University, Campus Sterre, Krijgslaan 281-S12, 9000 Ghent, Belgium*
2) *National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia*
3) *Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia*

*frank.vanhaecke@ugent.be*

The use of laser ablation (LA) as a means of sample introduction in ICP-mass spectrometry (ICP-MS) not only allows the *bulk* analysis of solid materials, but also enables the 2-dimensional (and sometimes even 3-dimensional) distribution of elements down to trace and ultra-trace level over the sample matrix to be revealed.

State-of-art software allows the data obtained upon line-by-line interrogation of materials of various origin to be converted into elemental maps. By using an ICP-MS unit equipped with a time-of-flight analyser for mass analysis, a(n almost) full elemental mass spectrum is obtained for every pixel of such map. Provided an ultra-fast ablation cell and adequate transfer line connecting such cell to the ICP torch are used, single pulse responses (SPRs) with a duration below 1 ms can be obtained, enabling pixel acquisition rates up to 1 kHz. Rapid evacuation of the LA-generated aerosol from the location of laser-sample interaction and its transport using He carrier gas flowing in a laminar regime also leads to largely improved signal-to-noise ratios, enabling the use of a laser beam with small diameter and thus, highly detailed elemental maps. By using a matrix-matched standard, this approach can be rendered quantitative.

When analyzing biological tissue sections, attention has to be devoted to the shape of the SPR for each element targeted. It has been demonstrated that several elements are (partially) transported under gaseous form [1], which can impact the image quality, unless the instrument settings and data acquisition parameters are adapted.

Throughout the presentation, step-by-step improvement of the LA-ICP-MS set-up used at UGent-A&MS towards current-state-of-art will be described. Tips and tricks will be shared and pitfalls highlighted. Real-world applications will illustrate the relevance and capabilities of LA-ICP-MS elemental mapping, also referred to as elemental bio-imaging.

References:

[1] T. Van Helden, K. Mervič, I. Nemet, J.T. van Elteren, F. Vanhaecke, S. Rončević, M. Šala and T. Van Acker, Anal. Chim. Acta, 1287, paper nr. 342089, 2024.

# Laser Ablation for ICP-MS: Simple Routine or Big Challenge?

**<u>M. Holá</u>[1], M. Kubeš[2,3], V. Wertich[2,3], J. Dobeš[1], Z. Salajková[4], J. Ondráček[5], V. Kanický[1]**

*1) Department of Chemistry, Masaryk University, Faculty of Science, Kamenice 5, 625 00 Brno, Czech Republic,*
*2) Department of Geological Sciences, Masaryk University, Kotlářská 2, 611 37, Brno, Czech Republic*
*3) Czech Geological Survey, Klárov 3, 118 21, Prague 1, Czech Republic*
*4) Center for Life Nano- and Neuro-Science, Istituto Italiano di Tecnologia, Viale Regina Elena 291, 00161, Rome, Italy*
*5) Research Group of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals of the ASCR, Rozvojová 135, 165 00 Prague, Czech Republic*

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Laser ablation for ICP-MS (Inductively Coupled Plasma Mass Spectrometry) analysis operates on the principle of laser pulse interaction with the sample surface, removing material which is then transported by a carrier gas to the ICP-MS device. While this method is routinely employed across various fields, the success of the analysis is not always guaranteed. The appropriate approach to sample analysis must be tailored to the specific analytical requirements, as both the laser ablation conditions, and the sample properties affect the extent and nature of laser-sample interaction and material transport to the ICP-MS. Numerous variables can be adjusted, including optimization of laser parameters, choice of ablation cell, flow rate and type of carrier gas, and sample surface treatment, etc.

Ensuring controlled sampling by laser ablation into the ICP mass spectrometer is crucial for achieving high-quality analytical results. Given that the laser beam is focused on a very small area (tens to thousands of square micrometres) and the sample is placed in a closed chamber, monitoring the quality of laser ablation using conventional laser system equipment is challenging. A microscope camera facilitates the basic assessment of the ablation process, capable of detecting undesirable phenomena like breakage, cracking, or crumbling of the sample, or conversely, resistance to the laser beam. For a detailed diagnosis of the sampling process, additional procedures must be employed, typically involving ablation crater characterization, characterization of the generated aerosol and processing of the time-resolved ICP-MS signal.

Each LA-ICP-MS instrumentation presents its own set of limitations, whether related to the laser system (such as scan speed and movement accuracy, repetition rate, wavelength, pulse length, etc.) or the ICP-MS (such as acquisition speed, accuracy, sensitivity, etc.).

However, the LA-ICP-MS method is constantly evolving and pushing its limits. The adoption of lasers with shorter pulses aims to mitigate fractionation issues, new calibration standards are being developed, and result processing is being refined to account for factors such as fractionation, varying sample ablation rates, and inhomogeneities. These advancements are propelling the method towards faster analyses, enhanced spatial resolution, lower detection limits, and broader applicability. Increasingly, the method is not only utilized for trace element analysis but also for precise determination of isotopic ratios, or for instance, the analysis of soft tissues and protein samples.

# ICP mass spectrometry approaches to the analysis of environmental nanopollutants

**J. Szpunar and J. Jimenez-Lamana**

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Nanopollutants are nanoparticles that have been released into the environment. The term encompasses accidentally released engineered nanoparticles as well as those (e.g., nanoplastics) resulting from the degradation of larger objects. Many of these particles have only recently been developed or described, leading to ongoing research to understand their origins, destinations, and the potential risks they pose to both human health and the environment [1]. The investigation of sources and fate of these emerging contaminants, as well as their effect on living organisms, requires the developments of analytical techniques suitable for their detection and analysis.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in the single particle mode (SP-ICP-MS) has been established as a method to study environmental contamination with metal-containing engineered nanoparticles [2]. It can be complemented by LA-ICP-MS imaging, and further insight into the processes occurring in their environmental cycling can be obtained by molecular MS to study products of their possible dissolution.

In tracking environmental pollution with nanoplastics, the choice of analytical techniques is hampered not only by their small size but also by their chemical composition, which is roughly identical to that of the organic matrix of many samples. Additionally, the expected number concentrations of nanoplastics in environmental samples are very low. In this context, SP-ICP-MS, which offers exceptional detection capabilities, has been investigated as a possible candidate for the analysis of nanoplastics. Different strategies, including monitoring of natural plastic particles as well as the use of metal tags, have been proposed.

The lecture will present an overview of ICP MS approaches for studies of environmental nanopollutants developed in the authors' laboratory, in a broader context of the related research carried out worldwide.

References:
[1] J. Szpunar, J. Jimenez-Lamana (eds), Environmental nanopollutants, RSC, Cambridge, 2022 (512 pp)
[2] F. Laborda, I. Abad-Álvaro, M.S. Jiménez, E. Bolea, Spectrochim. Acta B, 2023,199, 106570

## Towards a better understanding of indoor air pollution

**V.G. Mihucz**

*Institute of Chemistry, ELTE Eötvös Loránd University, H-1117, Budapest, Pázmány Péter sétány 1/A, Hungary*

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Recognition of the significance of exposure to pollution indoors has considerably grown in the last decades. In recent years, buildings have become more airtight to reduce energy loss and $CO_2$ emissions to combat climate change impacts. As energy efficiency measures are implemented, ventilation rates have been reduced in buildings. Therefore, a higher exposure to indoor air pollutants is expected in the future. Recently, the COVID-19 pandemic has also contributed to the acknowledgement of the importance of good indoor air quality (IAQ). However, compared to studies on air quality outdoors, IAQ is still underrated. A new framework for IAQ has been proposed in the frame of the INDAIRPOLLNET COST Action project (https://indairpollnet.york.ac.uk/resources). This framework has been applied for monitoring IAQ in vegan and vegetarian restaurants. Although emission of common pollutants such as fine particulate matter, polycyclic aromatic hydrocarbons, volatile organic compounds as well as aldehydes and ketones arising from vegan and vegetarian cooking has been demonstrated to be lower compared to emissions originating from cooking meat-based dishes, a good IAQ is also always subject to existence and proper operation of mechanical ventilation and adequate use of high-quality ingredients. Drawing adequate conclusions are also hampered by the lack of clear guideline values for indoor air pollutants for residential and commercial kitchens. Definition of such guidelines will gain more importance soon if we consider the challenges posed by the rapid urbanization. Attempt to define guideline values for air pollution in kitchens has also been made and will be presented during the lecture.

# Monitoring chemical processes in materials science – novel approaches for in situ measurements of elements and isotopes

**T. Prohaska**[1], **S. Wagner**[1], **G. Mukhametzianova**[1], **K. Thiele**[2], **S. Michelic**[2], **J. Irrgeher**[1]

*1) Department of General, Analytical and Physical Chemistry, Montanuniversität Leoben, Franz-Josef-Straße 24, 8700 Leoben, Austria*
*2) Department of Metallurgy, Montanuniversität Leoben, Franz-Josef-Straße 24, 8700 Leoben, Austria*

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Materials science has posed a challenge to analytical chemistry ever since. The variety of matrices and the physicochemical properties under investigation, as well as the demand for 2D and 3D information from bulk information to atomic resolution require a manifold of techniques coping with aspects required by industries: fast, accurate, cheap, and all information at once by keeping the highest level of analytical quality based on profound metrological concepts. Novel methods have been developed constantly to trace element fluxes or to monitor reactive processes on surfaces.

A novel approach to trace sources and sinks of element fluxes in technological processes is the application of enriched stable isotopes. [1] The addition of an enriched stable isotope does not alter the chemical property but leads to significant changes in the natural isotopic composition. Even smallest amounts of spikes can be monitored by applying isotope pattern deconvolution making an application of enriched spikes possible even at large scaled processes such as in steelmaking. In one selected example, sources of Mg within non-metallic inclusions in steel have been traced by enriched stable Mg isotopes.

A novel method to visualize and quantify chemical processes at reactive surfaces directly is based on multi-elemental mapping using passive, non-destructive Diffusive Gradients in Thin films (DGT) sampling in combination with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). [2, 3] The challenge of quantification was overcome by using matrix-matched DGT calibration standards with known analyte mass loadings. The method was applied to technologically important materials (Mg and Al) to better understand corrosion processes and improve material characteristics. In the selected examples, the localisation of analyte solute fluxes revealed the potential for multi-elemental mapping down to sub-picogram levels. The quantitative evaluation of the DGT flux provided quantitative information about the spatio-temporal reaction dynamics of corrosion processes.

References

[1] K. Thiele et al., Tracing sources of non-metallic inclusions by using enriched Mg spikes, 2024, in preparation

[2] S. Wagner et al., In situ spatiotemporal solute imaging of metal corrosion on the example of magnesium. Analytica Chimica Acta, vol. 1212, p. 339910-339919, 2022, DOI: 10.1016/j.aca.2022.339910.

[3] G. Mukhametzianova et al., Mapping elemental solutes at sub-picogram levels during aqueous corrosion of Al alloys using diffusive gradients in thin films (DGT) with LA-ICP-MS. Analytical and Bioanalytical Chemistry, 2024, DOI: 10.1007/s00216-024-05288-8

# Potential risk from the decommissioning of oil and gas infrastructure to the marine environment: a multimethod study

**L. Paton**[1], **T. Lindsay**[1,2], T. Thaíse Moro[1,3], **R. Gonzalez de Vega**[1], **D. Clases**[4], T. de Andrade Maranhão[3], **C. Doolette**[5], **E. Lombi**[5], **J. Feldmann**[1,2]

*1) TESLA – Analytical Chemistry, Institute of Chemistry, University of Graz, Universitätsplatz 1, 8044 Graz, Austria,*
*2) School of Natural and Computing Sciences, University of Aberdeen, Aberdeen AB24 3UE, Scotland, UK*
*3) Department of Chemistry, Universidade Federal de Santa Catarina, Florianopolis, SC Brazil*
*4) NanoMicroLab, Institute of Chemistry, University of Graz, Universitätsplatz 1, 8044 Graz, Austria*
*5) Institute for Future Industries, University of South Austria, Australia*

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Here in this lecture we explain the use of multiple analytical techniques when applied to biological and steel samples: the techniques used for elemental mapping, single particle ICPMS, and total element analysis: Micro-XANES, synchrotron-XRF mapping, RAMAN, LA-ICPMS, CV-AFS, HPLC-ICPMS, spICP-TOFMS, AF4-MALS-ICP-TOFMS.

We will show results Mercury in the marine environment is characterised by its ability to biomagnification in the food chain. We will demonstrate that whales accumulate in their organs high concentrations of mercury in a form of nanoparticles in which mercury is mainly bound to selenium[1]. It will be discussed if this is a detoxification mechanism, which might have a higher limit of mercury intake.

A threat that the mercury is increasing comes from the off-shore oil and gas industry. It will be shown that the corroded pipelines accumulate up to g levels of mercury per $m^2$.[2] The pipelines need to be decommissioned and there is a risk that they will remain on the seafloor. The solubility and bioavailability of mercury in the carbon steel depends strongly on their speciation. We will demonstrate that mercury will not only occur as elemental mercury, but also as Hg nanopartciles and Hg-Cu amalagam. The majority of these compounds have the potential to be introduced into the marine food chain and potentially threatens the health of the whales.

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# The unlimited power of combined spICP-MS with AF4-ICP-MS/Light scattering: Providing new insights into the fractionation of engineered nanomaterials in consumer products

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In recent years, metrological advances for inorganic engineered nanomaterials (NM) have been mainly driven by industrial needs to produce more effective and safer products as well as comply with emerging regulation. For example, many Notified Bodies (e.g. FDA, MHRA, EMA) require full biocompatibility test data for medical devices in compliance with ISO 10993 if (*i*) such new device products incorporate or produce nano-objects (1-100 nm) that can be released and, (*ii*) where over 50% of the material may be released as nanoparticles (NPs), rods and plates from any surface of the device in contact with the body. From a food perspective, although nanomaterials (NM) as food additives offer a potential new food technology they require authorization under the requirements of the Novel Foods Regulation 2015/2283, and their presence in food must be indicated on the label (EC Regulation 1169/2011). European legislation is underpinned by the Recommendation 2022/C 229/01 for the definition of NM, which describes the need for reliable identification of NM and determination of a percent content of nanoscale particles within a consumer product or an additive.

Improved metrological traceability of measurement methods and reference materials are required to characterise industrial products and help industry to comply with regulatory requirements. To this end, hyphenated platforms combining spICP-MS with AF4-ICP-MS/Light scattering have been demonstrated to be powerful for the detection and reliable quantification of mass and number concentration of inorganic NM in complex samples. However, remaining challenges include the accurate determination of mass and number concentration of NM with size in the few nm range combined with the high complexity of the matrix as commonly found in ‘real life’ applications.

This lecture will discuss how some of those challenges have been overcome through (*i*) development and application of a platform based on Single particle ICP-MS (spICP-MS), supported by asymmetrical flow field-flow fractionation (AF4) coupled on-line to ICP-MS and multi-angle light scattering (MALS) to the identification and number-based quantification of $TiO_2$ particles with sizes down to 15 nm, in the raw ingredient $TiO_2$ (E171) as well as in a range of food products [1] and (*ii*) development and validation of characterisation methods for mixtures of AgNPs leached from medical devices [2]. The importance of reference methods and materials that can help validate new and improved methods and/or can be directly implemented/used by industry will be highlighted. Finally, the relevance of international inter-laboratory comparisons for institutes to demonstrate competency and feasibility of existing methods will be discussed.

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# Infrared, Far-Infrared, and Raman Spectroscopy Studies of Minerals, Rocks, and Biogenic Minerals

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Attenuated total reflection infrared (ATR-IR), ATR-far-IR (ATR-FIR), and Raman spectroscopy were used to investigate polymorphism of minerals and biogenic minerals, differences in the crystal structure among aragonite and aragonite biogenic minerals, and water in the minerals and biogenic minerals [1]. The three kinds of vibrational spectra were measured for calcium carbonate, three kinds of minerals (calcite, aragonite, and quartz), two kinds of rocks (obsidian and pumice), and four kinds of biogenic minerals, i.e., coral (aragonite), Ruditapes philippinarum (aragonite), Meretrix lusoria (aragonite), and Corbicula japonica (aragonite). In this study, some emphasis was put on the low-frequency region of IR (FIR) and Raman spectra. The FT-IR/FIR instrument we used (FT/IR-6700FV, Jasco) covers from 6000 to 20 $cm^{-1}$ as a single scan [2]. The ATR-FIR spectra were obtained down to 50 $cm^{-1}$ and the Raman spectra were measured down to 10 $cm^{-1}$. Second derivative spectra were calculated for the FIR spectra to elucidate the small differences in the lattice vibrations of minerals and biogenic minerals. The present study revealed that the FIR spectra are the most powerful for exploring polymorphism and differences in the crystal structure among aragonite and aragonite biogenic minerals. A Boson peak, which is a characteristic low-frequency Raman band for amorphous materials, was observed at around 40 $cm^{-1}$ in the Raman spectra of obsidian and pumice. The present study has revealed that IR spectra are useful to investigate the amounts and structure of fluid and bound water. Moreover, it has also been found that Raman spectra can detect a very tiny amount of carotenoids in the shells due to the resonance Raman effect.

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# Current Status and Challenges in Sample Preparation for Atomic Spectrometry

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With few exceptions, most of equipment used in atomic spectrometry require a previous step for sample digestion that is generally necessary for a convenient analysis. Classical methods for sample digestion and further determination by atomic spectrometry involve the use of a relatively high volume of concentrated reagents (inorganic acids in case of further metals determination) and a relatively long time for digestion. Moreover, the digestion efficiency of these systems presents some limitations for many matrices. In this sense, even using methods based on microwave-assisted closed vessels some drawbacks can be present for some matrices and incompleteness of digestion is frequently reported. Nowadays, there is a trend for the development of methods requiring lower reagent consumption, less analytical steps and lower waste generation combined with high efficiency of digestion. In addition, it is important that digests are suitable for the determination techniques avoiding excessive dilution or high blank levels. On this aspect, some trends for sample preparation will be presented in this lecture for further metals and also non-metals determination. The use of diluted solutions using oxygen pressurized systems with or without UV radiation, use of combustion systems, etc, will be covered. Recent applications will be presented showing the advantages of methods using diluted reagents for metals and non-metals determination using ICP-MS and ICP-OES.

# Exploring the potential of hydride generation atomic fluorescence spectrometry for ultratrace elemental analysis

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The non-dispersive arrangement of atomic fluorescence spectrometry (AFS) is very simple and sensitive. It can provide extremely low limits of detection (LOD) and is cheap both in investment and in operation costs. The fundamental drawback of AFS is that it is affected by scattering and quenching problems, which are not easy to control. The potential of AFS to reach very low LODs can be fully achieved when using very mild atomization conditions which are compatible with the atomization of volatile species. This is the reason why AFS is currently associated prevalently with hydride generation (HG).

Our long-term ambition is the development of HG AFS for ultratrace element determination. To approach this target, we have been optimizing individual components of our laboratory- made non-dispersive atomic fluorescence spectrometer. The history of our investigations of the two essential components of a non-dispersive atomic fluorescence spectrometer, hydride atomizers and atomic lamps, will be outlined.

The miniature diffusion flame (MDF) is a standard hydride atomizer for AFS. We extensively studied advantages and limitations of this atomizer. The results motivated us to develop a new atomizer - flame-in-gas shield (FIGS) which is basically an argon shielded oxygen-hydrogen microflame. Compared with MDF, it is more complicated in construction as well as in operation but it offers better sensitivity and LOD and much greater potential for miniaturization. Employing spatially resolved laser induce fluorescence, we determined distributions of temperature, hydrogen radicals and free analyte atoms in both atomizers. This made us possible to discover the mechanism of hydride atomization in MDF as well as in FIGS.

Regarding atomic lamps, mainly two their types have been used: electrodeless discharge lamp (EDL) or boosted-discharge hollow cathode lamp. EDLs are said to provide higher radiation intensities, however, the range of elements for which the EDLs are manufactured is limited to certain volatile elements. Boosted-discharge hollow cathode lamps are widely applied in the current commercial AFS instruments whereas EDLs are usually used in experimental laboratory setups of AFS. The relevant lamp settings are namely: atomic lamp input power/current and its modulation pattern. In principle, the intensity of the fluorescence radiation is proportional to the radiation source intensity. Consequently, higher sensitivity and lower LOD can be reached simply by increasing the intensity of the radiation source. Our latest research on atomic lamps focusing on the absolute intensity of the lamp radiation will be presented. The positive impact of optimizations of the relevant lamp settings will also be illustrated. The potential of further development of HG AFS in terms of pushing down LODs of hydride forming elements will be outlined.

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# Atomic versus molecular mass spectrometry in speciation analysis

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Understanding that the reactivity of trace elements in biology depends on their chemical species has spurred interest in analytical methods targeting specifically the chemical forms of essential and toxic metals and metalloids. While earlier approaches focused on isolating a single metal-containing compound in sufficient amounts for NMR analysis, advancements in analytical techniques have dramatically increased the number of metal species detected and led to the emergence of a field of analytical chemistry known as speciation analysis. [1].

Element-specific plasma source detection in chromatography enabled the online detection of sub-picogram quantities of trace elements and shifted the focus from NMR molecule detection to detecting the metals within them. Molecular selectivity was achieved through high-resolution chromatography, which provided species specificity for anthropic contaminants or metallodrug metabolites but fell short for endogenous compounds.

Electrospray ionization and advances in high-resolution, high-mass-accuracy (HRAM) mass spectrometry (MS) transformed speciation analysis. Instead of detecting atoms, it became possible to target entire molecules based on accurate mass. This shifted the challenge from peak capacity in chromatography to peak capacity in a mass spectrum, focusing on molecular signatures like fine isotopic structure.

Recent developments in FT ICR and Orbitrap MS enable separate detection of two ions differing by a mass of one electron (0.5 mDa) and the measurement of their masses with sub-ppm accuracy. These advancements make possible comprehensive detection of element species in biological sample extracts.

The lecture discusses the recent advances in speciation analysis focusing on the analysis of large populations of chemical species of one or several elements at the same time and their correlation with the biological role (metallomics). A novel high-throughput approach to quantification of element species based on isotope dilution electrospray HRAM will be presented.

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# Advances in single event-ICP-MS

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Over the last decade, the potential of ICP-MS for the analysis of individual entities, such as nanoparticles (NPs), cells, or nano/microplastics, has been well documented.[1] Nevertheless, matrix effects still limit the application of single particle-ICP-MS to complex samples for which its use could be more beneficial. Several novel approaches for overcoming such matrix effects are discussed in this work. One such strategy is based on the application of the standard addition method in such a way that the calibration of the particle size is performed by two different methods: (i) by spiking a suspension of NPs standards of known size containing the analyte, or (ii) by spiking the sample with ionic standards; the measured sensitivity is finally used in combination with the transport efficiency (TE) for sizing the NPs. Moreover, such TE can also be obtained from this data set so that the particle number concentration can also be determined.[2]

Applying isotope dilution approaches is another possibility for elements with more than one nuclide. The importance of different factors in achieving the best possible precision and accuracy when using ICP-TOF-MS will be discussed in the context of AgNP characterization.[3] Finally, another approach makes use of the mass spectrometer (quadrupole) operating in bandpass mode, enhancing the sensitivity for the monitoring of NPs while also allowing for the detection of NPs of a different type in the same measurement run, such that they can serve as an internal standard.[4] Different examples of the abovementioned approaches for the characterization of NPs in complex matrixes will be discussed.

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# Multimodal platform towards non-target speciomics: from known to new molecules.

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Speciomics is a terminology adapted from biological area [1], and comprehends the study/evaluation of chemical species applied to omics studies, while the speciome is coined due to the synergism of both chemical speciation and omics, being defined as the entirety of the chemical species evaluated through omics strategies. Then, in simple words, this concept can be presented as the "umbrella" containing all omics approaches (i.e. metabolomics, proteomics, metallomics, genomics) devoted to speciation analysis [2]. In this sense, to exemplify this concept, we are presenting a study with a biotechnological material (soybean callus), which was added or not nanoparticles for preservation, and a marine animal (Turtle). Therefore, from a speciomics point-of-view, we are examining possible molecules present in such samples, and discovering new ones. From this multimodal platform some species containing As, Ca, Fe, Mg, Zn, lipids, and metabolites containing P were already identified, using a negative or positive mode of ionization, as well as a new molecule was discovered (Methyl-(Trimethylarseniumyl)acetate). This multimodal strategy opens up new opportunities for precise non-target speciomics of selected elements through a multi-specific evaluation.

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# Overcoming sample preparation challenges for halogen determination by mass spectrometry techniques

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The determination of non-metals, particularly halogens, provides crucial insights into their influence in various fields such as nutrition, health, and toxicology. Despite advancements in instrumentation, sample introduction typically involves converting samples into a solution. Traditional sample digestion methods, which often employ large volumes of concentrated reagents, are time-consuming and may necessitate dilution of digests prior to analyte determination, potentially compromising detection limits. Even with microwave-assisted closed vessel methods, issues such as incomplete digestion are common. Additionally, regarding halogen determination, they can also be lost in their unstable volatile compounds in an acid medium. There is a growing trend towards developing green analytical methods that minimize reagent use, reduce waste, streamline analytical steps, and achieve high-efficiency digestion. Ensuring the suitability of digests for subsequent determination techniques is equally critical. This lecture will present the latest advancements in sample preparation for food and biological matrices aimed at halogen determination using inductively coupled plasma mass spectrometry and ion chromatography with mass spectrometry detection. Topics will include the use of diluted solutions, combustion systems, and recent technological developments in this field.

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## Graphite and Carbon: Once Panacea, Redundant Today?

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Graphite and other carbon components revolutionized ultra trace analysis 50 years ago. Electrothermal atomization seemed to solve the challenging questions of analytical chemists. Sample digestion benefitted from the stability and chemical inertness of glassy carbon. Soon research electrothermal AAS made graphite and other carbon material to one of the most investigated fields with respect to chemical reactions, long term stability and dynamic temperature behaviour. Conferences were run focused merely on this very technique and ESAS started this way as a "Furnace Symposium". Absolute analysis was proclaimed. Electrothermal AAS indeed became an ultra- sensitive, reliable, and most extensive interference-free analytical method in the late eighties of the last century.

With the improvement of plasma OES and plasma MS the latter techniques inherited the typical ETA-AAS determinations in more and more laboratories. Research in the field of electrothermal atomization and volatilization declined to almost nil. Today ETA AAS seems to fade away into insignificance.

This contribution will highlight the important steps of achievements on the scientific road of the graphite furnace. Trends and methods will be illuminated with respect to benefit and meander. These trends did accompany the history of ESAS as well. We will show how, on the other hand, monetary aspects stopped promising developments and "killed" excellent products. There are still application areas where the technique is unique. This may be a stimulus not to completely forget this methodically sound technology.

# Unconventional quantification methods in microwave plasma - atomic emission spectrometry (MP-AES)

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MP-AES is an Agilent product launched in 2011 as an affordable alternative for ICP-AES and FAAS techniques. The most important MP-AES features include: (i) the use of a nitrogen generator and nitrogen plasma substantially reduces the operating cost of the instrument; (ii) the stable and robust plasma enables an ICP-like introduction system and tolerates up to 4% of TDS; (iii) atomic lines prevail, which simplifies the emission spectra compared to ICP. On the other hand, the temperature of microwave plasma is around 5000K so the excitation efficiency is lower and the risk of both chemical and spectral interferences increases relative to ICP. Therefore, MP-AES is suitable for the determination of major and trace elements, it is recommended to eliminate potential interferents through sample pretreatment and efficient baseline correction is necessary. In this talk, some examples of reliable quantification achieved in chemically complex samples will be presented. First, the application of Te(IV) as an internal standard for the determination of tAs in maize tortilla by hydride generation - MP-AES will be discussed. The IS was added directly to the sample, thus compensating for non-rigorous volume measurement/adjustment during sample preparation, as well as for imprecisions associated with sample introduction and signal fluctuations during instrumental measurements [1]. Next, the application of standard dilution and multi-energy calibration for the determination of selected metals in wine and in human urine will be presented [2,3]; in these works, diluted samples were introduced to MP-AES and baseline correction was not performed. In the third example, the feasibility of HG-MP-AES system and partial least square (PLS1) regression for Sb determination in PET and water samples will be shown [4]. Alkaline methanolysis was proposed for Sb release from PET at relatively mild conditions (60°C, 24 h); the samples were cleaned-up by elimination of partly depolymerized PET and by extraction of nonpolar products from acidified water-methanol solution to chloroform. In calibration, Sb-free PET was used for matrix-matching. When constructing PLS1 model, the 2nm spectral range near the intense emission line was used, ensuring good prediction quality without the need for baseline correction.

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# ORAL PRESENTATIONS

# Use of imaging and counting techniques for the identification and analysis of metal particles in unused legal and illegal cannabis vaping products

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Research on characterizing metal contaminants in cannabis vaping products is notably sparse. Current regulations mandate testing cannabis vapes solely for arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb). Previous studies concerning nicotine vape products have demonstrated potential contamination from metal components within the vaping devices.

Our investigation delved into the metal composition of 12 metals/metalloids present in both legal and illicit Canadian cannabis products. Alarmingly, cobalt, chromium, copper, nickel, lead, and vanadium concentrations in numerous products surpassed commonly accepted tolerance thresholds, exceeding limits by over 100-fold in certain instances. Particularly concerning were the elevated levels of lead, reaching milligrams per kilogram (mg/kg) in five illicit samples, alongside substantial nickel (up to 677 mg/kg), zinc (up to 426 mg/kg), and copper (up to 485 mg/kg) concentrations. Furthermore, significant variations in metal concentrations were observed among replicate subsamples, prompting further investigation into this variability.

Employing scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), we corroborated the presence of metal particles in the analyzed samples. Additionally, we optimized the single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) technique for organic mode analysis to better elucidate the composition and abundance of metal particles in cannabis vape products. Our findings, including encountered challenges such as matrix interferences, particle sedimentation, and selection of appropriate software for data treatment, will be discussed.

# Revealing the composition of coralline algae skeleton with LA-ICP-ToF-MS imaging

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is now a well-established elemental imaging technique that combines the advantages of laser microsampling with ICP-MS features. The capabilities of this technique can be expanded if LA systems are coupled with time-of-flight (ToF)-based mass spectrometers instead of more common, sequentially operating quadrupole (Q) mass analysers.

Modern ICP-ToF-MS instruments enable rapid full elemental mass spectra acquisition (at rates > 35 kHz) and continuous saving of binned mass spectra at rates exceeding 10 kHz, which promotes the fast imaging of elemental distributions in various samples.[1] This can be especially beneficial in analysing new specimens whose composition is unknown.

In our work, LA-ICP-ToF-MS imaging revealed elements which have not been described in the literature yet in the calcareous skeleton of coralline algae. The analysed samples were collected from the seas surrounding the Spitsbergen and obtained in cooperation with the Institute of Oceanology of the Polish Academy of Sciences.

Moreover, during the studies, the problematic aspect of calibration in LA-ICP-MS has occurred, which will be discussed during the presentation.

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# Tools for determination of specific proteins by LA-ICP-MS

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The determination of specific proteins is the key to understanding the processes in the organism or the development of diseases. Unfortunately, the determination of heteroatoms as are P, S, Fe, Cu, and Zn is insufficient for this purpose. Hence, the biorecognition tools for their determination by LA-ICP-MS are being developed. We describe labeling the antibodies by gold nanoparticles (AuNPs) with detection by LA-ICP-MS. As the target protein, p53 was chosen due to the high specificity of its appropriate antibody (i.e., DO-1). Nonspecific interactions with the sample matrix – was investigated and optimized using dot blot and Western blot assays. Finally, imaging of tissue sections was carried out.

# Determination of SP LA ICP MS transport efficiency using photon upconverting nanoparticles

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Inductively Coupled Plasma Mass Spectrometry (ICP MS) plays a pivotal role in elemental composition analysis across various disciplines, including analysis of nanomaterials. The accurate determination of transport efficiency (TE) is crucial for enhancing sensitivity in ICP-MS, enabling the precise determination of nanoparticle size and particle number concentration during single-particle (SP) experiments. Existing methods for TE determination, particularly in laser ablation ICP MS (LA ICP MS), face challenges due to the complex processes of aerosol generation and transport. Even so, a few methods for determining TE have been published, such as our previously published indirect method using gold nanoparticles and scanning electron microscopy as a reference method.[1]

In this context, we present a method for direct TE determination primarily applicable to SP soft tissue analysis. Our approach involves the immobilization of upconversion nanoparticles (UCNPs) in agarose gels, followed by upconversion fluorescence microscopy (UCM) analysis serving as a reliable reference for characterizing the number of nanoparticles immobilized within the gel.[2] Subsequent LA ICP MS analysis using the same sample for both SP LA ICP MS and UCM overcomes some limitations of conventional methods, leading to more accurate results. This includes addressing errors during sample preparation and potential issues caused by the aging of the nanoparticle suspension, such as the unknown degree of nanoparticle aggregation.

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# Elemental analysis of environmental and food samples by means microwave-sustained inductively coupled atmospheric-pressure plasma optical emission spectrometry: matrix effects and calibration strategies

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New instrumental developments have dramatically improved current analytical figures of merit of microwave-induced plasma optical emission spectrometry (MIP-OES) being on a par with those afforded by inductively coupled plasma optical emission spectrometry (ICP-OES) but with lower operational costs due to the use of nitrogen as the plasma gas instead of argon [1]. Among the emerging MIPs cavity designs, the microwave-sustained inductively coupled atmospheric-pressure plasma (MICAP) is noteworthy due to it is capable to maintain an annular plasma, similar to ICPs, using a dielectric resonator ring and a 2.45 GHz microwave field [2]. Previous studies have shown that MICAP-OES exhibits detection capabilities similar to ICP-OES, but the benefits and drawbacks of this system for real sample analysis have not yet been assessed, particularly matrix effects and calibration strategies. The goal of this work is to evaluate MICAP-OES capabilities for elemental analysis of complex samples of environmental and food origin. To this end, spectral and non-spectral interferences were evaluated for 19 elements (Ag, Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, Mg, Mn, Ni, Pb, Sr, Tl, Zn) in the presence of: (i) acid solutions (sulfuric and hydrochloric acid); (ii) organic solutions (glycerol, acetic acid and ethanol); and (iii) saline solutions (sodium chloride and calcium chloride), since they are usually employed in sample preparation or can be naturally present in the sample. Next, the selection of plasma experimental conditions and calibration strategies were examined. Finally, the developed procedure was validated by analysing different certified reference materials (BCR-146 sewage sludge industrial, BCR-483 Sewage sludge amended soil, BCR-185 bovine liver, BCR-278R mussel tissue, CRM-DW1 drinking water, NIST-1549 non-fat milk powder, and TITRIVIN BTA wine). Experimental data shown that, unlike previous MIPs, the optimum nebulizer gas flow rate for a given wavelength is unaffected by sample concomitants. In general, MICAP-OES exhibited high robustness operating inorganic acids and organic matrices, and it demonstrated lower susceptibility to changes in the excitation and ionization mechanisms in the presence of easily ionizable elements compared to other cavities previously described in the literature. On the other hand, because the MICAP is equipped with a simultaneous spectrometer, internal standardization could be easily employed to correct matrix effects and improve both sample throughput and instrument long-term performance. Consequently, elemental analysis of complex environmental and food samples could be accurately performed.

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# Investigating Trace Element and Radioisotope Migration in Solid Waste from Sewage Sludge Incineration

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Thermal treatment of sewage sludge is becoming more and more popular around the world. The study focuses on disposed fluidized beds (FB), sewage sludge ash (SSA), and air pollution control residues (APC) obtained from three Polish facilities engaged in the thermal treatment of sewage sludge. For the first time, natural radioactive isotopes were analysed in these materials, alongside the migration patterns of various trace elements across different waste fractions generated during sewage sludge combustion. In the research, so-called heavy metal fractionation analysis was performed, using modified BCR sequential extraction techniques. Additionally, the activity of the anthropogenic isotope $^{137}$Cs was examined. Results indicate a significant accumulation of both radioisotopes and trace elements in SSA and FB, contrasting with lower concentrations in the APC fraction. However, volatile compounds of mercury and selenium migrate to the exhaust gas dedusting system, accumulating in the APC fraction. Notably, potential concerns arise regarding the presence of the $^{226}$Ra isotope in SSA, surpassing typical activities found in standard building materials. Management of SSA and FB warrants careful consideration, particularly concerning metalloids such as arsenic, boron, and selenium, due to their high mobility within these materials, as confirmed by our findings.

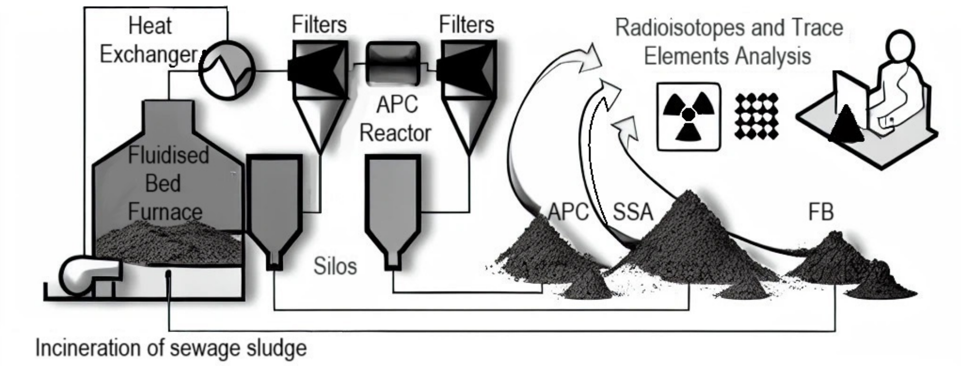

Figure 1. Sewage sludge thermal treatment installation with solid waste streams presentation. APC - Air Purification Control residues; SSA- Sewage Sludge Ash; FB- Disposed Fluidised Bed.

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# Terpenoic acid oxidation by hydroxyl radical in the aqueous phase: kinetics and product study

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**Secondary Organic Aerosols** (SOA) are formed in the atmosphere from organic precursors, which are continuously released in huge quantities on an everyday basis. These processes are driven by both human (e.g., car emissions) and biogenic activities (e.g., plant emissions). The ambient particles undergo **chemical changes,** which have a proven impact on **human health** and the earth's climate. In recent years, the atmospheric aqueous phase has been recognized as an important reaction media for the processing of water-soluble organic compounds. The currently poorly characterized **monoterpenes aqueous-phase processes are becoming an emerging topic** of interest in the field of atmospheric chemistry.

In the presented studies, we focused on reactions of **important SOA aging markers with hydroxyl radicals (OH) in the aqueous phase** by simulating reactions at pH=2, pH = 4 and pH=10 for temperatures ranginge from 288 K to 308 K. Additionally, **quantitative analysis** of reaction products was performed using high-performance liquid chromatography coupled to the electrospray ionization time-of-flight mass spectrometry (HPLC-ESI(-)-ToF-MS).

Our results show that in the reaction of pinonic acid + OH, four main products are formed i.e. pinic acid, norpinonic acid, norpinic acid and terepenylic acid with mass fractions 16.8 %, 11.9%, 10.7% and 18.5%, respectively. (Figure 1)

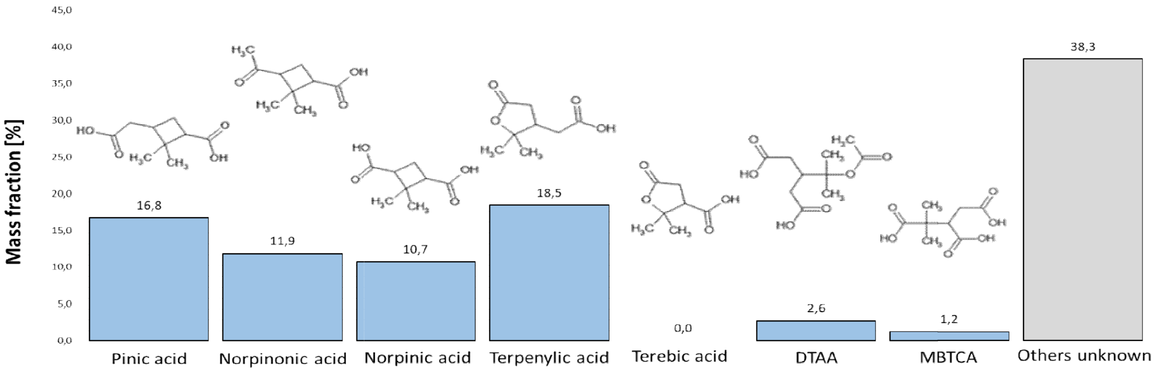

Figure 1. Products of oxidation of Pinonic acid reaction with OH radicals (pH = 2, T = 293K, $t_{reaction}$= 2h)

Surprisingly, we did not detect terebic acid, which is known as an important marker of the precursor of pinonic acid (α-pinene), showing that the studied compound is not a direct compound leading to this particular product. Our research provides direct information on the aqSOA formation mechanism and mass fraction of detected products.

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# Study of bioaccessible forms of Mn and Cu in rosemary (*Rosmarinus officinalis* L.) by SEC-ICP-MS and LC-MS/MS methods

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It is known that the effect of chemical elements on the human body depends not only on the dose but mainly on the form in which the element occurs. Therefore, it is essential to learn about the speciation forms of metals found in food, which may positively affect the human body. In plants, elements may occur in the form of complexes with various bioligands (e.g. polyphenols, polysaccharides, proteins and amino acids). Such a rich matrix indicates that determining only the total content of chemical elements in plants is insufficient to assess their bioaccessibility [1,2]. Bioaccessibility can be understood as the amount of a substance released from the food matrix in the gastrointestinal tract that becomes available for absorption. This process includes the digestive transformation of food into material ready for assimilation or absorption/assimilation into intestinal epithelium cells and intestinal and hepatic metabolism [3]. Knowing the exact composition and forms of the elements in food allows us to determine which metal compounds are more bioaccessible to the human body.

For this reason, our research focused on finding bioaccessible forms of Mn and Cu from rosemary (*Rosmarinus officinalis L.*). We also checked if the form of rosemary (fresh, freeze-dried, dried and dietary supplement) may affect the bioaccessibility of these metals. The dynamic *in vitro* digestion model was used to simulate conditions typical for the human digestive system. The size exclusion chromatography hyphenated with inductively coupled plasma-mass spectrometry (SEC-ICP-MS) method allowed for separating Mn and Cu bioaccessible forms in the obtained plant extracts. It has been shown that manganese in rosemary occurs mainly in the form of compounds with low molecular weight. On the other hand, copper in all tested forms of rosemary occurs mainly in compounds with high molecular weight. Additionally, in the case of fresh and freeze-dried rosemary, Cu may also be bound to compounds with a lower molecular weight. The different intensities of Cu signals in fresh and freeze-dried rosemary may indicate that the freeze-drying process affected this element's bioaccessibility. However, no significant differences were observed in the case of manganese in fresh and freeze-dried rosemary. Additionally, the use of two-dimensional liquid chromatography, SEC x LC using MS/MS detection, enabled the determination of bioligands from the group of polyphenols that may be associated with manganese and copper in rosemary.

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# Seasonal changes of the chemical speciation of arsenic, antimony, germanium and tellurium in Czech freshwater reservoirs

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Despite considerable advances in modern analytical methods, obtaining reliable analytical data and detection limits that allow the study of the cycling of elements and their species in natural environments remain a considerable challenge for certain elements. Some mature techniques, such as hydride generation, updated with modern ultrasensitive detection can provide a solution to this need. Here we present a method for the simultaneous analysis of germanium, arsenic and antimony species by hydride generation (HG), cryotrapping (CT) and ICP-MS/MS detection. Tellurium speciation was determined separately by selective HG-ICP-MS/MS and total As and Sb concentrations were determined by solution nebulization ICP-MS/MS. Details of the methods and analytical challenges of analyses at (sub)ng/L concentration levels will be discussed.

Two Czech reservoirs of contrasting chemistry and hydrological regime used as drinking water sources were chosen as study sites to observe changes of the chemical speciation of As, Sb, Ge and Te throughout the year. Vrchlice in Central Bohemia, is a eutrophic lake, which becomes anoxic in summer, while the oligotrophic or mesotrophic Souš in the mountainous area of North Bohemia remains well oxygenated throughout the year. In both reservoirs, depth profile samples were taken at monthly intervals over the course of a year and fully characterized in terms of their physical and chemical properties.

The different species of each element follow very different patterns. Arsenic speciation is the most influenced by the biota in the water reservoirs, leading to a higher presence of $iAs^{III}$ and methylated As species in the productivity period, while the presence of these species declines in winter. Likewise, iGe shows a nutrient profile controlled by biogenic uptake: scavenging and partial regeneration from sediments. In contrast, methylated Ge and Sb species show quite a conservative behaviour throughout the year with near vertical depth profiles, and $iSb^{III}$ was not found in the samples. For the first time, systematic data on $Te^{IV/VI}$ speciation in freshwater profiles are available.

*Acknowledgements*

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# Advantages and disadvantages of different sample preparation methods for ferrosilicon magnesium alloy analysis using X-ray fluorescence spectrometry

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FSM is a type of ferro-alloy obtained from a combination of iron, silica and magnesium. The main use of this alloy is the processing of spherical graphite in the production of cast iron and thus increasing its strength. This alloy plays a key role in providing magnesium for smelting cast iron. It can be used as a deoxidizing and desulfurizing alloy additive for steel, as well as a coating for electric welding. Thus, the chemical composition of the FSM alloy is essential and it must be characterized by accurate and valid analytical results. Moreover, as the alloy production is a high scale pyrometallurgical process, it requires using fast instrumental analytical methods, and the X-ray fluorescence spectrometry (XRF) is a first choice method.  The paper presents different possibilities of the preparation of FSM alloy samples for the XRF analysis using the thin layer technique, borate beads fusion, pressed pellets and pellets with internal standard. The presentation include detailed description of each preparation procedure, development of different type of calibration standards, traceability assurance, accuracy and analytical results for selected samples in comparison with the values obtained using other independent analytical methods. The XRF methods were validated and used in development of new certified reference materials in realization of the SILREF project: "Development of reference materials for silicon industry - improvement of quality assurance", which was carried out at the Łukasiewicz-IMN Center for Analytical Chemistry in cooperation with the Norwegian company ELKEM and completed in April this year. As part of this project, new certified reference materials were developed for silicon, silica fume and ferrosilicon magnesium alloy (FSM).

The SILREF project is financed by the Norwegian Funds, operated by the National Center for Research and Development. The project benefits from a subsidy of €444,930.14 from Norway and €78,517.08 from the state budget. The aim of the project is to develop new certified reference materials for the silicon industry.
The issues presented in the paper are part of the scope of work carried out as part of the implementation doctorate: Research on the development of new certified reference materials for selected silicon industry products.

# Exploring 2-propanol and its fluorinated derivatives using femtosecond optical Kerr effect spectroscopy and theoretical chemistry methods

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2-Propanol (IP) is a commonly used organic solvent for cleaning optics and electronic contacts, in DNA extraction, and as a sanitizer (70% solution in water) due to its antiseptic properties. Fluorinated alcohols, such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), are frequently employed as co-solvents having a significant impact on the structural and dynamic properties of proteins and peptides in aqueous solutions. In contrary to IP and HFIP, the less studied 1,1,1-trifluoro-2-propanol (TFIP) is a chiral molecule and exhibits some peculiar behavior when mixed with water. While IP and HFIP mix with water at any ratio, TFIP shows phase separation for some concentrations, which was previously attributed to low affinity between $CH_3$ and $CF_3$ groups, hindering micelle-like assembly formation [1]. Here, we employ femtosecond optical Kerr effect spectroscopy combined with molecular dynamics simulations and quantum-mechanical calculations to investigate the vibrational, translational, and rotational dynamics as well as the local structure of IP, TFIP, and HFIP molecules. For TFIP we present results for pure enantiomer and a racemic mixture.

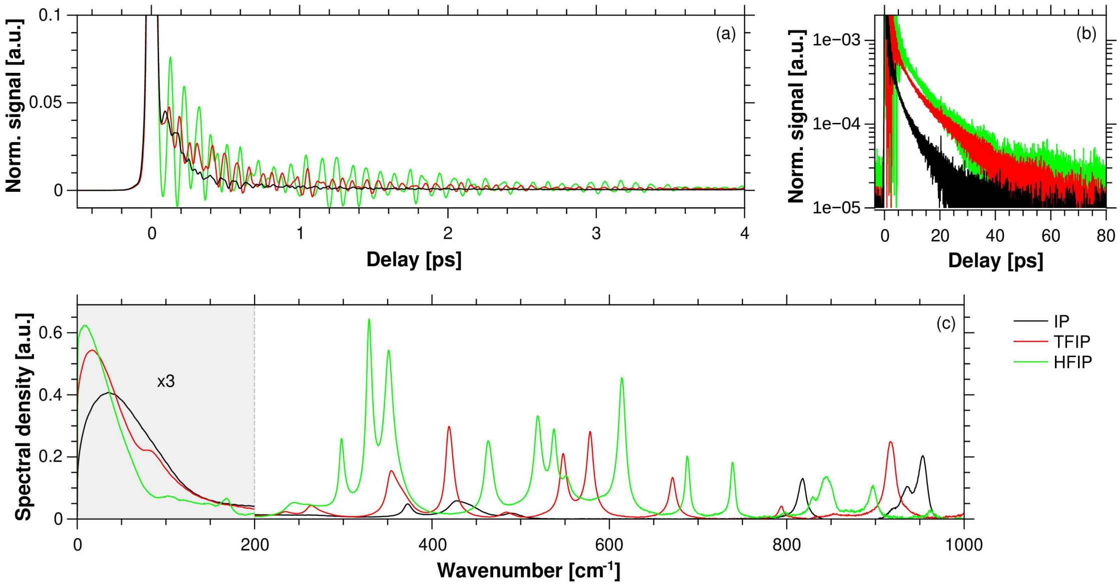

Figure 1. Femtosecond optical Kerr effect signal of IP, TFIP, and HFIP on short (a) and long (b) time-scale, together with the corresponding low-frequency spectrum (c). The part of the spectrum dominated by intermolecular dynamics (below 200 $cm^{-1}$) is enlarged.

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# Standardization of microwave-assisted extraction procedures for characterizing metallic nanoparticles by means single particle ICP-MS.

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Nanomaterials (NMs) present in solid sample are usually characterized by means single particle inductively coupled plasma mass spectrometry (spICP-MS) after an extraction treatment. To this end, different sample preparation strategies (e.g., liquid extraction at ambient temperature, ultrasound-assisted extraction, etc.) have been proposed in the literature but they do not always provide accurate results and show a limited sample throughput. Recently, our research group has recently demonstrated the benefits of using microwave-assisted extraction (MAE) treatment for extracting NMs from soils and air filter samples [1-2]. For instance, Au- and PtNPs were quantitatively recovered by treating samples with 20mL of a 0.1 M NaOH solution in a 800 W domestic microwave oven (DMO) for 6 minutes. Though the use of MAE overcomes main drawbacks shown by previous strategies, the use of DMO entails significant practical disadvantages (e.g., lack of sample heating control, poor reproducibility due to solution splashes, etc.). The aim of this work is to adapt previously developed MAE treatments with DMOs to state-of-the-art scientific microwave oven digestion systems (SMO). Thus, MAE treatments can be standardized for routine analysis and improve metrology for spICP-MS. By the appropriate optimization of operating conditions, metallic NMs could be efficiently isolated from soils and air samples using a MW power of 1200 W and 10mL of NaOH 0.1M solution in 10 and 6 min, respectively. When compared to DMO, the use of SMO provided better accuracy (Fig 1), precision, and sample throughput (6-fold).

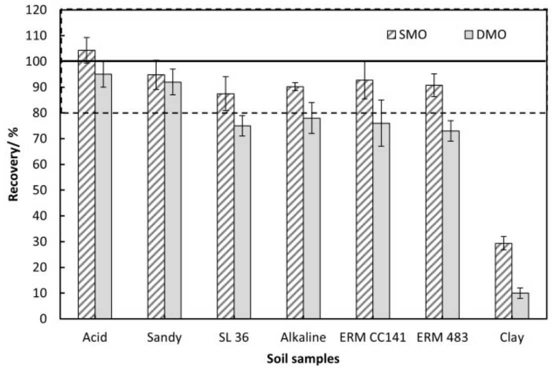

Figure 1. Comparison between the recoveries obtained in soil samples using the DMO and the SMO for 70nm PtNPs. Error bars: standard deviation, n=5. Dashed lines limit the quantitative recovery interval.

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# The determination of Ge by hydride generation–atmospheric pressure glow discharge optical emission spectrometry (HG–APGD OES)

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Miniaturized microplasmas are more and more used as excitation sources in optical emission spectrometry (OES). Such systems are characterized by a simple design and low media consumption (e.g., plasma-forming gas and electricity), which makes microplasma-based instrumentation very affordable. In this contribution, we present a novel analytical method based on an atmospheric pressure glow discharge (APGD) system for the OES determination of Ge in aqueous solutions. In this approach, an analyzed sample (pH=6.5) was submitted to hydride generation (HG) in the reaction with a 3% $NaBH_4$ solution. Generated $GeH_4$ along with accompanying $H_2$ (a by-product of the $NaBH_4$ decomposition), were swept by a carrier/discharge-supporting gas (He, 350 mL $min^{-1}$) and introduced into the APGD system (I=40 mA), where atomization and excitation processes took place. The effect of the design of the HG-APGD system (e.g., the volume of a gas-liquid separator and diameter of a gas nozzle) and its operating parameters on the Ge detectability was investigated. For example, it was found that high sensitivity of Ge measurements was assured when water vapor was removed from the gaseous phase leaving the HG unit and transferring into the APGD system, e.g., by using a dryer filled with NaOH. A beneficial effect on the SBR (signal-to-background ratio) of the Ge signals had the reduction of the interelectrode distance to 0.5 mm. Such a small discharge gap tended to hinder the diffusion of ambient air to the discharge phase, which limited the spectral interferences occurrence originating from the NO molecular bands. Finally, under optimal operating conditions, the analytical performance of HG-APGD OES was assessed in detail.

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# Atmospheric plasma discharges as hydride atomizers for trace element analysis: their development, applications and mechanistic studies

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Some analytically important elements such as As, Sb, Bi, Se, Pb, Sn, Te or Ge can be efficiently converted from a liquid sample into their volatile hydrides, yielding a 100% analyte introduction efficiency into the spectrometric detector, and surpassing thus, by an order of magnitude, the performance of common pneumatic nebulizers (5-10%). Atomic absorption spectrometry (AAS) is still the daily workhorse in trace element analysis, offering affordable instrumentation, method robustness and operator friendliness. Externally heated quartz tube atomizers (QTA) are the most common hydride atomizers in hydride generation (HG) AAS. Recently, the dielectric barrier discharges (DBD), i.e. low power and low temperature plasmas sustained by alternating voltage at atmospheric pressure, have been proven as promising hydride atomizers at least for some of the elements listed above. Other types of atmospheric plasma discharges, namely a RF plasma jet called plasma pencil, or a discharge sustained inside a quartz tube between two bare electrodes, i.e. with no dielectric barrier, have been investigated as alternative hydride atomizers, especially to overcome difficulties with atomization of Pb, Sn or Ge hydrides in DBD. Experimental conditions were optimized individually for each analyte in all three plasma atomizer designs. Sensitivities and limits of detection were determined as basic figures of merit to assess the atomizer applicability to routine measurements. Each atomizer design was also characterized in terms of plasma temperature, absolute concentration and spatial distribution of H radicals as important species responsible for hydride atomization determined by two photon laser induced fluorescence (TALIF). For selected elements, the absolute concentration of free analyte atoms and their spatial distribution was measured by LIF allowing to quantify atomization efficiency. Detailed insights into hydride atomization mechanisms, which are strongly element-dependent, will be shown using Ge and Se as target analytes. The sensitivity trends observed in AAS measurements correlate perfectly with atomization efficiency determined by LIF. Also the tendency of individual analytes to deposit in the discharge area, quantified by leaching experiments, seems to agree with element dependent life-time of free atoms. The advantages of plasma diagnostics by LIF and TALIF, and the importance of these methods for further improving the hydride atomizers performance will be discussed. Potential coupling of the plasma sources investigated with other atomic spectrometric detectors such as atomic fluorescence or optical emission spectrometry will be outlined.

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# Studies of uptake and translocation of metal nanoparticles in edible plants using single-particle ICP-MS/MS method

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The unique properties of metal nanoparticles (NPs) have made them an essential ingredient in an ever-growing number of products. In particular, they are used in popular goods such as personal care products, cosmetics, textiles, construction materials, and medicines [1]. They have recently been also used in agriculture to improve soil properties, as an alternative to conventional fertilizers for direct application to plants, and to protect plants against diseases It is worth noting that their impact on physiological processes and plant growth is very complex and not fully understood, and the benefits resulting from their use have stopped the emergence of obvious questions about the fate of nanoparticles in the environment and their toxicity.

The knowledge on migration and transformation of NPs in the environment, including their uptake by plants, is still incomplete due to some procedural and economic limitations of analytical methods used for their determination. Recently, the potential of *single particle*- ICP-MS for analysis of nanoparticles was displayed [1], but to date, little is known about the ability of this technique to detect NPs in complex matrices selectively. Therefore, the impact of the matrix effect on the accuracy of particle mass and corresponding size determination needs investigation. In addition, efficient and accurate procedures for extracting NPs from biological tissues are required to study their interaction with plants.

We will present research on the uptake and translocation of gold and titanium(IV) oxide nanoparticles in edible plants (potato, lettuce, tomato, radish, and green pea) [2,3]. The plants were grown in hydroponic or field conditions (in soil) with the addition of nanoparticles. The procedures for sample preparation for such analysis and their determination using the *sp* ICP-MS/MS method were optimized. On this basis, the extraction procedure characterized by accurate results in terms of both recovery and size of NPs was selected and used to determine the fate of NPs in plants.

We confirmed the uptake of both types of nanoparticles by the roots and their further transport to the above-ground parts of plants, and the fact that the results of nanoparticle translocation depended on the type of plant and type of metal. We have also proven that the *sp* ICP-MS/MS technique is well suited to studying the migration of metal-based nanoparticles inside the plant body.

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# Performance of single-cell ICP-MS/MS for investigating HSA-induced alterations in zinc uptake in paraformaldehyde-fixed HUVECs

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Single-cell inductively coupled plasma-mass spectrometry (scICP-MS) represents an analytical method employed for scrutinizing trace elements at the cellular level, facilitated by the heightened sensitivity of contemporary instrumentation [1]. Nonetheless, specific applications might encounter constraints due to both spectral and non-spectral interferences stemming from the intricate matrix. In this context, the efficacy of this approach hinges upon adequate sample preparation, crucial for maintaining cell stability before their introduction into the plasma [2]. Here, a technique was devised to gauge overall concentrations of Zn and Fe in human umbilical vein endothelial cells (HUVECs) using scICP-MS/MS. The Instrumental factors such as dwell time (3, 5, and 10 ms) were also examined. As a proof of concept, The analytical methodology optimized for scICP-MS was utilized to ascertain Zn levels in HUVECs undergoing four treatments aiming to assess the impact of human serum albumin (HSA) on the intracellular balance of this vital nutrient: 1. Culture medium (DMEM) containing 10% FBS, 2. DMEM containing 20 μM $Zn^{2+}$, 3. DMEM with 60 μM HSA (without zinc), and 4. DMEM with 20 μM $Zn^{2+}$ and 60 μM HSA. The results of this study show that fixing HUVECs with paraformaldehyde helped achieve good experimental consistency and reproducibility without substantially altering the baseline signal. For the 3 ms dwell time, the mass determined by scICP-MS/MS for Zn and Fe were 1.6 fg $cell^{-1}$ and 1.8 fg $cell^{-1}$ respectively. It is possible that for 5 ms, more than one cellular event is expressed in a single peak. Therefore, the dwell time of 3 ms was utilized as it presented better results. The method was applied to evaluate the effect of albumin on zinc homeostasis in HUVECs. The results revealed that the addition of 20 μM Zn alone led to Zn accumulation within the cell. The additional presence of 60 μM HSA reduced Zn uptake. This occurrence arises from the fact that HSA has at least two high-affinity Zn binding sites [3]. Consequently, despite the presence of HSA, it is known that an excess of free Zn can lead to toxic effects detrimental to cell growth in conditions similar to those evaluated here. Intricate details about the femtogram-level Zn mass distribution within HUVECs under the conditions tested were revealed. However, when comparing cells exposed to 60 μM HSA with 10% FBS, the mass distribution of Zn remains similar, which is likely indicative of the BSA in the FBS exerting an equivalent effect on Zn uptake to HSA. However, even with the addition of physiological concentrations of $Zn^{2+}$ (20 μM), the balance of this metal is compromised in the absence of albumin. This disparity could potentially impact the cell's metabolic activity, proliferation, and survival in certain culture conditions.

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# Speciation of ionic selenium and biogenic SeNPs by means of spICP-MS after an ion exchange resin treatment

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*Haloferax mediterranei*, a halophilic archaeon prevalent in hypersaline environments, has been identified as a cell biofactory producing a variety of compounds, including carotenoids, polyhydroxyalkanoates and nanoparticles, including Se nanoparticles (SeNPs) [1-3]. The characterization of biogenically produced SeNPs by this microorganism is particularly challenging due to: (i) spectral interferences from Ar-based polyatomic ions; (ii) non-spectral interferences caused by the high salt content in the medium (>20% w/w NaCl); and (iii) the high ionic selenium background caused either by the presence of selenite in the culture medium for nanomaterials production or SeNPs dissociation due to their high lability under standard conditions. This latter issue complicates mass balance studies aimed at understanding how this archaeon transforms selenite into SeNPs. This work evaluates the use of anion-exchange resins to speciate ionic selenium and SeNPs in salt-rich media. To this end, anion-exchange extraction parameters (e.g., resin amount, extraction time, extractant volume, etc.) were initially optimized to maximize both selenite retention and recovery. Next, this strategy was applied to characterize both Se species in *Haloferax mediterranei* culture medium by means of spICP-MS.

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# Is CE-ICP-MS/MS a proper tool for examining the encapsulation of active compounds in liposomes?

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Liposomes are nanometric vesicles built of a double phospholipid layer. Intensive work is being carried out on their wide application in the more effective transport/delivery of various chemical compounds. On the one hand, researchers' great attention is related to the biocompatibility of these chemical objects (imitating cell membranes with their structure), the diversity and simplicity of their synthesis processes, and the encapsulation of crucial chemical compounds inside them. On the other hand, it is essential to examine the mechanisms of their selective transportation into cancer cells (the effect of increased permeation and retention) or the effective incorporation into the membranes of skin cells.

Despite the advantages mentioned above, liposomal nanomaterials are problematic analytical objects of interest, making it difficult to understand the pathways of their transportation and release of active compounds in targets. This is due to the lack of unique properties of electromagnetic energy transposition and the poor isotopic composition, which makes it impossible to develop simple tools for their effective determination (especially when compared with metallic nanoparticles). These conditions create a unique research niche and motivation to propose innovative analytical tools to study the formation, stability, and changes of the liposome–active compound systems in variable matrices.

As a solution to the abovementioned problems in the frame of this presentation, a capillary electrophoresis hyphenated with an inductively coupled plasma tandem mass spectrometer (CE-ICP-MS/MS) is proposed. Its analytical potential in investigating liposome-containing samples will be verified, especially considering the resolution of the optimized methods. As active compounds encapsulated inside the liposomes, antiaging agent (tripeptide GHK complex with copper) and anticancer drug (cisplatin)[1,2] were chosen to monitor.

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# Estimation of measurement uncertainty and optimization of algorithms for signal processing in the Single Particle-ICP-MS technique

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The broad use of nanoparticles (NPs) inevitably leads to the release of nanoparticles into the environment, which may have a negative impact on the natural environment, accumulate in living organisms, and consequently affect human health. The detection and characterization of NPs in complex media, such as various consumer products and foods, is an essential element in understanding the potential benefits and risks associated with their use.

Studying the transformation of nanoparticles in the environment requires determining the number of their physicochemical parameters (size, concentration of metal in ionic and nanoparticle form, chemical composition of the nanoparticle, size distribution, dissolution, and agglomeration efficiency). Until recently, each of these parameters would require the use of a separate measurement technique often coupled to an extensive sample preparation stage.

Single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) is a promising technique for nanoparticle analysis [1]. It allows one to obtain quantitative information about the number, size, and size distribution of nanoparticles and the concentration of the ionic form of the element in the solution. The technique is distinguished by the ability to conduct analyzes for nanoparticle concentrations corresponding to those observed in the environment. This confirms the attractiveness of the SP-ICP-MS technique as a potential high-throughput characterization of nanoparticles in various studied systems.

SP-ICP-MS makes it possible to obtain the key physicochemical parameters of a nanosystem in one measurement act. The reliability of the results obtained and, consequently, the quality of the conclusions drawn are fundamentally related to the reduction of the current limitations of this technique. This requires action in the area of technical conditions and their confrontation with metrological aspects. One of the most important issue is the modification of the algorithms that process the signal and collected data [2]. The processing SP-ICP-MS signal consists of several numerical steps including: ionic background determination, peak detection, peak area determination and mass flux determination. Our goal is to optimize these algorithms and estimate uncertainties associated with their output.

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# Measurement uncertainty of complex measurements from correlated performance data: Determination of total Cr in yeast

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The objective interpretation of a measurement result requires knowing the associated uncertainty. After short introduction of the uncertainty concept, currently used approaches of its estimation will be shown and compared [1]. The detailed evaluation of the measurement uncertainty based on complex sample pretreatment and instrumental analysis of the processed sample is challenging. The application of bottom-up approach will be presented on practical example of total Cr determination in yeast samples frequently used in food industry.

The cost-effective collection of measurement performance data on the same day produces correlated values that can affect measurement uncertainty evaluation. This work describes a novel methodology for the bottom-up evaluation of measurements based on complex sample pretreatment and the instrumental quantification of the prepared sample applicable to correlated inputs. The numerical Kragten method is used to combine the uncertainty components shared in various analyte recovery determinations. The developed methodology was applied to the determination of total chromium in yeast samples by ICP-MS after microwave-assisted acid digestion. The developed analysis of yeast samples is fit for monitoring the contamination of this product since it is associated with a relative expanded uncertainty (U') lower than 20%, ranging from 8.4% to 10.0% in determinations of Cr between 0.125 mg/kg and 305.5 mg/kg [2].

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# Speciation Analysis of Organo-Tin in Environmental Samples *via* Electrothermal Vaporization/Inductively Coupled Plasma-Mass Spectrometry

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Shipping plays a significant role in the global trade. However, it is negatively impacted by the unwanted accumulation of marine organisms on the ship hulls. To prevent the so-called bio-fouling, antifoulant paints containing the organometallic compound tributyltin (TBT) have been used on ship hulls since the 1960s. Compared to the generally considered non-toxic inorganic tin, the endocrine disruptor TBT leads to the endangerment of non-target organisms. The most prominent effects are imposex in snails and shell deformation in oysters. This resulted in a global ban by the International Maritime Organization in 2008. Nevertheless, recent studies have found alarmingly high concentrations in sediment.

Organotin compounds (OTCs) are known to persist and accumulate in marine sediments, posing a long-term threat to the environment. Once released from the ship hull, TBT gets effectively absorbed into the sediment. Under anaerobic conditions and the absence of light, the half-life is extended up to several decades. The resuspension and transport of sediment remobilizes butyltin compounds, making them bioavailable even in distant regions. The monitoring of OTCs in sediment is inevitable to conduct a comprehensive risk assessment and a thorough monitoring of pollution. Conventionally, species-specific analysis of OTCs involves (gas-)chromatographic separation after extraction and pre-concentration of the analytes. However, the sample preparation is time-consuming, chemical-intensive, and prone to species-transformation, respectively incomplete extraction. In this context, electrothermal vaporization coupled with inductively coupled plasma-mass spectrometry (ETV/ICP-MS) shows high potential as a rapid and chemical-saving screening tool for OTCs in environmental samples.

The main challenge for obtaining correct, quantitative data with direct solid sampling techniques like ETV/ICP-MS is the application of a suitable calibration strategy. In this context, a new quantification method based on on-line isotope dilution analysis has been developed and validated by a reference material with certified OTC content. Our approach overcomes matrix effects while being compatible with commercially available ETV systems. Using an optimized multi-step ETV temperature program, the full separation of OTCs, inorganic tin, and major matrix components could be achieved. Since its use as a screening tool, analyzing OTCs as a sum parameter is beneficial and can complement chromatographic approaches.

# Dispersive micro-solid phase extraction for the determination of Cd by slurry sampling microplasma optical emission spectrometry

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A solution anode glow discharge (SAGD) is a novel miniaturized excitation source for the analysis of liquid samples by optical emission spectrometry (OES). SAGD OES offers outstanding measurement sensitivity, however, it is also very susceptible to matrix effects. So far, various approaches have been presented to reduce the appearance of chemical interferences, *e.g.,* the use of complexing agents to mask the foreign ions. In this contribution, for the first time, a dispersive micro-solid phase extraction (D-μSPE) based on graphene oxide was employed for the ultrasensitive determination of Cd by SAGD OES. It was found that in contact with microplasma, Cd bounded on the graphene oxide surface can be converted to its volatile species. As a result, it was possible to omit the elution step (a slurry sample was introduced), which allowed us to shorten the sample preparation time and reduce the risk of contamination. The effect of selected variables, *e.g.,* the type/concentration of interferents and the graphene oxide concentration, was studied in detail. It was established that using the D-μSPE-SAGD OES, matrix effects were remarkably reduced, and the improvement in the tolerance of Cd to alkali metals by a factor of 25 was reached. The detection limit of Cd for the developed method was 0.003 μg $L^{-1}$ (in the presence of a complex matrix). Under optimal operating conditions, D-μSPE-SAGD OES was successfully employed for the ultra-trace analysis of food and environmental samples containing a high alkali metals content, *i.e.,* wine and Baltic seawater.

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# The influence of mineralization conditions on the recovery of metals from sewage sludge ash: implication for analytical and technological applications

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The popularity of sewage sludge thermal treatment processes as the management method for the mentioned hazardous waste has increased in the last couple of years in EU countries. In the process several fractions of solid waste are generated, while the major faction is sewage sludge ash (SSA) – mineral residue after the combustion process. The possibility of SSA management in different manners is under consideration. One of the most important issues during SSA management is the high content of potentially toxic and hazardous metals in this material, such as Cd, Cr, Cu, Pb and Zn [1,2]. Thus, the analysis of the content of the mentioned elements is routinely carried out as a part of the research on chemical characteristics of this type of waste. Using of plasma-based spectrometry techniques requires the prior mineralization of the solid sample as a key stage of the sample preparation process. Sewage sludge ash is a particularly difficult matrix to dissolve, mainly due to the high content of chemically stable minerals like aluminosilicates and spinel structures [3]. Thus, using mineralization methods differing in the mixture composition, temperature and other parameters can lead to obtaining different recovery rates of elements. Moreover, the development of efficient and reliable procedures for the determination of metals in SSA is demanding because of the lack of certified reference material (CRM) for SSA on the market. Usually used CRMs for validating the mentioned analytical procedures (coal ash, wood ash) are characterized by significantly different matrix compositions. In the presented study, the influence of the mineralization method on the obtained results of metal determination in the SSA sample was examined. Three different mineralization mixtures commonly used by researchers were taken into account: $HNO_3$:$H_2O$ (1:1), concentrated $HNO_3$ and aqua regia. Mineralization was carried out using different temperatures and during different times of the process. To check the influence of tested parameters, the content of several routinely determined metals was quantified in prepared solutions after mineralization using the Microwave Induced Plasma Optical Emission Spectrometry (MIP-OES) technique. It was confirmed that both mixture composition and parameters of the process can affect the recovery rate. It follows that comparing of results of the determination of metals in SSA obtained using different parameters of mineralization is often unreliable. Thus, it is necessary to develop appropriate CRM and standard procedures for the determination of metals in SSA.

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# Recent advances in photochemical vapor generation with a focus on the less abundant elements

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Photochemical vapor generation (PVG) is an emerging alternative sample introduction technique for analytical atomic spectrometry, combining advantages of efficient separation of analyte from matrix and significantly higher introduction efficiency than possible with conventional pneumatic nebulization of solutions. Volatile analyte species are synthesized during UV irradiation of an aqueous photochemical medium typically containing low-molar mass carboxylic acids, mainly formic or acetic acid.

This presentation will be devoted to our most recent achievements in the PVG of several new analytes [1,2] belonging to the so-called group of technology-critical elements (TCEs). Despite increasing use in modern technologies, these elements are extremely rare in nature and require ultrasensitive detection methodologies. Evidence will be presented of efficient coupling of PVG to an inductively coupled plasma mass spectrometer to provide excellent detection power for determination of several TCEs (e.g., Ru and Ir), even in complex matrices such as seawater (limits of detection in single units to tens of ppq). Details relevant to optimization of PVG conditions, including the key role of metal ion sensitizers, will be highlighted. Attention will also be paid to efficient PVG of Ru, Re, and especially Ir, from dilute formic acid media (≈0.01 M HCOOH) and its related mechanistic aspects [3]. Finally, recent attempts to identify the form of some generated volatile species (metal carbonyls) using alternative ionization techniques combined with mass spectrometry will be discussed.

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# Graphite furnace and fluorine determination

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Graphite furnace atomic absorption spectrometry (GFAAS) was the title technique of the first conferences of the series of the present one. However, due to the extreme physicochemical properties of fluorine (e.g. the highest electronegativity), its determination using this technique has never been presented (and published).

The introduction of high-resolution continuum source equipment [1-4] gave the possibility of selecting any wavelength from the whole spectral range (~190->800 nm), excellent resolution and efficient background correction. Thus, opportunities have arisen for measurements of the absorption of molecules generated directly in GF. The high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GFMAS) turned out to be an excellent tool for fluorine determination. More than fifty papers have been published on the topic, devoted to the analysis of a wide variety of materials, including food and animal feed, environmental samples (e.g. water, soil, sewage sludge and inhalable particulate matter $PM_{10}$), dental hygiene products, cosmetics, raw materials (coal and copper concentrates), biological tissues, medicines and special materials (e.g. niobium oxide, alkylate, residual oil and calcium phosphate). Gallium or calcium monofluoride has been mostly used as the target molecule [2,4]. Using GaF, excellent sensitivity can be achieved with a characteristic mass of 2 pg.

The aim of this presentation will be to show the current state of knowledge and prospects for developing the HR-CS GFMAS technique for F determination [5].

Among others, the following issues will be considered: selection and investigation of chemical modifiers and analysis parameters, spectral interferences, various modes of background correction, chemical effects (among others, competitive reactions of fluorine or competitive reactions of complementary metal), relative sensitivity obtained using various target molecules, the effect of the chemical form of F on the analytical signal and the ways undertaken to diminish the problem of reagents contamination.

The most spectacular examples of analysis will be presented, such as the determination of extractable organically bound fluorine or per- and polyfluorinated alkyl substances (PFASs), the design and in vitro testing of antitumor drugs, the investigation of the release of fluorine from drugs into human sweat or the release of fluorides from dental fillings.

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# Fluorine mass balance analysis in wild boar organs from the Bohemian Forest National Park

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As PFAS are more and more widespread in the environment it is important to establish background contamination values in areas and animals. Wild boars can be used as sentinel animals for monitoring PFAS contamination in the environment, moreover their diet and widespread presence makes mapping possible.
Current research are focuses more on PFAS in wild boars that are close by contamination sites or are from urban areas, however, what happens with the wild boars that come from a pristine environment?
Bohemian Forest National Park is situated in the south Bohemian region of Czech Republic along the border with Germany and Austria. The area is a rural mountainous area which makes it the perfect place to study sentinel animals from a pristine environment.
In the following study we analysed kidneys and livers from 30 animals harvested from the national park (for population control purposes) to study the PFAS profile and concentration with a multi-method approach, using targeted – and non-targeted analysis, as well as total oxidizable precursor assay (TOPA) with liquid chromatography coupled to mass spectrometry and extractable organofluorine (EOF) and total fluorine (TF) content analysed with combustion ion chromatography (CIC). Results suggest that the main source of PFAS in the wild boars are from atmospheric deposition, however concentration of individual PFAS and PFOS contribution to the sum of PFAS suggest a nearby contamination source. Mass balance analysis showed that the sum of target PFAS compared to EOF accounted for a few % (<10%), moreover, TOPA and non-target analyses were not able to close the mass balance, suggesting that most of the PFAS in the wild boars from the national park contains PFAS that are not measurable and degradable with the routine PFAS analyser tools.

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# Does green mean better? A critical look at the green synthesis of selenium nanoparticles.

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Selenium is an important trace element for humans and animals. In recent years, selenium nanoparticles (SeNPs) have attracted great attention due to their higher bioactivity and lower toxicity in comparison to inorganic and organic selenium species [1]. They offer great potential in various biomedical applications, including potential use in the treatment of antibiotic-resistant bacteria infections. SeNPs can be synthesized by physical, chemical, and biological methods [2]. However, the growing popularity of the so-called green methods of selenium nanoparticles has been observed recently. Biologically synthesized SeNPs demonstrate greater compatibility with human organs and tissues and od not require chemical reagents which may be toxic, and hinder their utilization in biological systems [3]. A good alternative seems to be the use of plant extracts for the synthesis of SeNPs. The extract naturally contains compounds that can act as both selenium reducers and stabilizers, thus, this approach fits perfectly into the "green synthesis" trend [4].
The aim of the lecture is to compare chemical methods of SeNPs synthesis and green methods based on the use of plant extracts. Both the practical aspects of conducting the synthesis itself and the parameters of the obtained SeNPs will be compared. The issue of antibacterial and antioxidant capabilities of SeNPs will also be discussed.

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# Insight into the formation and evolution of secondary organic aerosol (SOA) in the forest atmosphere

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In Europe, depending on the region, coniferous trees like pines, spruces, and firs are the most common to build forest flora. Considering each species is characterized by a particular emission of gas-phase volatile organic compounds, the complex forest's atmosphere can be described as a chemical reactor, where a number of products react with oxidizing species such as ozone ($O_3$), OH/$NO_3$-radicals, and with each other making the composition analysis of forest atmosphere even more complicated.[1] Therefore, the model approach using an aerosol chamber system to study atmospheric processes will be used to mimic processes occurring in the forest atmosphere.

In the presented project, experiments were based on the reactivity of freshly distilled pine needle oil, representing tree emission. A number of experiments were conducted in Atmospheric Chemistry Department - Chamber (ACD-C) using a set of online instruments e.g. Aerosol Mass Spectrometer (AMS), Atmospheric Pressure Chemical Ionization Mass Spectrometer (APCI-ToF-MS) And Proton Transfer Reaction Mass Spectrometer (PTR-ToF-MS).

Overall, a set of chamber experiments were conducted with different amounts of pine oil (2 – 10 µL). The SOA yields and mass ranged from 2.5% and 12.0 µg × $m^3$, for experiments with 2 µL precursor to 3.7% and 85.7 µg × $m^3$, for experiments with 10 µL precursor. (**Figure 1**)

**Figure 1** Concentration of organic mass (µg × $m^3$) measured during smog chamber experiments..

Experiments performed only with *α*-pinene and *δ*-*3*-carene show lower organic mass and yields (14.5 µg × $m^3$ and 2.1%, respectively) than experiments with pine oil. Results show that components occurring in smaller concentrations in the atmosphere greatly impact the formation and growth of SOA particles in the forest troposphere.

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# Determination of potentially toxic elements in tobacco products in the perspective of consumer exposure

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Chronic obstructive pulmonary disease is expected to became one of the leading reasons of deaths globally, predominantly due to predicted increases in smoking combustible tobacco products (CTPs) [1]. Studies are mostly limited to cigarette products, despite the fact tobacco market offers wide spectrum of products. Cigars appear to be of particular interest, which, due to their often-considerable size and popularity, can deliver significant doses of toxic elements (compared to smaller cigarettes) into the bodies of significant numbers of people [2]. Moreover, there is a lack of methods for analysing the smoke of non-cigarette CTPs. Therefore, the determination of the content of potentially toxic elements in the non-cigarette products is justified and contributes important data to comprehensive knowledge of the subject. To estimate consumer exposure to potentially toxic elements in non-cigarette products (cigars, pipe tobacco and bidis) elemental analysis of samples conditioned at 135-275 °C was also performed. This approach simulates smoking on a laboratory scale. As a result, 13 out of 14 determined elements contents decreased with conditioning temperature increasement. This implies the likely transmission of these elements to the volatile fraction, which is of particular importance for heavy metals with known adverse effects on human health through inhalation, such as As, Cd, Co, Ni or Cr. Determination of the total content of potentially toxic elements in tobacco and an initial estimate of their possible transmission into smoke is a necessary first step in a wider study of the exposure of non-cigarette CTPs consumers to these elements.

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# Analytical approaches to the comprehensive characterization of the mineral content and elemental speciation in Shilajit, a traditional Asian medicine

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Shilajit, a naturally occurring rock exudate of predominantly biological origin sourced from mountain cliffs, holds prominence in traditional medicine in Afghanistan, India, Iran, China, Pakistan, Nepal, Central Asia and Tibet. [1]. Nowadays, Shilajit is widely used as a health promoting product in complementary medicine worldwide [2].

The existing literature on Shilajit reveals the presence of varying concentrations of mineral components, including not only the essential metals such as Ca, Mg, Fe and Zn, but also potentially toxic ones, such as, Al, As, Hg, Pb, Cd and Cr [2]. The presence of heavy metals raises concerns about potential toxicity related to Shilajit intake by vulnerable patients seeking its beneficial effects. The available reports on Shilajit greatly differ in terms of determined contents of individual elements which is most probably related not only to the natural variability but also to the lack of validation of the different analytical methods used.

The work aims at the comprehensive characterization of mineral content of Shilajit to better understand its beneficial effects, establish its safety and possibly highlight the variability of samples of different origin. The analytical approach developed involved ICP MS multielemental fingerprinting for fast differentiation of samples of different origin followed by determination of the elements of therapeutic interest or toxicological concern. Elemental speciation by HPLC - ICP MS allowed an insight into the complexation of metals with macromolecules present in rich organic Shilajit matrix. The issue of bioaccessibility of mineral components of Shilajit is also addressed.

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# Application of graphene oxide foams in preconcentration of ultratrace amounts of metal ions via X-ray fluorescence spectrometry

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Metal contamination poses a significant threat to environmental and human health, necessitating highly sensitive and efficient detection methods. The importance of this topic is vital for various fields, including environmental monitoring, industrial processes, and public health. Despite the low detection limits offered by spectroscopic techniques, direct determination of metal ions remains challenging due to their low concentrations in environmental samples and the presence of chemical and physical interferences in complex matrices. This necessitates the introduction of an additional sample pretreatment step, such as preconcentration of analytes before actual measerment [1,2].

The aim of this research was to explore the capabilities of graphene oxide foams (GOF) in preconcentration of several heavy metal ions (chromium, cobalt, nickel, copper and lead) and to investigate factors influencing the analytical procedure combining dispersive solid-phase microextraction (DMSPE) and detection by X-ray fluorescence spectrometry techniques: energy-dispersive X-ray fluorescence (EDXRF) and total-reflection X-ray fluorescence (TXRF)). Carbonaceous nanomaterials have garnered considerable attention in analytical chemistry owing to their exceptional properties and versatile applications. 3D-carbonaceous nanomaterials typically possess a highly porous structure with interconnected channels and voids. This architecture results in an exceptionally high surface area, providing ample active sites for adsorption of target molecules or ions [3]. In the realm of X-ray fluorescence (XRF) spectrometry, these materials offer promising avenues for enhancing preconcentration methods, thereby improving the sensitivity and accuracy of element determination.

The obtained results highlight the positive synergic effect of microextraction-based preconcentration and X-ray fluorescence detection, which is an aftermath of the sample preparation method imposed by both measurement techniques, such as preparation of sample in the form of thin layers. Parameters affecting adsorption of heavy metal ions on the surface of GOF, such as acidity of the solution, adsorbent mass, adsorption time, influence of ionic strength and potentially interfering ions were verified. The adsorption behavior of GOF towards analytes was investigated by the means of kinetics studies and adsorption isotherms. Furthermore, the validation of the analytical procedure ensured its applicability in real-world scenarios, thereby addressing pressing environmental and health concerns associated with metal contamination.

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# Spectrophotometric study of oxytetracycline derivatives and their use in analysis

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Oxytetracycline (OTC) is a broad-spectrum tetracycline antibiotic that effectively treats various diseases in animals and humans.OTC is often used in combined veterinary drugs, which include several antimicrobial substances of different classes, which is a reason for an effective fight against various infections.

Oxytetracycline is included in a structurally diverse class of aromatic polyketide antibiotics and contains phenolic hydroxyls. This chemical structure allows the OTC interaction with diazo salts of primary aromatic amines, forming colored azo compounds. Such derivatives are effectively used for the spectrophotometric determination of many organic compounds.

As reagents for obtaining OTC azo compounds, 1-diazo-2-naphthol-4-sulfonic acid (DNSA) and previously diazotized Fuchsin were chosen. As a result of the azo coupling reaction of OTC with DNSA and diazotized Fuchsin orange and yellow-colored products are formed respectively. The optimum conditions for obtaining the OTC-colored derivatives with the examined reagents are presented in Table 1.

Table 1. The optimum interaction conditions and spectral characteristics of the obtained azo compounds

| Reagent | $\lambda_{max,}$ nm | $\varepsilon \cdot 10^{-4}$, $L \cdot mol^{-1} \cdot cm^{-1}$ | OTC: Reagent, Stability | Conditions | |
|---|---|---|---|---|---|
| | | | | Diazotization | Azo coupling |
| Fuchsin | 440 | 3.14 | 3:1<br>3 hours | C(HCl) = 1.0 $mol \cdot L^{-1}$, (≥10-multiple excess $NaNO_2$ to Fuchsin) within 10 min | 1.33- multiple excess OTC to Fuchsin),<br>C(BR buf)=0.01 $mol \cdot L^{-1}$ pH=10.5 |
| DNSA | 470 | 0,30 | 1:1<br>5 min | – | 2.5- multiple excess DNSA to OTC<br>C(NaOH)=10 $mol \cdot L^{-1}$ |

The linearity of the analytical signal is observed within the OTC concentration limits: for Fuchsin in the range of 5.0–42.2 $\mu g \cdot ml^{-1}$ (LOD $3.17 \cdot 10^{-6}$ M), and for DNSA 12.4–198.6 $\mu g \cdot ml^{-1}$ (LOD $1.11 \cdot 10^{-5}$ M). The sensitivity of the OTC reaction with Fuchsin is three times higher than with DNSA. The developed methods have been successfully tested at the OTC determination in veterinary drugs, in particular:

| OTC (regulated amount in medecines) | The determined OTC content in the solution for injection "Oxy-100" Interchemie Werken De Adelaar Estonia AS (1 ml of the drug contains (mg): oxytetracycline hydrochloride - 100.0, benzyl alcohol - 1, magnesium chloride - 200, sodium formaldehyde sulfoxylate - 5, monoethanolamine, polyethylene glycol - 20, water for injections up to 1 ml) | | | |
|---|---|---|---|---|
| | DNSA | | Fuchsin | |
| | $x \pm S \cdot t_{\alpha} / \sqrt{n}$ | $S_r$ | $x \pm S \cdot t_{\alpha} / \sqrt{n}$ | $S_r$ |
| 100±10 $mg \cdot ml^{-1}$ | 137.0 ± 1.5 | 0.009 | 135.8 ± 1.98 | 0.012 |

# Micro-Discharge Optical Emission Spectroscopy – On-site analysis of lithium process samples by generating micro-plasmas

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The fast and precise on-site analysis of main components and trace elements in highly saline solutions, e.g. brines or process solutions, is still a challenge. Established techniques, like ICP-OES or ICP-MS, are usually limited to laboratory use due to high plasma gas flow rates and power consumption, making them not suitable for real-time analysis and monitoring of industrial processes on-site. Therefore, a fast and precise on-site method would be preferable. Here we investigated the potential of the Micro-Discharge Optical Emission Spectroscopy (μDOES) for the on-site and on-line analysis of the lithium hydroxide production, whose end product is an essential precursor for the battery industry. The technology is based on a micro-plasma, which is directly created inside the aqueous sample without any carrier gas by using electrodes and high voltage pulses enabling optical emission spectroscopy on-site[1] (cf. Figure 1). After optimisation of several parameters like sample conductivity, plasma discharge energy or signal integration setting, measurements were carried out at an industrial pilot plant. Various process steps, starting with the raw material (calcined lithium ore) through different intermediate products to the end product (lithium hydroxide monohydrate), were monitored. The technique proved to be useful for a fast and precise on-site main component and trace analysis of saline solutions, whereby a good agreement with established methods like laboratory ICP-OES or ion chromatography was achieved for the elements Li, Na, K, Ca and Mg with deviations < 10% for most samples.

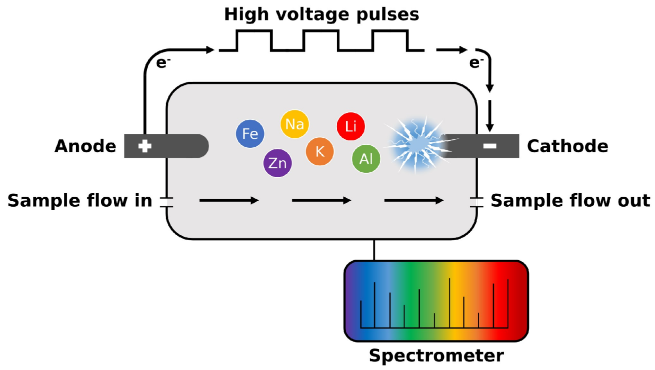

Figure 1. By applying high-voltage pulses to the electrodes, a micro-plasma is generated by a corona discharge at the cathode directly inside the liquid sample enabling optical emission spectroscopy[1].

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# Simultaneous determination of selected metals in Dried Blood Spot (DBS) by EDX

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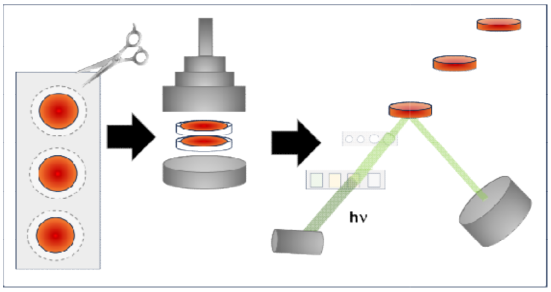

Figure 1. The scheme of analytical procedure

The most prominent use of Dried Blood Spot (DBS) samples dates back to the early 1960s when Robert Guthrie developed an assay to detect phenylketonuria [1]. Recently, the application of DBS was expanded to amino acids to screen neonates for congenital and inherited metabolic disorders. The collection of DBS samples is typically conducted by pricking the finger, heel, or toe with a lancet, and single blood drops are then spotted onto preprinted circles on specially manufactured paper. Next, blood is dried for at least 2–3 h in an open space at room temperature. Major advantages of using DBS are (a) easy, non-invasive, and economical collection of a small volume of blood (single drops); (b) minimal risk of bacterial contamination and/or hemolysis; (c) good stability and long storage time in room temperature enabling low-cost delivery by post [1].

Nowadays, humans are exposed to high levels of different metals from many sources (air, food, food supplements, or pharmaceuticals), many organic compounds administrated to humans, or metabolism disorders can lead to increased excretion of microelements [2]. Therefore, determining toxic and essential elements in human fluids and tissues accurately and precisely is critical. Metals in blood or blood extracts are most frequently determined by absorption atomic spectrometry with graphite furnace (GF AAS) or inductively coupled plasma mass spectrometry (ICP MS) [2].

The study aimed to optimize a new method for the simultaneous determination of metals in DBS using Energy-Dispersive X-ray spectrometry (EDX). EDX does not require sample dissolution, and metals were determined directly in DBS in the specially constructed vessels, enabling sample immersion and blocking in the autosampler necessary to obtain an appropriate vacuum level in the detector chamber.

The method was optimized for determining 11 elements (e.g., Mg, Na, S, K, Ca, Fe, Cu, Zn, Se, Br, Pb, and Hg) and validated against ICP MS/MS results for blood CRM samples. It should be noted that the method enabled accurate determination of K and Fe, the content corresponding to the hematocrit level, which enables the normalization of the metal amount against iron and/or potassium. The study includes modification of detection chamber vessels, optimization of EDX and ICP MS/MS (including extraction conditions) detection parameters, and study on metal distribution within DBS, which significantly influences method precision using ICP MS/MS analysis for metal extracted from 3 mm discs cut out from DBS.

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# Challenges of integrating metallome analysis in exposomics workflows

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Over the last decade, the concept of the "human exposome" has emerged as a useful framework for understanding the complex connections between environment and human health. It encompasses the totality of environmental exposures that individuals encounter throughout their lifetime, including chemical, physical, biological and even social factors. [1] Until now, exposome research has been dominated by techniques of some classical "-omics" disciplines. However, for a holistic understanding, investigation of the metallome (i.e., the concentrations of "all" metals, metalloids and eventually also non-metals) is required as well, considering the ubiquitous occurrence and wide array of known detrimental effects on human health.

While multi-element analysis via inductively coupled plasma mass spectrometry (ICP-MS) is considered a routine task in many laboratories, the integration into existing workflows for exposome research poses several challenges, especially concerning sample collection and preparation.

Often, the amount of available sample is very limited, e.g. in the case of human biopsies, and therefore, samples cannot be prepared for organic and inorganic analysis individually. Instead, metal analysis has to be achieved with solutions originally prepared for the investigation of organic compounds.

In addition, high throughput is required for the investigation of large cohorts, and low limits of detection are necessary for the detection of background levels and smallest differences in concentration of numerous elements at the same time.

Therefore, we aimed to develop fit-for-purpose workflows for quantitative determination of metals and metalloids within existing protocols for exposomics research using,e.g., placenta samples [2] and blood samples from volumetric absorptive microsampling devices from pilot studies. Anticipated and unforeseen challenges will be presented, as well as potential solutions.

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# Application of mass spectrometry to analyze interactions between flavonoids and G-tetrad

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Guanosine-rich fragments of nucleic acids form a structure called G-quadruplex. The unit that builds the G-quadruplex is the G-tetrad, i.e. four guanosines interacting with each other. This structure can be stabilized by the ligands with which the G-quadruplex interacts [1].

Electrospray mass spectrometry can be effectively used to identify molecules/complexes and to determine the stability of nucleic acids and their components [2]. Flavonoids make a large group of polyphenolic compounds which are known for its health-promoting properties [3]. There are studies that say that flavonoids will readily interact with guanine. Flavonoids are known for their antioxidant properties, while guanine is the most easily oxidized nucleobase [4].

Electrospray ionization with collision-induced dissociation (ESI-CID-MS) mass spectrometry was used to study the interactions between G-tetrad and quercetin and its derivatives. To assess the stability of the fragmented ions, the survival yield (SY) method was used. The strength of the interactions in the resulting complexes was possible thanks to the determination of the $E_{com\delta 50}$. This value is characteristic for each complex and means the energy that caused the fragmentation of half of the tested ion. Experience has shown that quercetin glycosides form more stable complexes than free aglycones, and the strongest complexes were those containing rutin. However, due to the fact that aglycones have greater biological activity, it should be noted that among the flavonols, the most effective bonds are formed by 3-*O*-methylquercetin The study also showed that the interactions of flavonols with the guanosine tetrad are stronger than with the deoxyguanosine tetrad [5].

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# Isotopic Tracing in Amino Acid Biosynthesis: Insights from *Galleria mellonella* and MEF Cells.

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**Background**: This study employs mass spectrometry analytical techniques to investigate amino acid biosynthesis in *Galleria mellonella* larvae and mammalian Mouse Embryonic Fibroblast (MEF) cells. These models are utilized to examine the effects of bio-compounds on metabolic pathways, with *G. mellonella* serving as a biological model and the use of deuterium in MEF cells providing insights into metabolic synthesis. **Methods:** We utilize LC-MS in MRM mode to analyze amino acid isotopic distributions, offering insights into metabolic pathways. Precolumn derivatization with APDS [2] enhances ionization efficiency, facilitating the detection of amino acids. This methodology, combined with optimized chromatographic separation and electrospray ionization, enables measurement of isotopologue molar excess percentages, emphasizing isotopic incorporation of $^{13}$C, $^{15}$N, and $^{2}$H into amino acids. Such detail is crucial for delineating biosynthetic pathways and understanding the modulation of amino acid synthesis and discovery of transamination inhibitors.

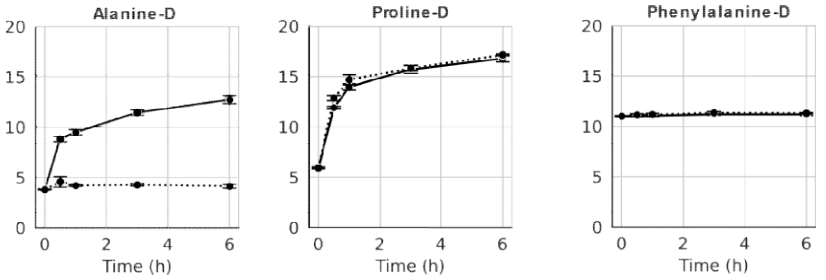

**Figure 1**. Isotopic Ratio Analysis in MEF Cells. This section displays the relative intensity, as a percentage, of the second most abundant ion in amino acid extracts from MEF cells cultured in DMEM medium with 5% deuterated water (D2O), without alanine. The solid line shows the change in relative ion intensity over time with D2O exposure. The dashed line represents the intensity when D2O and PAG are present together.

**Results:** The study outlines amino acid biosynthesis in *G. mellonella*, validating its utility for metabolic research. The application of $^{15}$N and [U-$^{13}$C] glucose, alongside $^{2}$H labelling, enabled precise quantification of isotopic molar excess in amino acids, illustrating metabolic adjustments in *G. mellonella* and MEF cells in response to inhibitors targeting pyridoxal 5-phosphate-containing enzymes. **Conclusions**: Our findings unveil the extensive biosynthetic capabilities of *G. mellonella* and the utilization of inorganic ammonia ($^{15}\mathrm{NH}_4^+$), as evidenced by the de novo synthesis of endogenous amino acids. The application of analytical methods, including isotopic labeling, not only confirms the larvae's metabolic flexibility but also mirrors similar biosynthetic patterns in mammalian cells, suggesting *G. mellonella* as a viable model for biochemical research.

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# Comparison of XRF and ICP-OES measurements in investigation of selected metal cations removal from aqueous solutions using poly(sodium acrylate)

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These days industry plays a big role in our daily lives. While it is crucial for the growing world to keep producing new, better products, one has to keep in mind that industry byproducts also take a toll on the ecological system. Researchers around the world keep trying to find new, more efficient yet cheap ways to remove various waste e.g. from water. Toxic metal ions are a big part of inorganic industry waste. These include ions of thallium, copper, lead, zinc, cadmium, nickel and much more [1,2]. Sorption of those cations has a potential to be one of the most effective methods for wastewater purification. One can divide sorbents into three main groups: organic sorbents (chitosan, copolymers, cellulose [3 – 5]), inorganic sorbents (zeolites and clay, carbon nanotubes, metal oxide nanoparticles [6 – 8]), hybrid sorbents [9, 10].

During our research, we focused on removal of copper (II), lead (II), silver (I) and thallium (I) ions from aqueous solutions using poly(sodium) acrylate hydrogel sorbent. To understand the studied material, the equilibrium and kinetic studies were performed. The efficiency of sorption of poly(sodium) acrylate in acidified solutions was also studied in an attempt to imitate industry wastewaters conditions. It turned out that, in such systems, the sorption capacities of the studied sorbent towards selected cations were still extraordinary compared to other hydrogel composites. For example, in the case of copper(II) cations, maximal sorption capacity in acidified conditions was ca. 270 $mg \cdot g^{-1}$, while the maximal sorption capacity towards lead(II) cations was ca. 650 $mg \cdot g^{-1}$. In the case of thallium(I) and silver(I) cations, the highest capacities exceeded 600 $mg \cdot g^{-1}$ as well. In order to test the sorbent's reusability, a series of sorption – desorption experiments were performed as well. The other aspect of our work was to compare the measurements performed by the X-Ray Fluorescence Spectroscopy (XRF) technique with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) technique. The XRF Spectroscopy in the handheld version is usually used to study solid samples. During our research, we wanted to test its ability to measure liquid samples. The ICP-OES technique was picked as a reference method to validate the XRF measurements. As a result, we achieved a good correspondence between both techniques.

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# POSTERS

## TUESDAY 25 June 2024: POSTERS P1-P30

## WEDNESDAY 26 June 2024: POSTERS P31-P60

# ICP Mass Spectrometry Assessment of the Bioavailability of Iron and Zinc from Edible Insects Available on the European Market

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Iron and zinc deficiencies are significant global health issues, causing problems such as anemia and weakened immune function. Foods rich in animal protein are important for combating these deficiencies due to their high levels of readily absorbable iron and zinc [1,2]. In this context, insects are emerging as a sustainable, protein-rich food source with a minimal environmental footprint, presenting a viable alternative for addressing micronutrient deficiencies [3].

Over 2,000 insect species are proposed for human consumption, necessitating thorough evaluation to understand their nutritional profiles. This study aims to assess the bioavailability of iron and zinc in various edible insects currently available on the European market to determine their potential inclusion in conventional diets. The species analyzed include a wide range of commercially available insects such as crickets, ants, mealworms, and sand and palm worms.

The goal of this work is to gain insights into the bioavailability of iron and zinc from edible insects available on the European market in view of their integration into mainstream diet. The species examined included a broad spectrum of commercially available species, including crickets, ants, mealworms, as well as sand and palm worms. However, because the composition of insects varies widely, the presented results may not be indicative for iron and zinc absorption from edible insects other than studied.

The study involved examining not only total elemental contents of the edible insects but also employing *in-vitro* assays for the evaluation of the release of iron and zinc from the food matrix at different steps of the digestion process: oral, gastric and intestinal. Gastric juice was found to be the most efficient in digesting the iron and zinc containing food components with only a negligible fraction digested by saliva. In addition, size-exclusion-ICP MS allowed the estimation of the MW of the species released.

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# Monitoring of Indoor Air Quality in Vegan and Vegetarian Restaurants

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Indoor air quality has become an important aspect of human life nowadays, while people may spend most of their time indoors [1]. WHO reports yearly about 3.2 million deaths due to indoor air pollution [2]. Pollution in indoor environment can be very high [3]. Several studies have been conducted in different indoor environments such as residences, schools, offices, hospitals, vehicles, and retail stores [4]. Information obtained from indoor air monitoring may contribute to the assessment of its health and environmental impacts, and subsequently to the mitigation of human exposure to indoor pollutants and [5,6]. Residential homes and schools have been the most frequent monitored indoor environments. Usually, $PM_{2.5}$, $PM_{10}$, volatile organic compounds (VOCs), nitrogen dioxide ($NO_2$), ozone ($O_3$), and carbon monoxide (CO) are monitored [7]. Sensors are the most generally used devices for long-term monitoring [6]. Interest for the investigation of indoor air pollution, especially from cooking emissions has increased in the last years, but no studies have been conducted in vegan and vegetarian restaurants. Therefore, present study focused on the monitoring of ultrafine particles, $CO_2$, $O_3$, $NO_2$, total volatile organic compounds (TVOCs) and formaldehyde (HCHO) in vegan and vegetarian restaurants in the warm and cold seasons using online monitoring devices. Detailed results will be presented on the poster.

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# Analysis of Polycyclic Aromatic Hydrocarbons (PAHs) in $PM_{2.5}$ Aerosol Collected at Granica Monitoring Station in Kampinoski National Park during Summer and Autumn Periods

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Polycyclic aromatic hydrocarbons (PAHs) are a large group of compounds emitted from natural and anthropogenic sources, typically during incomplete combustion. Over the years, they drew attention due to their potential toxicity, including carcinogenic, mutagenic, immunologic, and reproductive effects.[1] Since their highly negative influence on human health, their emission and concentration in the air need to be controlled.

In the presented study, we collected $PM_{2.5}$ samples at the meteorological station Granica, located in the Kampinoski National Park (Fig. 1), in autumn 2022 and summer 2023. Analysis of PAHs was performed using capillary gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) operated in the multiple reaction monitoring (MRM) mode.

**Figure 1** Kampinoski National Park (station Granica).

Overall, 70 samples were analyzed for the presence of 12 different PAHs. The most dominant were 5 and 6-ring PAHs: benzo[b]fluoranthene, benzo[a]pyrene, Indeno[1,2,3-c,d]pyrene and benzo[g,h,i]perylene. Additionally, our research showed a clear difference between the PAHs concentrations during summer and autumn periods. Higher overall concentration was measured during the autumn campaign, which is connected with intensified residential heating.

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# Optimization and validation of a highly sensitive method for determining glyphosate in food safety area

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Glyphosate is one of the most widely used herbicides. Its operation is: inhibiting the activity of the 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase enzyme, which is the key factor in the Shikimate acidic pathway. Glyphosate is impeding biosynthesis ofaromatic and amino acids, leading in consequences to plant death. In crops, glyphosate is used in the form of an ammonium, sodium or, isopropylammonium salt in order to eliminate weeds. European Union (EU), established the maximum residue levels (MRLs) for glyphosate, which are set for most plant and animal commodities at the limit of quantification (LOQ) of 0.1 mg/kg. Due to the constantly changing legislation and the market requirements for food safety, there is a need to develop a new analytical protocol for glyphosate quantification with low detection limits.

This work presents a new, modified method for the determination of glyphosate QuPPe (Quick Polar Pesticides Method) reference method. The method is based on the HPLC-MS/MS technique. The method was validated in accordance to the requirements presented in the document SANTE/11312/2021 for different matrices.

The developed method meets all validation requirements of the SANTE document,including LOQ of 0.01 mg/kg. Obtained recoveries are in the range (70 -120)% with expanded uncertainty <30%.

On this poster we present a comparison of the analytical parameters of the methods used for glyphosate determination along with their possible modifications. All compared methods are based on the HPLC-MS/MS technique. Following factors were investigated: different chromatographic columns, the addition of medronic acid into mobile phase and modifications in sample preparation process. The aim of the study was to develop and validate the most optimal method enabling quick, easy, cheap and stable analysis.

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# Improvement in the calibration strategy for sizing of selenium nanopowder using microwave plasma optical emission spectrometry operating in a single particle mode (SP-MWP-OES)

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Single particle microwave plasma optical emission spectrometry (SP-MWP-OES) is a real-time fast detection technique that allows capture of the light radiation events when single particles are vaporized, atomized and excited in the plasma, providing information such as particle count, size and stoichiometry. Due to the use of simultaneous multi-element specific detection, the proposed technique can significantly contribute to the characterization of multicomponent nanoparticles (NPs) [1]. However, the calibration of detection system for sizing NPs suffers from the lack of monodispersed nanopowder standards.

Recently, selenium nanoparticles (SeNPs) gained wide interest of many researchers due to their higher bioactivity compared with other chemical forms of selenium. Potential applications of SeNPs in biological systems strongly depends on their physicochemical properties. Thus, the careful evaluation of SeNPs size and chemical composition is required [2,3].

In this study, we proposed the use of SP-MWP-OES technique for determining size distribution and chemical composition of SeNPs synthesized based on microwave-assisted protocol using citrus juices as a source of reducing and stabilizing agents. It should be mentioned that the size of the resulting NPs can be controlled by adjusting the synthesis parameters such as microwave power. Thus, the calibration of the optical detection system for sizing SeNP was performed using pneumatic nebulization of powdered in-house synthesized nanomaterials, by correlating recorded light pulses from NPs entering MWP-OES, at specific emission wavelength, for 3 SeNPs standards with different size characteristics. The particle characteristics were established based on the results obtained by using scanning electron microscopy and single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). On the other hand, the elemental composition of each analysed particle was evaluated by examining the simultaneity of recorded pulses. A plot of the time-correlated signals of selenium and carbon confirmed that SeNPs were functionalized by biomolecules which contain carbon in their structure. Particle size distributions, average particle sizes and plots of the time-correlated signals were calculated by using an in-house developed single particle calculation tool.

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# Advancements in Lithium Quantification in Geological Samples using Sci-Trace/M-Trace LIBS Technology

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In the contemporary landscape of technology and energy, the demand for lithium, a critical component in batteries for electric vehicles, portable electronics, and renewable energy storage systems, is escalating rapidly. This surge is primarily driven by the global shift towards greener technologies and the increasing prevalence of electric vehicles, necessitating efficient and precise methods for lithium extraction and processing [1] . Our study presents advancements in the quantification of lithium in geological samples, utilizing the state-of-the-art Sci-Trace/M-Trace LIBS devices. These instruments have been pivotal in addressing the challenges associated with lithium analysis in diverse geological matrices. The focus of our research was on granites with lithium-rich micas and rhyolites, which are significant sources of lithium. We employed an approach of analyzing lithium content in pressed pellets, a standard technique that enhances the accuracy and reliability of the measurements while also dealing with the effect of sample both chemical and physical (dimensional) heterogeneity. A key feature of our methodology was the performance of measurements under an inert argon atmosphere. This environment is crucial for reducing atmospheric interference, thereby improving the precision of the lithium quantification. The study extensively evaluated three lithium spectral lines: Li I 610.36 nm, Li I 670.78 nm, and Li I 812.60 nm. The selection of these lines was based on their sensitivity and the ability to provide a comprehensive analysis of lithium concentrations in various geological samples.

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# Microwave-Induced Combustion in Disposable Vessels as a Sample Preparation Method for La Determination in Carbon Nanotubes

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Most of the detection techniques require the sample introduction in liquid form.[1] Depending on the matrix characteristics, the analyte to be determined, as well as its concentration and the selected detection technique, the sample preparation method must to be chosen appropriately [2]. The digestion of carbon nanotubes (CNT) is still a challenging matrix to be digested due to its refractoriness, requiring the use of large amounts of reagents to ensure the complete digestion, as well as longer reaction times. This work aims the use of microwave-induced combustion in disposables vessels (MIC-DV) as an approach for CNT digestion and further La determination by inductively coupled plasma optical emission spectrometry (ICP-OES). The parameters of MIC-DV that were not adapted from the literature were optimized, such as sample mass, volume, type and concentration of absorbing solution, and pressure applied into the disposable vessels. The optimized conditions of MIC-DV were applied for the digestion of two CNT samples for further La determination. The results were compared with those obtained after sample digestion by microwave-assisted digestion with single reaction chamber (MAD-SRC) and MIC and determination by ICP-OES, with agreement for both samples ranging from 92 to 99%. The method provided suitable relative standard deviation values (< 8%), considering the difficulties concerning to the CNT digestion. The limit of detection (LOD) and limit of quantification (LOQ) values for MIC-DV/ICP-OES were 1.3 and 3.5 µg $g^{-1}$, respectively. The proposed method overcomes some limitations presented by CNT digestion proposed in the literature, such as the long time for sample digestion and the use of large amounts of reagents, as well as the mixing of reagents for the complete matrix digestion.[3,4,5] Another advantage of the proposed method is its good performance under the aspects of the Green Analytical Chemistry, comparing with MAD-SRC and MIC.[6] To conclude, the proposed method was considered a simple, low-cost and fast sample preparation for the digestion of CNT, which is an extremely hard to digest sample. It was possible to determine La by ICP-OES after MIC-DV with suitable LOQ values. Considering all the advantages, the proposed method (MIC-DV/ICP-OES) is a suitable alternative for routine CNT analysis for further trace elements determination, such as La.

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# Speciation analysis of Gd complexes in river water using HPLC-ICP-MS

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Magnetic resonance imaging (MRI) is now one of the requisite imaging methods for medical diagnostics. Gadolinium (Gd) is used as a contrast agent for MRI to enhance the contrast of an image because of its strong paramagnetic property. Gadolinium-based contrast agents are administrated to patients in chelated form, because $Gd^{3+}$ is well known for its toxicity. In recent decades, several studies reported that the apparent positive anomalies of Gd in the REE pattern are shown in rivers running through metropolitan areas [1-3]. It shows that a part of the Gd-based contrast agents is emitted to river water without being processed during the sewage treatments, even though the long-term risks of Gd-based contrast agents for living organisms are not well elucidated so far.

Recently, our group has developed a HPLC-ICP-MS technique using the hydrophilic interaction chromatography (HILIC) column with the water-based eluent for the separation of Gd-based contrast agents [4]. In this study, the presented technique was applied to the speciation analysis to identify Gd-based contrast agents in river water in Japan.

River water samples were collected from the Muko River (Hyogo, Japan) in June 2018 and November 2020 near Sanda City, which is a suburban city with a population of 200,000. The concentrations of Gd in the samples collected in 2018 and 2020 (2018-O and 2020-O) were 97 ng $L^{-1}$ and 51 ng $L^{-1}$, and the magnitudes of the anomalies were calculated 39 and 17, respectively.

Gd-species in the river water samples were also investigated using the HILIC-ICP-MS technique with the water-based eluent. As a result, 3 kinds of the macrocyclic type of Gd-based contrast agents were found in 2018-O and 2020-O, although the linear type of reagents were not observed. The former were highly recommended to be used by authorities in Japan. The concentration of these Gd-species makes up 70% of the anthropogenic Gd. The results clearly indicate that a part of Gd-based contrast agents pass through the WWTP without being treated.

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# Combining mass spectrometry with electrochemical simulation to study mechanisms of alkaloid metabolism *in vivo*

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In recent years, a combined approach integrating electrochemical methods with mass spectrometry (EC-MS) has been gaining increasing popularity in research on the metabolism and degradation of biologically active compounds in the human body. This approach not only complements existing biochemical methods but also offers efficiency and cost-effectiveness in studying metabolic reactions. Specifically, the use of EC-MS facilitates the identification of products from electrochemical reactions and expands understanding of their potential roles in biological systems, which is valuable information for the fields of metabolomics and bioanalytical chemistry.

In this study, we focused on investigating the metabolism process of alkaloids, pharmaceutical substances, in the human body. It is known that alkaloids undergo metabolism to form N-oxides of alkaloids in the living organism under the action of liver enzymes. Therefore, our work aimed to obtain alkaloid N-oxides, establish their structure, and investigate the course of the reduction reaction. We used alkaloids of various origins and uses in our study: alkaloids of plant origin, which may be present in herbal raw materials, and synthetically derived alkaloids. For the synthesis of alkaloid N-oxides, an oxidation reaction was employed. The potassium peroxymonosulfate as the oxidizing agent in this reaction was served. The identification of the obtained metabolites and determination of their structure were conducted using high-resolution mass spectrometry.

For a deeper understanding of the metabolism and degradation mechanisms of alkaloid N-oxides in biological systems, an electrochemical approach using voltammetry was employed, which is an attractive method for studying drug metabolism. From a pharmaceutical standpoint, such an approach offers several advantages, such as cost-effectiveness, ease of use, and avoidance of ethical issues associated with the use of human or animal materials. We proposed a mechanism for the reduction of alkaloid N-oxides on the surface of electrodes, confirming the obtained reduction products using mass spectrometry. The reduction mechanisms involve electron and proton transfer, leading to the formation of derivative anion-nitroxide radicals or original alkaloids. The data obtained enable an understanding of the structural characteristics and electrochemical behavior of alkaloid N -oxides, which is significant for pharmacological and biochemical applications.

Therefore, the obtained results contribute to a better understanding of the metabolism and degradation processes of alkaloids in living organisms and provide a new impetus for research in medical, biological, and pharmaceutical fields.

# Evaluating multi-point and one-point calibration strategies for bioimaging by LA-ICP-TOFMS

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Laser ablation (LA) in combination with inductively coupled plasma mass spectrometry (ICP-MS) has become an established bioimaging technique, providing high sensitivity, high-speed mapping and spatial resolution in the low µm range [1]. The growing interest in quantitative elemental imaging is reflected by a plethora of proposed calibration strategies [2].

Especially for bioimaging applications there is a lack of certified reference materials for the preparation of matrix-matched calibration standards. In this context, gelatin has emerged as a fit-for-purpose calibrant for bioimaging by LA-ICP-MS. Due to its similarity to biological tissues, the matrix is widely used for external multi-element calibration.

In our laboratory, an external multi-point calibration approach based on multi-element gelatin standards produced by a robotic micro-dispensing device has been developed and validated [3]. With the established standards, everything is in place to streamline the calibration approach in the direction of one-point calibration, allowing to further reduce the analysis time [4]. We will test micro-droplets of certified serum reference materials for this purpose, and compare this high throughput method with multi-point calibration approaches.

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# Plasma assisted vapor generation of platinum group elements

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In this work, preliminary results achieved with a new plasma assisted vapor generation (PAVG) as an alternative and more efficient sample introduction technique for ICP-MS will be presented [1]. The PAVG was constructed using a tubular dielectric-barrier discharge (DBD) and a Meinhard type nebulizer (MicroMist) as liquid sample introduction into the DBD. An in-lab built power source was used for plasma generation. The platinum group elements (PGEs) were chosen for the preliminary studies, including Ir, Pd, Pt, Rh [2], Os and Ru. The early development of this new PAVG was focused mainly on the proper and robust construction of the PAVG generator, different electrode configuration and the power source modulation/input voltage for a stable plasma generation. ICP-MS/MS was utilized as a detection technique using He as a collision gas for preliminary experiments.

Once the device exhibited a robust performance, the research was subsequently focused on the examination of various conditions affecting the efficiency of vapor generation. Mineral acids ($HNO_3$ and HCl) and organic acids (acetic acid and formic acid) in different concentrations were tested as the carrier medium. The observed effects for individual PGEs differed significantly, suggesting the optimal conditions for vapor generation is different depending on the element. Using Cs as the element, which is assumed not to produce any volatile species by the PAVG, it appears that an important part of the measured analytical signal is obtained due to an increment in the sample aerosol transfer efficiency by the PAVG rather than in a generation of volatile species. Regarding generation of truly volatile species by the PAVG, the results are especially promising for Ir, Rh and Os. The constructed protype of the DBD device will be the base for future research on this topic.

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The support of the Czech Science Foundation (23-06530S) and Czech Academy of Sciences (Institutional support RVO: 68081715) is gratefully acknowledged.

# Infrared microspectroscopy in the study of biodistribution, kinetics and fate of microplastics in the body

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Synthetic polymers are currently among the most commonly used materials of everyday use. This is connected with the accumulation of plastic waste in the environment, which then breaks down into smaller pieces due to physicochemical factors. Micro- and nanoparticles of plastics can be easily ingested by living organisms, and their presence in the body may causes pathological changes in tissues and organs. Therefore, it is important to use appropriate methods for detecting micro- and nanoplastics and evaluating their impact on cells and tissues. An excellent method for both detection and identification as well as for assessing biochemical changes occurring in tissues is Fourier-transform infrared microspectroscopy (FTIRM).

In the study, FTIRM was used to determine the distribution and accumulation of administered orally standard polystyrene microplastics in the body of rats. Moreover, the mentioned technique was utilized to identify potential biochemical changes occurring in organs due to exposure and/or accumulation of these microparticles. Thirty-day-old female Wistar rats were used for the study. For two weeks, the animals obtained drinking water with polystyrene particles with a diameter of 20 and 30 μm. After the exposure period, kidneys, heart, liver, and spleen were collected for examination, as well as peripheral blood samples of the rats. Analysis of the collected organ fragments and blood smears did not show the presence of microplastics in them. Nevertheless, biochemical changes were observed in the organs of animals receiving water with polystyrene particles.

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**P13**

# Mass-spectrometry based, targeted analysis if amino acids reveals metabolic changes induced by low doses of cadmium (II) in vertebrates

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As a result of environmental exposure to Cd(II), it is important to understand the effects of low doses of Cd(II) and the mechanisms driving persistent accumulation. Here, we identified that treatment with low doses of Cd(II) results in defective integrated stress response (ISR) with distinctive metabolic reprogramming accompanied by mitochondrial cataplerotic depletion in mouse embryonic fibroblasts (MEFs), resulting in changes in amino acid (AA) profiles (Fig. 1A). The AA profile was determined using a Shimadzu 8030 liquid chromatograph LC-MS coupled to a triple quadrupole mass spectrometer using electrospray ionization in positive mode. The spectrometer employed a multiple reaction monitoring (MRM) approach. For derivatization, APDS (3-aminopyridyl-N-hydroxysuccinimide carbamate) was used, synthesized from the adapted procedure [1]. Additionally, the impact of low doses of Cd(II) on metabolism was evaluated using a metabolic labeling method for the detection of AA isotopologues using heavy water (D2O) or [U-$^{13}$C] glucose as tracers. We confirmed ISR induction using ATF4 protein as a marker in lysates of Cd(II)-treated cells. The inhibitor BCH was used to confirm the contribution of ATF4 target and the transporter Lat1 to the accumulation of branched-chain amino acids (BCAA) through their AA profiles. We evaluated cell synthetic capacity by labeling AA with $D_2O$ (Fig. 1B), which we confirmed with uniformly labeled $^{13}$C-glucose flux studies. The flux of main carbon chains from glucose to Glu, Asp, and their derivatives Pro and Asn decreased in Cd(II)-treated cells (Fig. 1C), and this dysfunction explains the observed deficiency in AA levels. Directed AA analysis revealed that changes in AA homeostasis induced by low doses of Cd(II) are partly the result of induced activity of membrane transporters and mitochondrial dysfunction. Similar pattern of changes was observed in 3-day-old zebrafish (*Danio rerio*) larvae.

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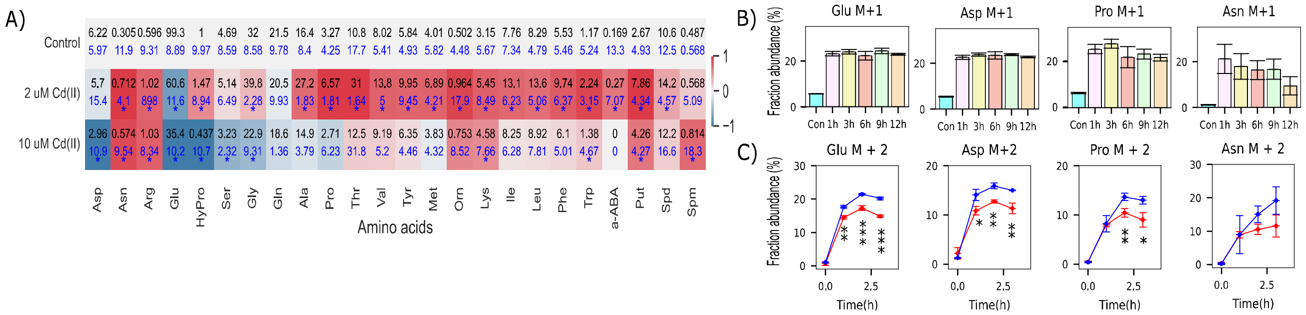

| | Asp | Asn | Arg | Glu | HyPro | Ser | Gly | Gln | Ala | Pro | Thr | Val | Tyr | Met | Orn | Lys | Ile | Leu | Phe | Trp | a-ABA | Put | Spd | Spm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Control | 6.22<br>5.97 | 0.305<br>11.9 | 0.596<br>9.31 | 99.3<br>8.89 | 1<br>9.97 | 4.69<br>8.59 | 32<br>8.58 | 21.5<br>9.78 | 16.4<br>8.4 | 3.27<br>4.25 | 10.8<br>17.7 | 8.02<br>5.41 | 5.84<br>4.93 | 4.01<br>5.82 | 0.502<br>4.48 | 3.15<br>5.67 | 7.76<br>7.34 | 8.29<br>4.79 | 5.53<br>5.46 | 1.17<br>5.24 | 0.169<br>13.3 | 2.67<br>4.93 | 10.6<br>12.5 | 0.487<br>0.568 |
| 2 uM Cd(II) | 5.7<br>15.4 | 0.712<br>4.1 * | 1.02<br>898 * | 60.6<br>11.6 * | 1.47<br>8.94 * | 5.14<br>6.49 | 39.8<br>2.28 * | 20.5<br>9.93 | 27.2<br>1.83 * | 6.57<br>1.81 * | 31<br>1.64 * | 13.8<br>5 * | 9.95<br>9.45 * | 6.89<br>4.21 * | 0.964<br>17.9 * | 5.45<br>8.49 * | 13.1<br>6.23 * | 13.6<br>5.06 * | 9.74<br>6.37 * | 2.24<br>3.15 * | 0.27<br>7.07 * | 7.86<br>4.34 * | 14.2<br>4.57 * | 0.568<br>5.09 |
| 10 uM Cd(II) | 2.96<br>10.9 * | 0.574<br>9.54 * | 1.03<br>8.34 * | 35.4<br>10.2 * | 0.437<br>10.7 * | 3.23<br>2.32 * | 22.9<br>9.31 * | 18.6<br>1.36 | 14.9<br>3.79 | 2.71<br>6.23 | 12.5<br>31.8 | 9.19<br>5.2 | 6.35<br>4.46 | 3.83<br>4.32 | 0.753<br>8.52 | 4.58<br>7.66 * | 8.25<br>6.28 | 8.92<br>7.81 | 6.1<br>5.01 | 1.38<br>4.67 * | 0<br>0 | 4.26<br>4.27 * | 12.2<br>16.6 | 0.814<br>18.3 * |

Fig. 1. Cadmium induced changes in AA metabolism. A) Amino acids levels in in Mouse Embryonic Fibroblasts, B) Metabolic labelling with $D_2O$, C) $^{13}$C Glucose flux, control (blue), Cd μM (red).

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# In *vivo* assessment of $TiO_2$ based wear nanoparticles in periprosthetic tissues

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Total hip arthroplasty is usually the only option for patients with advanced damage to their joints to prolong active life without considerable restrictions. Titanium and its alloys are considered the perfect material for implant manufacturing. However, when placed in the body titanium in ionic or particle form may be released from the implant to the surrounding tissue representing a potential health risk to the patient [1]. Thus, this study aimed to develop an analytical tool capable of investigating both forms of the released titanium with a focus on further characterization of the particle form. A multimodal approach combining inductively coupled plasma mass spectrometry (ICP-MS), single particle ICP-MS (spICP-MS), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) and Raman spectroscopy has been chosen to determine the total Ti, ionic Ti, and particle Ti levels. Additionally, the chosen approach is capable of providing information on the number, size, shape, and elemental composition of the titanium-derived particles. Periprosthetic tissue samples from 21 patients were analysed utilizing the multimodal approach. Lyophilized and homogenized samples were digested using two different microwave acid digestion procedures. One utilises hydrofluoric acid (HF), allowing for a complete dissolution of $TiO_2$ particles, this way a total Ti load in the sample was studied. The second digestion without HF left the particles intact enabling their separation a further examination. The solution ICP-MS revealed that up to 94% of the total titanium load could be present in the form of $TiO_2$ wear particles. The spICP-MS analysis confirmed the presence of the $TiO_2$ derived (nano)particles (NPs) with a 39 to 187 nm median size and particle count up to $2.3 \times 10^{11}$ particles per gram of tissue. On top of that, the SEM-EDS confirmed the presence of the $TiO^2$ nanoparticles with 230 nm median size and an anatase crystal phase determined by a Raman spectroscopy. The case study on a patient with a failed hip implant revealing the titanium nature in a tissue sample is shown in the contribution. The proposed multimodal approach enabled the first in vivo detection and characterization of titanium-derived particles in the periprosthetic tissue of patients with failing joint implants. This methodology can become a strong tool in future investigation of the effects of released titanium on the patient's well-being.

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# Microwave-sustained inductively coupled atmospheric-pressure plasma optical emission spectroscopy (MICAP-OES) for elemental analysis of clinical samples

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Microwave-induced plasma optical emission spectrometry (MIP-OES) has gained significant interest for trace element analysis in the last years as an alternative to inductively coupled plasma optical emission spectrometry, primarily due to its use of nitrogen as the plasma gas and a simpler hardware setup.[1] Among the latest advancements in MIP technology, the microwave-sustained inductively coupled atmospheric-pressure plasma (MICAP) deserves special attention. Previous studies have demonstrated that MICAP-OES offers a more robust discharge than other high-power ($N_2$)-MIP cavities, making it a suitable technique for analysing trace elements in samples with complex matrices. Even though it is still prone to matrix effects caused by high concentrations of easily ionizable elements, these can be appropriately overcome by means of matrix-matching of the calibration standards and the use of internal standardization without compromising sample throughput. [2] Thus, the goal of this study is to evaluate MICAP-OES suitability for elemental analysis of clinical samples (i.e., urine and human blood serum). To this end, spectral and non-spectral interferences were evaluated for major and trace elements (e.g., Mg, Ca, Na, Cu, Fe, Zn, etc.) across different dilution rates of the samples (i.e., undiluted, 1:5, 1:10 and 1:100-fold dilutions) with the subsequent selection of the optimal experimental conditions. Next, the analytical capabilities of the MICAP-OES were tested by means of recovery assays and the analysis of the Seronorm™ Trace Elements Serum L-2 certified reference material using external calibration strategies (with and without matrix-matching) and different internal standards (i.e., Pt, Rh and Sc).

Experimental results demonstrated that, MICAP-OES exhibits a remarkable robustness operating different matrices with high-solid contents regarding previous high-power ($N_2$)-MIP cavity designs, since a common nebulizer gas flow rate could be used for the different wavelengths irrespective of the characteristics of the sample dilution rated used. Moreover, matrix effects were only significant for the undiluted samples and the 1:5-fold dilution rate, whereas the 1:10 and 1:100-fold dilution rates did not present changes in the emission signal. Finally, MICAP-OES proved to be a successful analytical method for elemental analysis of clinical samples like urine and human blood serum.

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# Target and non-target analysis via HR-ToF-MS of particulate matter collected on two sites in Poland

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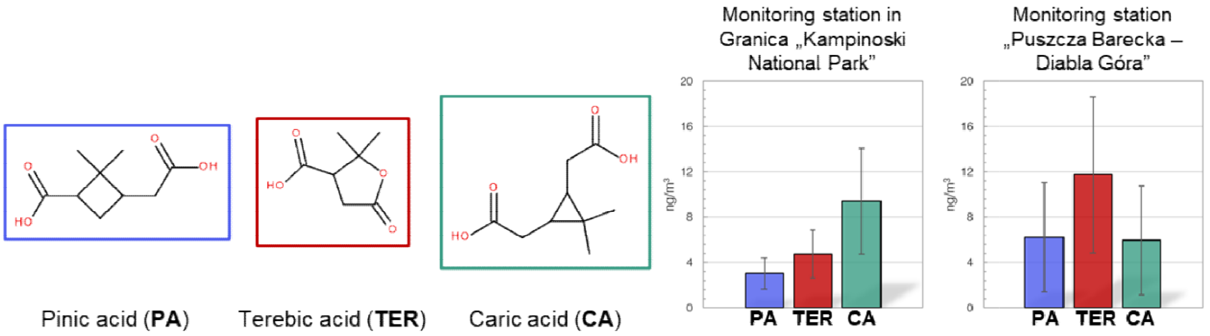
Secondary organic aerosol (SOA) is widely investigated because of its proven impact on air quality, people's health, and climate change. Important biogenic sources of SOA are biogenic volatile organic compounds (BVOCs) emitted from terrestrial areas. The amount of biogenic SOA in the troposphere is measured to be much higher than primary organic aerosol (POA).[1] Despite intensive research on SOA, it is still not fully described, and its formation is not completely understood.[2]

Our research focuses on studying an SOA formation in two forest areas in Poland – a monitoring station in Granica "Kampinoski National Park" and Puszcza Borecka - Diabla Góra. During two monthly campaigns in August and September 2022, we collected a series of samples of particulate matter ($PM_{2.5}$). Using the high-performance liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) we performed target and non-target analysis of collected samples to study the exact composition and sources of the formed SOA.

Our results show that the average concentrations of studied SOA traces i.e. pinic acid, terebic acid, and caric acid were 3.04 ± 1.37 ng$\times$m$^{-3}$, 4.77 ± 2.11 ng$\times$m$^{-3}$, 9.40 ± 4.64 ng$\times$m$^{-3}$ for samples collected in "Kampinoski National Park" station and 6.23 ± 4.82 ng$\times$m$^{-3}$, 11.75 ± 6.88 ng$\times$m$^{-3}$, 5.97 ± 4.78 ng$\times$m$^{-3}$ for samples collected in "Puszcza Borecka – Diabla Góra" station, respectively.(**Figure 1**)



Pinic acid (**PA**) Terebic acid (**TER**) Caric acid (**CA**)

Figure 1. Average concentrations of pinic acid (**PA**), terebic acid (**TER**) and caric acid (**CA**) with their mean deviations measured on two sites.

As an outcome of "non-target" analysis, we have observed the domination of compounds with a molar mass around 240 - 250 g$\times$mol$^{-1}$ or around 140 g$\times$mol$^{-1}$. Their concentration in the air was around 1 mg$\times$m$^{-3}$ or even higher.

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# Comparison of fluorine determination by high-resolution continuum source graphite furnace molecular absorption spectrometry and ion-selective electrode potentiometry with respect to animal feed safety

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Fluorine, depending on its concentration and chemical form, is essential or toxic to humans and animals. Therefore, it is crucial to be able to determine it reliably. In this work, fluorine was determined in animal feed after extraction to hydrochloric acid (gastric juices simulation) using the newly developed high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GFMAS) method and standard potentiometric method with a fluoride-selective electrode (ISE).

Feed samples turned out to be a challenge for HR-CS GFMAS. Chemical interferences (formation of competing molecules, CaF, GaCl and GaP, instead of the target GaF molecule) and spectral effects (including a phosphorous molecule spectrum and atomic lines) were identified. An additional difficulty was reagent contamination, as well as memory effects.

In the ISE method, the non-linearity of the calibration relationship at the concentration of $F^-$ bellow 0.1 mg $L^{-1}$ (which excludes standard addition calibration) and the reaction of fluorides with some cations ($Al^{3+}$ or $Fe^{3+}$) create some risk of inaccuracy. However, the results of HR-CS GFMAS and ISE methods (obtained for various kinds of feed and a wide range of F content) were consistent, which confirms the accuracy of both methods and informs that the extracted fluorine is in the fluoride form. The quantification limits of HR-CS GFMAS and ISE methods are comparable and satisfactory (1.5 and 1.0 mg $kg^{-1}$, respectively), as well as the precision (relative standard deviation at the level of a few per cent).

Generally, it was confirmed that the ISE method is simple, fast and cost-effective and is a good tool for routine control of F content in the feed. The HR-CS GFMAS can be used alternatively. The application of both methods enables their cross-validation.

The presented results obtained by the HR-CS GFMAS method and the results of extensive ISE tests conducted in Poland in 2021-2023 have shown that, in most investigated cases, the fluoride content is significantly lower than the threshold values published in the Directive 2002/32/EC of the European Parliament and of the Council of the 7th May 2002 on undesirable substances in animal feed (OJ L 140, 30.5.2002, p.10.).

# Selection of target molecule for investigation of fluorine release from dental fillings using high-resolution continuum source flame molecular absorption spectrometry

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The presence of fluorine in the oral cavity is necessary for teeth development and health. On the other hand, an excessive fluoride content leads to fluorosis, impaired thyroid, endocrine system and nervous system functions. The safest fluorine delivery route is topical application. One of the ways of F delivery is the introduction of fluorine compounds to dental fillings such as composites and glass ionomer cement. Under the influence of saliva and food, the gradual leaching of F takes place, which efficiency and kinetics should be known.

In this presentation, fluorine determination in 0.9% NaCl as a substitution for saliva will be discussed. The preliminary experiments showed that the amount of released F can be quite high (several dozen to several hundred mg of $L^{-1}$). Therefore, high-resolution continuum source molecular absorption spectrometry with flame (HR-CS FMAS) was selected as an analytical technique.

In HR-CS FMAS, fluorine is measured indirectly via molecular absorption of a target molecule, a monofluoride. A few monofluorides have been selected for testing, including GaF, CaF and SrF, known from the literature [1-3] (bond energy 577, 527 and 542 kJ $mol^{-1}$, respectively). However, the molecule of dreams was NaF (bond energy 519 kJ $mol^{-1}$), which was expected to be formed spontaneously in the investigated environment without the need to use additional reagents.

The main difficulty turned out to be spectral effects. The presence of complementary metals (1% Ga, 2% Ca and 5% Sr) caused a structured background which overlapped the target molecules' spectra. The OH, CaOH and SrOH molecules were responsible for that. Unfortunately, apart from many efforts, the NaF molecule was not synthesized in flame at all (on the other hand, Na atomic line, CS and OH molecule spectra were observed). Using the optimized conditions the best sensitivity (characteristic concentration of 6 mg $L^{-1}$) and detection limit (2 mg $L^{-1}$) were obtained in the experiments with the GaF molecule.

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# Determination of selected metals in food supplements using graphite furnace atomic absorption spectrometry.

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Food supplements are food items that are meant to supplement a standard diet and are concentrated sources of nutrients (vitamins, minerals) or other substances with a nutritional or physiological impact.[1] Besides vitamins and minerals, food supplements can also include other organic substances such as amino acids, alkaloids, fatty acids, dietary fiber, lutein, probiotics and prebiotics, etc. The composition and quality of food supplements must ensure that the normal use of these products according to the manufacturer's instructions is safe for the consumer. The popularity of these commercially available products is growing. The general view is that supplements are safe for health, but when these are taken too much or when the supplements are originating from a suspicious sources their impact on our body can be negative.[2] Unfortunately, dietary supplements are not subject to legal restrictions and regulations like medicines, so their composition (along with the raw materials used for the supplements formulation) is frequently not fully tested. Taking them from an unreliable source may result in health damage.[3] In this work, we have examined several commercially purchased food supplements for the content of harmful to health heavy metals (Fe, Mn, Zn, Pb, Ni, Cr, Cd). Food supplements (spirulina, chlorella, antaxanthin and kelp) based on marine algae were tested. Marine algae, frequently cultivated in urban areas, have an easy ability to accumulate heavy metals.

In this study, food supplements were mineralized and analyzed using graphite furnace atomic absorption spectrometry. Graphite furnace atomic absorption spectrometry (GFAAS) is a popular analytical method for determining trace levels of selected atoms. The main advantages of this technique are the low detection limit at the ppb level and the ability to test complex matrices.

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# Trace element levels in urban soil samples from central Poland (Lodz region)

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Soil is the outer, biologically active layer of the earth's crust, whose main substrate is the crucial, among other factors that determine soil composition. The two main factors playing a role in the case of heavy metal levels in soil are industry and traffic (exhaust emissions). The distribution of same metals can be influenced by the nature of the parent materials, the climate and their relative mobility [1,2]. One of the largest source of heavy metals, including platinum group metals (PGE), is vehicle emissions. PGEs occur naturally in very low concentrations. However, their levels are changing in time with the release of PGEs from vehicle catalytic converters [2]. Currently in the studies involving pollution of selected regions by heavy metals contamination are increasingly using a combination of geographic information technology (GIS) with geostatistical techniques are employed along with multivariate chemometric analysis. T. As a result of the combination of several approaches, the results obtained and their appropriate interpretation can have important implications for the development of strategies and policies to prevent widespread heavy metal contamination. [3]. In the present study, based on studies performed by the following techniques: ICP-OES (Cd, Cr, Cu, Ni, Pb, Zn, Fe), AAS (Hg, Pt, Pd, Rh), an attempt was made to determine the variability of the levels of toxic elements as the degree of contamination of the investigated soil samples assisted by the spatial and multivariate analyses. Optimization of the decomposition parameters was carried out using the NCS DC 73326a soil standard. Various reagents proportions were tested of the sample mineralization and conditions. An additional aim of this work was to confirm the usefulness of the applied statistical tests, multivariate analyses and geographical information systems in identifying the influence of spatial variability on the elemental composition of the studied samples. The obtained results in this project can be used to assess the extent of heavy metal contamination in soils, including PGE elements, and provide a basis for further monitoring to assess changes in levels in the future.

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# Assessment of the safety of the use of dietary supplements by women who are planning a pregnancy, are pregnant or are breastfeeding

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In recent years, there has been a growing interest in dietary supplements in Poland and around the world. There are many types of preparations available on the consumer market today, offering a variety of health benefits. These include special products for specific groups, such as supplements for women who are planning a pregnancy, pregnant women or women who are breastfeeding.

Pregnancy is a unique time in a woman's life. A series of developmental changes that transform these two gametes into a complex organism begins with fertilisation, the moment when the egg and sperm combine. In just forty weeks, a human body is created with an average birth weight of 3,338 g. During this time, a series of dynamic changes occur in the mother's body that accompany foetal development, with hormones playing an important role [1].

Pregnancy should be a time of peace and waiting for a woman. It should give her the opportunity to focus on her health and that of her baby. During this time, microelements play a key role in metabolism. An inadequate supply of essential nutrients can have an impact on the course of pregnancy, leading to: weakened placental function, increased risk of premature birth and developmental defects in the foetus. Therefore, it is important that a pregnant woman's diet is balanced and varied, and that it is enriched with appropriate vitamins and minerals in optimal amounts to promote proper foetal development and good maternal health [2].

It is recommended that the diet be modified and supplemented with essential ingredients that support the proper and undisturbed development of the foetus. For future mothers, supplements such as iron, DHA, vitamin D, iodine and folic acid are recommended [3].

The market for food supplements is constantly on the move. However, it is important to remember that supplements only complement a healthy diet, not replace it. The most important thing is to maintain a rational approach to a healthy diet and a healthy way of life.

The study included different types of supplements for: i) women planning pregnancy, ii) pregnant women, iii) breastfeeding women. A total of 34 samples were taken, including tablets (solid) and capsules containing oils. The samples were mineralised by reverse aqua regia using the Milestone UltraWave system, and then the elemental composition of the samples tested was analysed using the Thermo Fisher Scientific iCAP 7000 Series ICP-OES spectrometer. The following elements were determined in the tested samples Ag, Al, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, P, Pb, S, Sb, Sn, Sr, Ti, Zn.

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# Interaction of selected porphyrin derivatives with DNA

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Photodynamic therapy (PDT) is a promising treatment for both cancer and microbial infections. Photodynamic deactivation of microorganisms can be an effective complement to antibiotic therapy, contributing in particular to the elimination of bacterial resistance. PDT uses photosensitizers (PS) - substances that are characterized by minimal or no activity in the dark and maximum activity after exposure to light. The emerging singlet oxygen plays an important role [1]. PSs can be used as therapeutic agents or imaging agents in diagnosis. Photosensitizers interact with various cellular components, such as organelles, nucleic acids, lipids and proteins. They cause cell destruction.

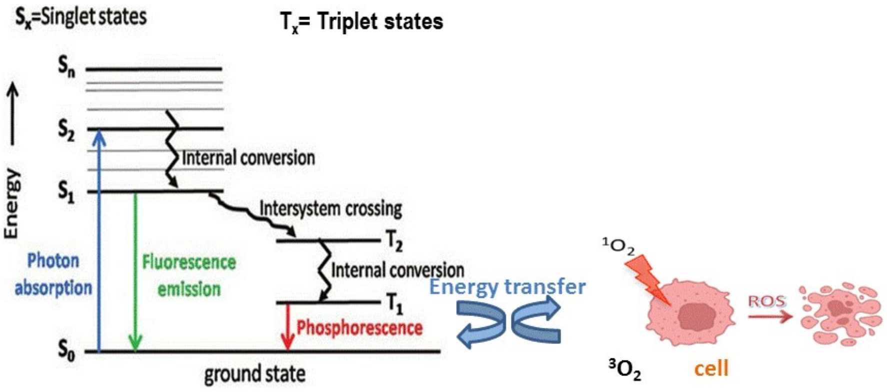

Figure 1. Jablonski diagram taking into account the emerging singlet oxygen

The interactions of six porphyrin (PS) derivatives with oligonucleotides with known nucleobase sequences were examined under conditions of darkness and white light irradiation of the tested solutions. It was found that there is a correlation between the results of spectroscopic and electrochemical methods. The conducted research confirmed the interactions of all compounds with oligonucleotides, confirmed the difference in the interaction in the dark and after illumination, and in the presence and absence of oxygen dissolved in the solution. Their effectiveness was also tested on selected cell lines.

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# Nicotine pouches - a new alternative to tobacco products

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In recent years, we have observed a dynamic development of the tobacco products market, and one of the interesting trends is the increasing popularity of nicotine pouches, whose roots date back to Sweden in the early 18th century. Nicotine pouches are small sachets that contain nicotine-based powders, they are also recognised as new, tobacco-free products. According to the manufacturer, nicotine salts are used, which are mixed with microcrystalline cellulose, various other salts (including sodium carbonate and hydrogen carbonate), citric acid and flavourings. Their attractiveness results from discreet use, variety of flavors and higher nicotine content compared to traditional cigarettes. Nicotine is fast and efficiently delivered by placing the sachet under the top one or lower lip, where it is absorbed through the mucous membranes. Even though tobacco-free pouches have been present on the Polish market since 2021, there are currently no proper legal regulations regarding their use, which raises concerns about increased addiction and health risks among young people. Situation is expected to change at the beginning of the new year and the introduction of excise tax [1-2].

The aim of this study was to assess the diversity of elemental composition of selected nicotine-containing pouches originating from various manufacturers and available in Poland market. The obtained results were evaluated against the selected parameters, i.e. brand or type of nicotine pouches used with appropriate statistical tests and multivariate principal component analysis PCA. In total, 60 types of pouches by 11 producers were analysed in two replicates. The sachets were different in terms of the type (nicotine, herbal, caffeine), taste and level of nicotine. Samples were decomposed in a mixture of nitric and hydrogen peroxide in a closed pressure system supported with microwave energy (UltraWave, Milestone). The total concentration of: Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Ni, P, Pb, S, Sr, Ti, Zn was measured by optical emission spectrometer with inductively coupled plasma (iCAP7400, Thermo). As part of the research, a survey was conducted regarding consumer preferences connected with the use of products containing nicotine, with particular emphasis on nicotine pouches. The questionnaire was completed by the 114 responders, among whom contribution of people using nicotine pouches reached 19%. Quantitative analysis of the sachets proved that their composition, despite the theoretically small amount of contaminants present, is quite varied. Elements, which concentrations influenced the most the discrimination of samples according to the manufacturer were: Al, Ca, Fe, K, Mg, Mn, P, S, Sr, Ti, while the type of nicotine pouches was defined mostly by the levels of: Ca, Cr, Cu, Fe, Mg, P, Ti. Considering the limits recognised as safe for the so-called smokeless tobacco products and amounting: 1.0 mg/kg for Cd, 2.0 mg/kg for Pb, 4.5 mg/kg for Ni and 3.0 mg/kg for Cr, these values have slightly been exceeded only in the case of Cr levels in two samples.

The data presented in this work and limited to the information about the elemental composition of nicotine pouches can suggest that these products may serve as a low-risk alternative to cigarettes or conventional, tobacco-based oral products.

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# Food authenticity studies supported by multivariate analyses

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Economic globalization and the rapidly expanding worldwide food trade have provided consumers with an unprecedented variety of food products on the market. At the same time, numerous cases of detected poisonings and adulterations have significantly increased consumer awareness of the quality and authenticity of the food they buy and consume. In Europe, geographical origin is one of the main factors influencing the authenticity of food. High-quality products with indications of origin, a special production method or a specific breeding method achieve higher retail prices and bring greater financial benefits to producers. There is therefore a justified need to protect such products against possible fraud, especially since the production of counterfeit food and illegal trade are ubiquitous phenomena. Food authentication is based on the analysis of measurable features that allow distinguishing products of different origins. Therefore, there is a growing need for reliable analytical methods that will provide a clear answer about the authenticity of products. As technology improves and the sensitivity of techniques increases, it becomes possible to perform measurements for an increasingly wider spectrum of determined variables, also due to improved detection limits. Analytical methods are often supported by multivariate analyses and statistical tests, thanks to which complex data sets are reduced or similarity between the considered groups of objects is established [1-3].

The aim of this research was to assess the diversity of the elemental composition of selected food products available on the Polish market in terms of verifying their authenticity using statistical tests and chemometric methods. The study was carried out on the group of single and multicomponent spices/herbs and their mixtures, which were simulating the potential adulteration. The results obtained for the prepared mixtures were compared with the data gathered for single-component spices/herbs. Before quantitative measurements, the milled material was treated with a mixture of concentrated nitric acid and hydrogen peroxide and placed in a closed pressure system with a support of a microwave energy (UltraWAVE, Milestone). The levels of the chosen elements were determined using optical emission spectroscopy with inductively coupled plasma, ICP-OES (iCAP7400, Thermo) and graphite furnace atomic absorption spectroscopy, AAS (Solar, Thermo). The correctness of the procedure was assessed by analysing the certified reference materials of Rice Flour IRMM 804, Spinach Leaves NIST 1570a, Apple Leaves NIST 1515 and Tobacco Leaves INCT-OBTL-5. Based on information from non-parametric tests and multivariate analysis, it was possible to determine the characteristic ingredients of specific types of spices/herbs. The research revealed that the limited number of measured elements can be used as markers for so-called food authenticity studies. PCA analysis proved its usefulness in detecting potential adulterations - samples acting as additives in the prepared mixtures formed separate clusters, distant in terms of their position from the original products in the projection of cases diagram.

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# Elemental signature of dried blood spots SARS-COV-2 patients

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On May 5, 2023, the World Health Organization canceled the status of the COVID-19 pandemic. However, this does not mean that the coronavirus has ceased to be a threat. This viral disease develops with severe clinical symptoms such as viral pneumonia, characterized by fever, fatigue, cough, shortness of breath, and other complications. Symptoms vary from mild to critical conditions, which often lead to the death of the patient. Therefore, the WHO has developed a strategic plan for preparedness and response for 2023-2025, designed to guide countries in transitioning to long-term treatment and alternative diagnostics of COVID-19. Additionally, it has been observed that individuals with severe COVID-19 exhibit significantly elevated levels of immunoglobulin antibodies against the SARS-CoV-2 virus. This discovery confirms a positive correlation between antibody levels and the severity of the disease, representing a significant advancement in recommending modern serological tests for rapid COVID-19 detection.

In clinical diagnostics, immunoglobulin M (IgM) and immunoglobulin G (IgG) tests based on enzyme-linked immunosorbent assay (ELISA) are used to assess COVID-19-induced pneumonia. Typically, the analysis requires several drops of patient blood on filter paper. Filter paper stabilizes the samples, meaning that dried blood spot (DBS) samples do not require stringent storage or transportation procedures, as with liquid samples. Moreover, safely stored DBS samples are suitable for postal delivery.

A vital tool in the elemental analysis of dried blood spots is laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This technique allows for the determination of blood elements without transferring samples to solutions. Laser ablation enables the direct sampling of microsamples, eliminating the need for complicated sample preparation.

The main objective of the study was to develop a new method for measuring the number of antibodies associated with the COVID-19 virus using DBS chemical analysis. During the method development, signals of seventy-eight elements were recorded using ICP-MS technique in the aerosol generated after Nd:YAG laser ablation. As a result of the conducted research, differences in the contents of some elements (Na, Mg, K, I, Ba, Hg) were observed in DBS samples obtained from healthy individuals compared to COVID-19 patients. The obtained results were subjected to statistical analysis. Linear discriminant analysis and principal component analysis were used to classify samples based on antibody levels in patient blood. The results of LA-ICP-MS analysis were compared with serological tests for IgG antibody presence. Such a study focuses on evaluating the correlation between blood elemental composition and IgG antibody levels against SARS-CoV-2 using LA-ICP-MS, representing an innovative approach to understanding the consequences of infection with this virus.

# Sorption and fractionation study of Te(IV) and Te(VI) in soil matrix

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Constant development of new technologies, including new ways of acquiring and converting energy, involves wider use of elements that have not previously been commonly present in industry. We refer to these elements as technology-critical elements and call them TCEs for short. These elements include Ge, Ga, In, Nb, Sb, Ta, Te, Tl, platinum group elements (Pt, Pd, Rh, Os, Ir, Ru), and most of the rare earth metals (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu). Tellurium is one of those elements for which we do not have much data regarding its behaviour in the environment, especially in the pedosphere. Within the framework of the presented research, it was decided to take a closer look at the interaction of different forms of Te with soils of distinct origins, to indicate the physicochemical transformations occurring in the soil environment, and to determine the mobility of tellurium species. Firstly, time-dependent sorption/desorption of Te(IV) and Te(VI) was compared in the presence of additives mimicking different soil systems. Findings showed that Te(IV) and Te(VI) interact differently with the studied matrices and that the sorption capacity is strongly dependent on the soil composition (organic carbon content and Mn and Fe oxides), as well as the presence of compounds produced by the rhizosphere activity. A series of single extractions was carried out to verify the fractions for which Te(IV) and Te(VI) have a higher affinity. The fractions were defined as follows: (i) the easily leachable/exchangeable and carbonate fraction (0.1 mol $L^{-1}$ $CH_3COOH$), (ii) the reducible fraction (0.1 mol $L^{-1}$ ascorbic acid in oxalate buffer) and (iii) the organic fraction (30% $H_2O_2$ at 85°C followed by 0.5 mol $L^{-1}$ $CH_3COONH_4$). The fractionation study showed a significant difference in the mobility of the two forms of tellurium, indicating that the mobility of Te(VI) is much higher. Furthermore, it has been demonstrated that organic matter plays a pivotal role in the binding of Te(IV), while Mn and Fe (hydr)oxides in the binding of Te(VI). These studies are of particular importance in light of a significant difference in the toxicity of both forms of tellurium.

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# How can be distinguished metallic and ionic platinum forms present in soil samples

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Platinum belongs to platinum group metals and is also an important element of technology-critical elements TCEs. It is mostly used in catalytic converters, so the highest Pt contents are observed in the vicinity of motorways [1]. The emitted particles containing PGEs are mainly of micron size range. It is reported that, on average, 66 % of emitted PGE-containing particles are greater than 10 μm, 21 % of particles are in the range 3–10 μm, and 13 % of particles are smaller than 3 μm.

Soil, as an important element of ecosystem, significantly affects the mobility and bioavailability of xenobiotics. As a result of its activity, it can limit the migration of introduced sub-micro particles or ionic forms of pollutants through retention. On the other hand, lowering the pH as a consequence of acid rain, or exposure to sunlight may increase the mobility and bioavailability of xenobiotics, and thus increase the risk of contamination of other ecosystems. In humic soil, Pt particles undergo a significant transformation, potentially leading to bioavailable Pt species, that can be taken up by plants.

The study is focused on distinguishing of ionic from metallic forms of platinum present in environmental matrix and assessing sorption capacity of soil [2]. Solid-liquid extraction, cross-comparison of the results of two determination techniques and two decomposition methods enable quantitative determination of the ionic form and, indirectly, NPs in soil. Information about ionic form is obtained after sample digestion with conc. $HNO_3$ and AdSV determination, and total Pt content is determined after digestion using mixture of conc. $HNO_3$ and conc. HCl. The recovery of Pt was in the range 99–110 % for both forms. The mobility (0.43 mol $L^{-1}$ 1 HAc) of Pt-NPs and Pt (II) was below 1 % even in the presence of citrates added to soil matrix. The long-term sorption study indicated that Pt retention (both forms) in the organic soil is related to formation of organic complexes, and the equilibrium is achieved after 2 days.

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# How to ensure stability of particular As and Tl species

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Speciation analysis is subject to errors resulting from the very fact of sampling, when the primary equilibrium is altered due to many transformations. It is quite difficult to prevent changes occurring between individual chemical forms of analytes during sample collection, but also during transport and storage in the laboratory. Importantly, sample preservation itself also affects speciation [1]. Having a simple separation procedure is extremely important from the point of view of water monitoring considering Tl and As species determination. Extremely fast reduction of Tl(III) and oxidation of As(III), which are unstable forms of mentioned elements, start just after sampling as a result of disturbed chemical equilibrium [2,3]. Separation of inorganic Tl and As compounds, unchanged, is thus crucial for reliable results of speciation analysis in water systems.

Presented studies describes a simple and fast sample pretreatment, based on ion exchange cartridges, which gives the possibility to separate Tl and As species already on the sampling site [3]. The use of SCX-3 allows for Tl(III) and SAX for As(III) separation, which are then quantitated in the effluent by ICP-MS. Determination of non-retained species was done after reduction of the sample volume to 2 mL (50-fold preconcentration), which allowed for detection of As concentrations <0.1 ppb and Tl <0.01 ppb. It should be stressed up that observed reduction of Tl(III) - about 15% - is in the range of losses typical for standard procedures based on Tl(III) fixation.

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# Analysis of the Drangsong collection of manuscripts using X-ray fluorescence spectrometry

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The investigations were carried out within the framework of the project "Protecting the Kingdom with Tibetan Manuscripts: Codicological and Historical Analyses of the Royal Drangsong Collection From Mustang, Nepal" (No. 2018/30/M/HS3/00372, funded by the National Science Centre)

The Drangsong collection of manuscripts, consisting of 336 different items with a total of 2900 folios, cards, or individual sheets of paper, represents the ritual repertoire of the priests of the kings of Mustang, once a Tibetan kingdom and now a district of Nepal. The texts have not been used since the priestly line ended in the 1950s or 60s. The value of this collection is twofold: first, the collection was assembled from different parts of Tibet and the Himalaya over six centuries, and offers a rich body of material which can be retrieved by material and codicological analyses that will contribute to our understanding of book and paper making traditions in the region, as well as social aspects of Tibetan manuscript production.

Fragments of papers from the Drangsong collection were examined using energy dispersive X-ray fluorescence spectroscopy (Tracer-III-SD, Bruker). All measurements were performed at a voltage of 45 kV, a current of 23.1 μA and in a partial vacuum. The spectrum of each sample of manuscript was measured for 60 seconds. Based on the obtained quantitative and qualitative data, similarities between the analysed fragments were searched for. The focus was on the determination of the relationship between the region of origin and the authors of the manuscripts in the information received. One of the goals of the experiments was to check whether, based on the XRF analysis, it is possible to assign manuscripts of unspecified origin to specific regions and, possibly authors.

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# A comparative analysis of the elemental composition of micro-samples of historical manuscripts with varying degrees of ink corrosion

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Inks found in historical documents present a unique challenge for conservators and researchers due to their diverse compositions and mechanisms of degradation. The most popular iron-gall inks have been used since ancient times until they were replaced by synthetically produced inks. Chemical composition this inks were fairly simple. The main ingredients are gall extract, vitriol (soluble salts) and binder (gum arabic). [1] Ink's additives were optional and depended on the availability of raw materials. The diversity of the chemical composition was the result of mixing different ingredients. This could result in chemical instability of the inks and then lead to degradation of the paper. Historical manuscripts may degrade over time. Apart from natural paper aging processes may result damage caused by the presence of free transition metal ions in the inks. Such we describe the mechanisms as ink corrosion. For the dominant mechanisms of this the process is considered to be hydrolysis or oxidation of cellulose. Acid hydrolysis induced is caused by the formed sulfuric acid (VI) and oxidation is a process catalyzed by $Fe^{2+}$ ions leading to depolymerization. Due to corrosion ink printing is the loss of the mechanical properities of the paper. For corrosion of inks, gallic acid and gum arabic may also be responsible. [2] Neevel indicators are papers soaked in bathophenantroline. This relationship looks like as follows and has a characteristic red colour when it forms a complex with iron in the secod oxidation state. The procedure for performing such a test is simple: wet paper should be applied to the recorded part of the object for a time that allows the migration of ions iron (II) on the indicator and the creation of a complex with bathophenantroline. [3] Original manuscripts can be examined using non-destructive methods. In archaeometry, the most popular method is XRF, which intervenes at the molecular level in the object. Nevela indicators allow for more detailed studies using destructive techniques without damaging the original artifacts. The method used to determine the elemental composition of inks is LA-ICP-MS. By utilizing both methods, one can obtain a comprehensive understanding of archival or library collections, thus delving deeper into the history they contain.

The research is devoted to a comparative analysis of the total elemental composition and an attempt to correlate the proportions of detected elements with the intensity of destruction of manuscripts by ink corrosion processes

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# Bioaccumulation of cadmium in fly *Lucilia sericata* - prospects for use as novel feed and food

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Farming of edible insects for animal or human consumption is growing due to their nutritional benefits such as high contents of good-quality protein and various micronutrients. However, insects should not contain any undesirable substances (such as heavy metals and other contaminants) to be safe for consumption. Cadmium is a toxic metal absorbed by organisms through the digestive tract along with contaminated diet. Therefore, research on Cd bioaccumulation by insects is important for the feed and food sector.

The aim of this work was to study the bioaccumulation of cadmium by the common green bottle fly *Lucilia sericata* (Calliphoridae), its transfer between developmental stages of the fly (larvae, puparial cases, and adults) and the effect on bioaccumulation of essential metals such as Cu, Mn, and Zn. Pork liver with natural Cd content and spiked with different inorganic compounds of cadmium ($CdCl_2$ and CdO) at four different concentration levels were used as feeding substrate for *L. sericata* larvae. Concentrations of metals in digested biological samples were determined by ICP-MS. The method quantification limits were equal to 0.21 ng/g for feeding substrate, 8.1 ng/g for larvae, 19.7 ng/g for adults, and 38.8 ng/g for puparial cases.

Cadmium was determined in all developmental stages of *L. sericata* collected from control treatment and Cd-enriched treatments, and accumulation of this heavy metal was positively correlated with its concentrations in an insect diet. The Cd bioaccumulation factors (BAF) in larvae and adults were dependent on the chemical form of cadmium, being higher for cadmium originally present in the feeding substrate (BAF: 1.3 – 3.9) than for its inorganic compounds added to this feed (BAF: 0.4 – 0.9). The study also showed that cadmium exposure may influence the content of microelements such as Zn, Cu, and Mn in edible insects. Moreover, cadmium concentrations in larvae and adults of *L. sericata* from non-spiked treatments exceeded almost all allowable levels established for insects intended for human consumption. It can be concluded that insects must be carefully tested for heavy metals to prove their safety as alternative feed and food products.

# Per and polyfluoroalkylated substances (PFAS) target and EOF analyses in ski wax, snowmelts, and soil from skiing areas

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Per and polyfluoroalkylated substances (PFAS) are common additives in ski waxes for their water repellent characteristic. Abrasion of ski wax leaves PFAS on the snow surface, however, little is known about the distribution and concentration of PFAS in snow and soil due to skiing. In this study we analysed different ski waxes, snowmelts and soil from family skiing areas from Alpine locations using targeted high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) to understand more about PFAS distribution in the environment. In general, we found a very diverse PFAS pattern in the analysed media. PFAS level was higher in skiing areas compared to the non-skiing ones that were used as control. Σtarget PFAS ranged between <1.7 ng L $^{-1}$ and 143 ng L $^{-1}$ in snowmelt, <0.62 ng g $^{-1}$ and 5.35 ng g $^{-1}$ in soil and <1.89 and 874 ± 240 ng g $^{-1}$ in ski wax samples. Snowmelt was dominated by short-chained PFAS, while soil and wax contained both short and long-chained PFAS. Extractable organic fluorine (EOF) was several orders of magnitude higher for waxes (0.5 - 2 mg g– 1) than for soils (up to 0.3 μg g $^{-1}$), while total fluorine (TF) content of the waxes was even higher, up to 31210 ± 420 μg g $^{-1}$. We also showed that the Σtarget PFAS accounts for up to 1.5 % in EOF content, showing that targeted LC-MS/MS gives a limited measure of the pollution originated from ski waxes and non-targeted analysis and EOF is necessary for a better overview on PFAS distribution.

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# Tryptophan modified fullerene[60] linked with graphene oxide in simultaneous toxic metal sorption and water purification

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Scientists are intrigued by carbon adsorption materials due to their notable characteristics, such as large specific surface areas, physical and chemical resilience, and the potential for surface oxidation and modification. Of particular interest are fullerenes, which possess a unique spherical structure formed by interconnected carbon hexagons. However, their hydrophobic nature and small size pose challenges for their use in aqueous solutions, complicating their separation from the solution.[1]

This study aimed to functionalize the surface of oxidized fullerene C60 by incorporating tryptophan. The resulting amino acid fullerene exhibited remarkable hydrophilic properties to the extent that it became partially soluble in water. This solubility stemmed from the deprotonation of numerous functional groups from the attached amino acid and the small size of fullerene particles. The amino acid fullerene was anchored onto graphene oxide to solve the abovementioned issue, stabilizing the resulting adsorbent in aqueous environments.

The presence of specific tryptophan functional groups facilitated the efficient complexation of Cr(III), Cu(II), Hg(II), and Pb(II) cations at pH 4.5, or selectively adsorbed Pb(II) ions at pH 3. The study delved into the mechanisms of ion adsorption using various adsorption isotherms (Freundlich, Langmuir, Temkin, and Elovich) and determined pseudo-first- and second-order kinetic equations. Additionally, the impact of ionic strength and coexisting ions on the adsorption process, as well as the affinity of the mentioned cations towards the adsorbent, were examined.

Preliminary findings suggest several potential applications for the adsorbent, including dispersive micro-solid phase extraction for concentrating and detecting Cr(III), Cu(II), Hg(II), and Pb(II) metals using spectroscopic techniques, as well as water purification.

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# Non-targeted analysis of wood-burning pollutants with liquid chromatography coupled to high-resolution mass spectrometry

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Globally, biomass burning (BB) is one of the major sources of emission of greenhouse gasses, non-methane volatile organic compounds, black carbon aerosols, and light-absorbing organic aerosols (atmospheric brown carbon, BrC) into the atmosphere. These pollutants are climate-forcing agents; they contribute to climate change by absorption of sunlight, alter the properties of clouds [1], and are a considerable health hazard [2]. Pollution associated with the combustion of biomass is likely to increase in the foreseeable future due to the widespread residential and industrial uses of wood and pellet fuel, and more frequent wildfires caused by progressing man-made climate change.

In this work, controlled, small-scale wood-burning experiments were carried out using a custom-designed laboratory combustor. To simulate the formation of the light-absorbing BrC during vegetation fires (smoldering conditions), the combustion of wood was carried out at low temperatures (250-400°C) in an oxygen-free atmosphere. The fine fraction of BrC aerosols generated in the combustor was collected and analyzed with ultra-high performance liquid chromatography (UHPLC) coupled with the electrospray ionization time-of-flight mass spectrometry (ESI-ToF/MS).

To gain insights into the molecular composition of the chemically complex BrC aerosols, UHPLC-ESI-ToF/MS analyses were carried out in data-dependant analysis (DDA) mode, yielding high-resolution fragmentation spectra of the ions corresponding to the major chromatographic peaks. Subsequently, MS-DIAL, MS-FINDER (mass spectrometric data-mining software) were used for data deconvolution and compound annotation using MS and MS/MS libraries [3]. Our workflow also included library-independent annotation of organic compounds under investigation with MS/MS spectra prediction algorithms embedded in CFM-ID software [4]. The performance of the developed workflow was evaluated using a standard mixture of 60 organic compounds typically encountered in BrC aerosols; >65% of standards were identified correctly. Initial analysis of BrC generated by the pyrolysis of commercial pellet fuel revealed >3000 unique features in both positive and negative ionization modes; complete or tentative annotation was achieved for >1200 molecules.

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# Overall efficiency of photochemical vapor generation: $TiO_2$ catalyzed PVG of Se

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Vapor generation improves the introduction of analytes compared to common solution nebulization and reduces some of the associated interferences. Photochemical vapor generation (PVG) uses UV radiation and solutions of low molecular carboxylic acids to produce volatile species of selected pnictogens, chalcogens, halogens, transition and noble metals. [1] These volatile species are usually hydrides, carbonyls, oxides or free atoms. [2]

Titanium dioxide has been established as an efficient photocatalyst for the on-line reduction of Se(VI) during the PVG of $SeH_2$ for the gas-phase introduction of Se into atomic spectrometers. The unknowns of this approach are the actual overall PVG efficiency of $TiO_2$-aided PVG and the experimental verification of the effect of $TiO_2$ properties on the overall PVG efficiency. This contribution compares two forms of $TiO_2$ (pure anatase and nanosized mixed phase $TiO_2$) for PVG of $SeH_2$ from Se(IV) and Se(VI) on the basis of the overall PVG efficiencies and figures of merit obtained, and supplements the information by investigating their particle size and crystal phase. Significantly better analytical figures of merit and generation efficiencies were obtained with nano-sized $TiO_2$ illustrating the greater importance of surface size over the crystal phase, because this photocatalyst was found to consist of approximately 87% anatase phase and 13% rutile phase. The optimum PVG conditions included 3.0 M formic acid, 0.02% (m/v) $TiO_2$ suspension and also 375 ng $mL^{-1}$ Co(II) and Ni(II) as sensitizers.

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# Plasma Spectroscopy in Pulsed Laser Ablation in Liquid (PLAL) for the Production of Metallic Nanoparticles

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Pulsed laser ablation in liquid (PLAL) plays an increasingly important role as the method for producing nanostructures without using chemicals and stabilizers. For example, it is a reliable, simple, and highly effective technique for generating metal nanoparticles. Monitoring the processes involved in the PLAL during nanoparticle production is very important to optimize the experimental parameters or if a new type of nanoparticle formation is requested.

The basic principle of the method is a material ejection, which is obtained by focusing a laser pulse on a metal target immersed in liquid. After the laser-matter interaction, the main processes include laser-induced plasma (LIP) generation and cavitation bubble formation. Spectroscopic analysis of LIP emission offers a powerful method for monitoring the processes taking place during the ablation generation of nanoparticles.

This work compares the spectral characteristics of laser-induced plasma generated on different metal targets in air or immersed in various liquids. It was shown that the responses of LIP spectroscopy signals in air, water, and organic solvents are different. Differences were attributed to the different plasma growth mechanisms in air and liquids. Generated nanoparticles were separated, and their size distribution and chemical composition were determined.

The essential task is to find the relationship between the spectroscopic data and the properties of the generated particles which will be also demonstrated in this work.

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# Selenium-enriched broccoli sprouts as candidate certified reference material for speciation analysis - specific study, selenium distribution, and characteristics

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Selenium plays a crucial role as a micronutrient in promoting human health and supporting plant physiology. To elucidate possible variations of selenium species in plant tissues, this study investigated the distribution of selenium in broccoli seedlings, including its accumulation in stems with roots and leaves. Total selenium content was determined using advanced analytical techniques, including inductively coupled plasma mass spectrometry (ICP-MS), and selenium speciation analysis using high-performance liquid chromatography (HPLC) coupled with ICP-MS. The results show different patterns of selenium accumulation in different parts of the broccoli plants. The highest selenium concentration was found in the roots, indicating a close relationship between selenium uptake and accumulation. Organic substances such as selenomethionine and Se-methyl-selenocysteine were found in all parts of the plant, as observed by selenium speciation studies. Inorganic forms of selenium, such as selenite, were also found, with lower concentrations varying between stem, root, and leaf. This study sheds light on the distribution and properties of selenium in broccoli sprouts and its potential impact also on human nutrition. Understanding the specific forms of selenium found in plant tissues can help in the development of strategies to increase the bioavailability of selenium and maximize its health benefits. Furthermore, these findings enhance our comprehension of selenium metabolism in plants and provide insights into the optimal approach for enriching broccoli sprouts with sodium selenite. This selenium enrichment process serves as an initial basis to increase the content of selenium in the broccoli sprouts to be produced as certified reference material (CRM), which in turn aids in the validation of methods for similar matrices.

# Methodological developments for selenium speciation in edible insects by elemental and molecular mass spectrometry

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The environmental and economic benefits of substituting traditional sources of animal proteins with those that require less feed, produce less waste, and result in fewer greenhouse gas emissions stimulate a growing interest in the introduction of edible insects into the European diet. However, the high diversity among insect species and their complexity as organisms make the characterization of these novel food products a challenge. In particular, there is an interest in assessing insects as a potential source of easily bioavailable essential elements [1].

Selenium (Se) is an essential element for both animals and humans, with its bioavailability critically depending on the speciation. In general, organic Se forms, such as selenomethionine (SeMet), are more bioavailable than inorganic ones [2]. Information on the selenium content in edible insects is very scarce, and the only published speciation report shows a very high content of inorganic selenium forms (in black soldier fly) [3].

The goal of this work was to revisit existing Se speciation methodologies to adapt them to different insect matrices. This allowed the assessment of Se distribution among different molecular forms in a broad spectrum of commercially available edible insect species, including crickets, ants, mealworms, as well as sand and palm worms.

At the same time, insects have the potential to be biofortified with different nutrients to improve their nutritional characteristics. The evolution of Se speciation during the enrichment of crickets with increasing doses of Se was also studied.

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# Speciation analysis of arsenic based on volatile species generation and in-situ preconcentration in a dielectric barrier discharge plasma

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Volatile species generation (VSG) comprises a group of techniques based on analyte derivatization in order to form a volatile compound prior to spectrometric detection. Selective analyte conversion from liquid to gas phase results in enhanced analyte introduction efficiency, but also in matrix separation and reduced risk of interferences. Moreover, VSG step can be utilized for speciation analysis or analyte preconcentration. Hydride generation (HG) induced by chemical reaction with $NaBH_4$ is the most common approach to VSG.

A significant difference in toxicity of various species of the same element leads to urgent need to develop strategies for speciation analysis. Various approaches to speciation analysis of toxicologically relevant arsenic species including inorganic As (III) and As (V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAsO) by HG-AAS were investigated in this work. All these species can be converted to volatile compounds. i.e. arsane and its methylated analogues. In atomic absorption spectrometry (AAS), the most frequent atomizers of volatile species are externally heated quartz tubes (QTA). Dielectric barrier discharge (DBD) atomizers have been proven to be alternative hydride atomizers to QTA. However, individual species have to be separated from each other prior to detection.

First, the ability of both atomizers, QTA and DBD, to atomize volatile As species was investigated. Comparable sensitivity was found among the species and between the atomizers under the optimized conditions. Secondly, two approaches to speciation analysis were compared. The first one employed a cryotrap device (CT) to separate and also preconcentrate the As species at the same time. This strategy is compatible with both atomizers, with QTA reaching better sensitivity and limits of detection.

A novel approach was based on HPLC separation of the species in the liquid phase and post-column HG followed by atomization in DBD with the in-situ preconcentration of individual species resulting into narrow peaks in the chromatogram and AAS detection in a fully automated procedure. Analyte trapping occurred in the presence of oxygen admixed to the discharge gas while fast analyte release and atomization is achieved by switching off the $O_2$ flow in presence of $H_2$ evolved from HG. QTA cannot be employed for in-situ preconcentration in that way. The method developed was validated by analysis of certified reference materials of human urine (NIST-2669) and marine tissue samples (TORT-3). A “hybrid” mode of determination was found useful for samples with greater difference in concentration of individual As species. Only the species present at low concentrations are preconcentrated while the others can be quantified in the same run but without preconcentration.

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# Radiolarite artefacts provenance: multimodal elemental analysis

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Radiolarites, siliceous sedimentary rocks composed mainly of micro-remains of radiolarians (marine plankton), have been considered an important raw material in the Palaeolithic assemblages of Central Europe. The rock was used for the manufacture of flaked stone artefacts and transported on large distances; thus, providing a unique material for studying the mobility of Upper Palaeolithic cultures: the Aurignacian (ca. 42 - 34 thousand years BP) and the Gravettian (ca. 34 - 24 thousand years BP). The multimodal approach combining petrological evaluation, X-ray fluorescence (XRF) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to determine the characteristic chemical fingerprint of the radiolarite artefacts. The presented study focused on the mobility of hunters from the Northern Calcareous Alps to the eastern fringes of the Pieniny Klippen Belt.
The developed approach was applied to 160 radiolarites collected in seven different areas, namely 1. Northern Calcareous Alps (NCA; AUT), 2. St. Veit Klippenbelt in and around Vienna (AUT), 3. Gerecse Mts. (HUN), 4. Miocene gravels under the Pálava Hills (CZE),
5. White Carpathians (SVK), 6. Pieniny Mts. (PL) and 7. Bakony Mts. (HUN). The advanced chemometric data evaluation (Linear Discriminant Analysis) classified the geographically specific radiolarite groups based on their Fe, Co, Ba, Nd, W, $^{206}$Pb, $^{207}$Pb, $^{208}$Pb and Ti features. We achieved a complete differentiation of the NCA, Vienna and Gerecse Mts. locations, while Western Slovakia and Southern Poland radiolarites formed an overlapping cluster. The LDA analyses allowed to trace radiolarite artefacts from Moravian Aurignacian, and Gravettian sites. [2] In addition, an online application was created to facilitate the provenancing of radiolarite artefacts with some degree of confidence for other researchers.

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# Is it worth becoming a coffee drinker? Application of spectroscopic techniques for the determination of selected elements in coffee

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The human body is constantly exposed to various elements in food, water, or air. Nowadays, there is growing interest in assessing the quality of food and, therefore, the amount of different elements present in it because of their nutritional importance as well as their harmful health effects. Food is the main source of these elements, so it is becoming necessary to monitor the elemental content of products for daily consumption [1]. Coffee is one of the most popular drinks in the world. Its prevalence entails assessing the quality of this product, which is why it is subjected to many analyses to determine the effects of coffee consumption on human health. The determination of elements in coffee is a broad topic that can be of great importance to the food industry. Also, consumers, increasingly, want to choose better-quality products [2].

In this study, the composition of selected coffee samples was considered in terms of the selected chemical elements present in them. Fifteen samples were prepared for the study, differing in manufacturer, degree of grinding, and price. The elements determined included sodium, potassium, calcium, magnesium, nickel, lead, cadmium, and mercury. Two methods were used to determine the elements: microwave-induced plasma optical emission spectrometry (MIP-OES) and cold vapour atomic absorption spectrometry (CV AAS). Based on the tests performed, the average concentrations of selected elements were determined with high repeatability, as confirmed by the low values of standard deviations. The highest concentrations in the analyzed samples were obtained for potassium (from 51 to 63 mg/kg), while the lowest concentrations were determined for mercury (from 0.55 to 34 μg/kg).

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# Evaluation of new extractants for arsenic speciation in microalgae

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Consumers are looking for healthy foods that contain various nutrients and exceptional health benefits. Today's consumers are demanding more natural foods with health benefits, and as a result, microalgae are expected to play an important role in the novel food industry in the future. Microalgae contain substances of high biological value, such as polyunsaturated fatty acids, proteins, pigments, antioxidants, vitamins, and minerals [1, 2]. The widespread interest in algal foods and/or their novel food potential is evident in numerous recent reviews and books [3, 4]. Microalgae have been used for centuries as a human food source or dietary supplement and are a good source of arsenic - the trace element important for the human organism.

The primary objective of this investigation was to search for new extractants (e.g. enzyme mixtures) of arsenic compounds for speciation analysis. The extraction of arsenic was optimised for selected microalgal species (*Arthrospira platensis*, *Ascophyllum nodonuri*, *Fucus vesiculosus*, L.). The total arsenic content in the algal species was also determined by inductively coupled plasma mass spectrometry (ICP-MS/MS). The highest total arsenic content in the tested microalgae species was found in brown algae (*Ascophyllum nodonuri*) - 62.113 μg $g^{-1}$, and the lowest - 0.682 μg $g^{-1}$, in spirulina (*Arthrospira platensis*). The total arsenic content in microalgae was used to determine the efficiency of arsenic extraction from microalgae, which also revealed differences in the effects of extractants. Certified reference materials were tested to validate the method used to determine the total content.

The second objective was the speciation analysis of arsenic in selected microalgal species using liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS/MS). The inorganic and organic forms (arsenobetaine (AB), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA)) were identified in all analysed microalgae.

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# The content of trace elements and heavy metals in seeds of leguminous plants when grown by eco-friendly and traditional methods

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Legumes from the legume family are one of the largest groups of plants very important for humans from an economic and nutritional point of view. The seeds of soybeans, beans lentils and broad beans are used as a source of protein, vitamins and mineral elements in human nutrition and for animal feeding. The aim of our work was to study the trace element composition of leguminous plant seeds and the content of heavy metals in plants grown in eco-friendly way and by traditional agriculture. Research was carried out on six types of leguminous plants: soybean (*Glycine max (L.) Merr.*), red and green lentils (*Lens culinaris Medik.*), chickpeas (*Cicer arietinum L.*), green peas (*Pisum sativum L.*), white beans (*Phaseolus vulgaris L.*). The seeds, grown in eco-friendly way on certified farms, were purchased in eco-products stores in Poland. Seeds grown by the traditional method were purchased at a grocery store. Content of mineral elements and heavy metals was determined using atomic absorption spectrometer Varian model AA240Z with the Zeeman effect, after preliminary mineralization of the samples.

The highest content of Mn was discovered in the seeds of chickpeas (219 mg/kg) and soybeans (199 mg/kg), and the lowest – in green peas (74 mg/kg), both under the conditions of traditional plant growing as well as of ecological cultivation. The highest Cu content was found in the seeds of white beans (11 mg/kg) and green lentils (102 mg/kg). The rest of seeds contained Cu at the level of 65-75 mg/kg. As in the previous case, the highest Zn content was also found in the seeds of white beans (640 mg/kg) and green lentils (568 mg/kg). Zn content in other seeds was at the level of 300 – 430 mg/kg. In terms of selenium content, seeds of green lentils and soybeans (1.6 mg/kg) in the case of traditional growing, and soybeans (1.2 mg/kg) when eco-friendly grown are worth noting.

Considering the content of heavy metals, our research showed the highest content of Pb, in green lentil seeds (1.8 μg/kg) comparing to other seeds (0.4-0.9 μg/kg) regardless of the method of growing plants. Average cadmium content ranged from 0.3 μg/kg for soybean seeds to 0.01 mg/kg for red lentils. When comparing the methods of seed cultivation, Cd content was significantly lower when eco-friendly approach was applied: 0.17 μg/kg versus 0.39 μg/kg for soybean seeds. Thus, even organically grown plants may contain traces of naturally occurring toxic elements, and the location may also play a specific role.

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# The use of natural deep eutectic solvents to study the speciation of copper and zinc in herbs by hyphenated techniques

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Natural deep eutectic solvents (NADES) are a class of solvents formed by combining at least one hydrogen bond acceptor and one hydrogen bond donor. These solvents are characterized by low toxicity and good biodegradability. They usually contain two or three substances, such as choline derivatives, organic acids, sugars and alcohols. They can be used to extract compounds from the groups of phenols, flavonoids, isoflavones, as well as proteins and sugars [1,2].

This work presents the obtained research results on the determination of speciation forms of copper and zinc in herbal extracts using combined techniques: size exclusion chromatography coupled to a mass spectrometer with inductively coupled plasma (SEC-ICP-MS) and liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). The plants tested were basil (*Ocimum basilicum* L.), thyme (*Thymus vulgaris* L.), and rosemary (*Rosmarinus officinalis* L.). Metal compounds were extracted from herbs with different types of NADES: (a) choline chloride with ethylene glycol (1:2), (b) choline chloride with urea (1:1, 30% $H_2O$), (c) choline chloride with glucose and water (1:1:10).

Research carried out using the SEC-ICP-MS method showed that NADES enable the extraction of copper and zinc compounds with different masses from plants. The signals obtained by this method for NADES extracts prepared from ethylene glycol indicate the presence of tested metals in several fractions with masses ranging from 13.7 to 44.3 kDa (for Cu) and from 0.14 to 44.3 kDa (for Zn). Plant extracts based on NADES prepared from urea gave Cu and Zn signals with retention times corresponding mainly to high molecular weight fractions (13.7-66.4 kDa). NADES prepared from glucose indicated the occurrence of copper and zinc compounds with masses of 0.14-44.3 kDa in plants. Moreover, signals for sulfur were obtained at the same retention times as for copper and zinc in NADES extracts prepared from glucose. This may indicate the presence of Cu and Zn in plants in combination with high-molecular compounds, which may be proteins.

In order to evaluate the speciation forms of Cu and Zn, two-dimensional liquid chromatography was used: SEC x LC using MS/MS detection. The presence of compounds from the polyphenol group (quercetin, caffeic acid and rosmarinic acid) in the fractions after SEC separation with a retention time corresponding to high-molecular compounds (13,7-44,3 kDa) may indicate the occurrence of these analytes in the form of phenol-protein-polysaccharide complexes in plants.

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# Determination of germanium species by hydride generation atomic absorption spectrometry: searching for efficient atomizer

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Concentration trends of Ge species in the environment are now in focus as the industrial consumption of Ge as a technology critical element is increasing. This study included three types of hydride atomizers: diffusion flame (DF), multiple microflame quartz tube atomizer (MMQTA), and dielectric barrier discharge (DBD) for Ge species detection by atomic absorption spectrometry (AAS) after hydride generation (HG). The atomization conditions of three volatile Ge species, which encompass germane ($GeH_4$), monomethyl germanium hydride ($CH_3GeH_3$) and dimethyl germanium hydride ($(CH_3)_2GeH_2$), were thoroughly optimized. Comparable sensitivity was observed among Ge species within each atomizer type. However, sensitivity values were extremely low for Ge, when compared with those reached by HG-AAS for other hydride forming elements. As generation efficiency of Ge species was found quantitative by means of ICP-MS, low sensitivity in HG-AAS is caused either by low atomization efficiency or by the rapid decay of free Ge atoms.

The atomization processes and the fate of free Ge atoms were studied by several advanced spectrometric techniques including laser induced fluorescence (LIF), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) employing $GeH_4$ as a model species. Spatial distribution of free Ge atoms can be visualized and their absolute concentration quantified by LIF. Free atoms were found only in the central part of the DBD discharge by LIF at a concentration 20 times lower than expected theoretically. The analyte deposited by decay reactions of free atoms at inner surface of the DF atomizer was characterized by SEM and EDS, implying that Ge is deposited as particles containing elemental Ge rather than Ge oxide. The deposited fraction was also quantified by leaching experiments with ICP-MS detection being around 80% in DBD and MMQTA and below 10% in DF. The results indicate fast decay of free Ge atoms.

Another type of hydride atomizer based on a plasma sustained between two tip-shaped rod electrodes in a quartz tube without a dielectric barrier was optimized for atomization of Ge species. The potential of HG-AAS to determine Ge species and mechanism of their atomization in flame and plasma atomizers will be discussed.

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# Feasibility of Reversed-Phase Dispersive Liquid-Liquid Microextraction for further Elemental Impurity Determination in Oily Pharmaceutical Excipients by ICP-MS

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Pharmaceutical excipients are inactive ingredients, which are included in drug formulations to ensure the stability of pharmaceutical products, improve the performance, and the bioavailability of active ingredients, providing a more efficient and safe treatment [1-3]. Among the several types of excipients available for the pharmaceutical industry, oily excipients have been recommended as a vehicle for some oily injectable drugs. However, these oily pharmaceutical excipients are not completely free from elemental impurities, such as As, Cd, and Pb, among others. Generally, these impurities are originated from the soil, pesticides, and catalytic processes during production, among other sources, and they can accelerate the oxidation and degradation of the oil, impairing the quality of the final product [6, 8]. Thus, in this study, the reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) method was proposed for the further elemental impurity of class 1 (As, Cd, Hg, and Pb) and class 2A (Co, Ni, and V) determination in oily pharmaceutical excipients to attend the International Council for Harmonisation (ICH) Q3D guideline recommendations. Analyte determinations were performed by inductively coupled plasma mass spectrometry (ICP-MS). The following parameters were evaluated: dispersant and extractant solvents, volume of extraction solution, sample mass, temperature, heating time, centrifugation, and stirring. Suitable results were obtained by using 5 g of oil, 1 mL of n-propanol and 1 mL of $HNO_3$ (3 mol $L^{-1}$ $HNO_3$ for all analytes and 6 mol $L^{-1}$ HCl for Hg), 20 min of heating at 85 °C, 1 min of stirring, and 10 min of centrifugation. Accuracy was evaluated by using certified reference materials (CRMs) of mineral oil, by comparison with results obtained after microwave-assisted wet digestion (MAWD), and also by analyte recovery experiments in three concentration levels according to the ICH Q3D recommendations and the United States Pharmacopeia (USP) for injectable drugs. No statistical difference was observed for the accuracy evaluation performed. Low quantification limits were achieved, such as 0.045, 0.006, 0.009, 0.020, 0.006, 0.040, and 0.102 μg $g^{-1}$ for As, Cd, Hg, Pb, Co, Ni, and V, respectively, which were lower than the maximum level allowed by ICH guideline. The proposed method presented several advantages for routine analysis, such as simplicity, high throughput, use of diluted solutions, and consequently low amount of laboratory waste generation.

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# Atomization of hydride-forming elements in atmospheric-pressure discharges

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The coupling of a hydride generation to atomic absorption or fluorescence spectrometry is a well-known method to trace element and speciation analysis. It enables efficient and "matrix-free" analyte introduction into the detector. Heated quartz tube atomizers or diffusion flames are the most common hydride atomizers. Nowadays also plasma atomizers based either on a dielectric barrier discharge or an atmospheric-pressure discharge (APD) are reported as alternative hydride atomizers. The dielectric barrier discharge is capable of efficient atomization of As, Se, Sb, and Bi hydrides while reaching poor sensitivity for Pb, Sn, and Ge. Besides dielectric barrier discharge, Ge is detected with low sensitivity even in the most common hydride atomizers.

Consequently, an APD-based atomizer was investigated in this work to overcome the low sensitivity observed in dielectric barrier discharge for elements mentioned above. Several APD designs were developed and tested using As, Se, and Ge. The first APD construction resembled the design of the diffusion flame. However, the discharge was unstable and suffered from low sensitivity due to a short optical path. The other two APD designs tested were derived from the quartz tube atomizer. In the first arrangement, analyte hydride was introduced through a quartz capillary in a parallel direction with the plasma. In the second arrangement, analyte hydride was introduced through an inlet arm perpendicularly to the plasma and the electrodes. The latter was selected as the best design its performance was compared to other hydride atomizers. The current-voltage characteristics of the APD power supply sources were also measured.

Moreover, the distribution and absolute concentration of hydrogen radicals/free analyte atoms in the APD were studied by two-photon/laser-induced fluorescence, and the results will be correlated with atomic absorption spectrometry experiments.

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# Elemental markers in identifying adulterations related to age and type of whisky

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The importance of copper in whisky production has been known for a long time. The source of Cu origin may be an alembic - a distillation vessel dedicated to the production of single malt whisky. This metal reacts with the distillate and, in a way, "extracts" undesirable sulfur aromas from it. Literature indicates that volatile sulfur compounds generated in the whisky production process have a significant negative impact on its quality. Selected alkyl sulfides (DMS, DMDS, DMTS) have been considered markers of the age of whisky because their level decreases significantly with the time the alcohol remains in the barrel [1,2]. This is particularly important in the context of assessing age-related adulteration of whisky.

The concentrations of a total of 30 elements were determined using ICP-QMS techniques (Ag, Al, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Sb, Sn, Sr, Te, Tl , U and V) and ICP-OES (Ca, Fe, K, Mg, P, S, Ti and Zn). The influence of factors such as the type (single malt and blended) and age of alcohols on their elemental profiles was verified. The product authenticity parameter was verified based on the analysis of 170 authentic whisky and 35 spirit samples of unidentified identity.

Differences in the concentration of copper, a metal whose presence is directly related to the vessel used to produce alcohol, made it possible to identify Scotch whisky according to its type (single malt and blended). Based on the analyses, a mutual relationship was found between age and the authenticity of products. Significantly higher concentrations of Mn, P and K were recorded for the original samples which were traditionally aged in wooden barrels for a minimum of three years. This may be related to the chemical composition of the wood, the process of burning the inside of wooden barrels and the agents used to impregnate them. Another element enabling the identification of age-related adulterations in whisky was sulfur. The concentration of this non-metal in the group of false samples (not aged or with a false aging period) was higher compared to the group of original samples (subjected to a minimum aging period of three years). A decrease in the content of alkyl sulfides with age is a characteristic phenomenon for alcohols matured for a long time in wooden barrels. The obtained results allow us to conclude about the influence of the whisky aging time on the levels of phosphorus, manganese, potassium and sulfur in the tested alcohol. These elements can be considered markers identifying the authenticity of whisky samples in terms of age.

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# Petrogenesis of concretions within sedimentary rocks using Raman spectroscopy

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Concretions are hard, massive, and spherical materials occasionally found in sedimentary rocks. They are filled with minerals such as calcium carbonate between clastic particles and sometimes contain well-preserved fossils. Recent studies[1][2][3] have shown that concretions form much faster than previously thought, from months to years, due to the reaction of calcium in seawater with carbon released from the remains of dead organisms. Various analytical methods have been used to study concretions, however, not much research has been done using Raman spectroscopy. In this study, we analyzed concretions by micro-Raman spectroscopy technique to obtain information about the generation and formation processes of concretions. Concretion samples were obtained from sedimentary rocks of the Cretaceous Izumi Group and the Miocene Morozaki Group, southwestern Japan. Firstly, we focused on apatite for the samples from the Izumi Group. Apatite is a calcium phosphate mineral contained in concretions. The band position and FWHM of the $v_1$ band of apatite can be used to infer whether apatite is of biogenic origin. Micro-Raman spectroscopic analysis of apatite was performed on both fossil-bearing and non-fossil-bearing concretions. Two types of apatite were found: one that appears to be biogenic and one that is inorganic. Apatite of possible biogenic origin was found in both concretion samples. The inorganic apatite is thought to have been formed by later diagenesis[4]. Secondly, the gigantic spherical dolomite concretion in the Morozaki Group was analyzed. Raman imaging, multivariate curve resolution (MCR), and classical least squares (CLS) methods were performed to identify the components of the concretion, and analyzed their distribution[5]. The concretion is composed of dolomite, kerogen, anatase, quartz, plagioclase and carbon materials. In particular, the Raman bands around 3000-2800 $cm^{-1}$ (CH stretching) and 1658 (amide I), 1585, 1455 ($CH_2$ bending), 1323 (amide III), and 1261 (amide III) $cm^{-1}$ in CLS suggests the presence of decomposed organic matter in the concretion. These results provide direct evidence that the giant concretion is of bioorganic origin. The concretion may have formed faster than the decomposition of organic matter, which supports the model that the formation rate is very fast. Additionally, the formation of the concretion had a carbonate sealing effect that prevented internal material changes even under the influence of temperature and pressure due to burial, up to 2 km below the surface after formation. This means that the original condition can be preserved for more than 10 million years. The use of Raman micro-spectroscopy and chemometrics provides direct and valuable information on the genesis and mechanism of concretion formation.

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# Development of a novel hydride atomizer based on atmospheric pressure plasma discharge for atomic absorption spectrometry

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Several analytically important elements (As, Se, Sb, Bi, Pb, Sn, Te and Ge) can be converted to their corresponding hydrides resulting in enhanced analyte introduction efficiency and reduced risk of interferences when compared to nebulization. Hydride generation (HG) is thus an elegant analyte derivatization and sample introduction step, compatible with atomic spectrometric detectors: atomic absorption (AAS), fluorescence (AFS) and optical emission (OES) spectrometry. The most common hydride atomizers in AAS include externally heated quartz tubes (QTA). Recently, plasma atomizers based on dielectric barrier discharge (DBD) have been successfully used for determination of As, Se, Sb and Te, while reaching not satisfactory sensitivity for Bi, Pb, Sn and Ge.

The motivation of this work was to explore the feasibility of plasma discharges other than DBD to serve as hydride atomizers for AAS. A novel hydride atomizer was constructed making use of the quartz body of a QTA atomizer. However, instead of resistive heating of the optical arm, two electrodes were inserted in its central part to sustain the discharge (0.5 kV, 30 mA). Subsequently, atomization conditions have been optimized individually for each hydride forming element including As, Se, Sb, Pb and Sn. The parameters optimized included discharge gas nature (Ar, He) and flow rate as well as the power delivered from the supply source. The effect of water vapor and aerosol co-generated together with analyte hydride on discharge stability and analyte response was also studied.

Finally, the sensitivity and limit of detection (LOD) were determined in this novel hydride atomizer under the optimum atomization conditions. They were compared with those observed earlier in QTA and DBD atomizers, respectively. The LOD values found in the proposed atomizer for arsenic and selenium (0.14 ng ml$^{-1}$ As and 0.11 ng ml$^{-1}$ Se, respectively) can compete very well with those found either in QTA (0.15 ng ml$^{-1}$ for both elements), or DBD (0.16 ng ml$^{-1}$ As and 0.24 ng ml$^{-1}$ Se, respectively). The analytical figures of merit achieved for other elements will be discussed. Another important feature regarding applicability of each type of hydride atomizer to routine analysis, i.e. is its resistance towards interferences, will be outlined.

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# Rapid Analysis of Phenolic Compounds in Plant-Based Milk Alternatives: A Smartphone-Based Approach

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The popularity of plant-based or non-dairy milk alternatives is steadily increasing as a dietary preference [1]. Phenolic compounds, essential constituents of these alternatives, contribute to their health benefits as abundant antioxidants. However, conventional methods for determining total phenolic content are often time-consuming and involve complex procedures especially in the presence of complex matrix analysis [2]. This study aims to develop a novel and miniaturized method for determining phenolic compounds in plant-based milk using digital image colorimetry on smartphones as a fast and cost-effective analysis method, along with the possibility of in-situ analysis. The procedure involves the application of the classically used Folin-Ciocalteu reagent for performing a color-forming reaction, followed by the extraction of derivative into the in-situ generated supramolecular solvent (Fig.1). The formation of such a solvent is observed due to the application of the green surfactant alkyl polyglycoside $C_8$-$C_{10}$ as an amphiphile and heptanoic acid as coacervation agent. The micellar solution facilitates efficient extraction, overcoming challenges posed by matrix components such as ash, protein, carbohydrate, crude fibre, and other interfering substances contents [3]. Digital images were captured inside a box under controlled lighting conditions and analyzed with image processing algorithms. Various types of plant-based milk substitutes, including plant extracts of cereals, legumes, nuts, seeds, and pseudocereals, have been analyzed. The results obtained, compared with reference methods involving methanol extraction and spectrophotometric detection, demonstrate significant findings, with a slope of the Passing-Bablok equal to 1.0024, indicating results are in good agreement. Moreover, assessments of the greenness based on the AGREE tool show a total score of 0.85, meaning that the procedure is environmentally friendly with a low environmental footprint [4].

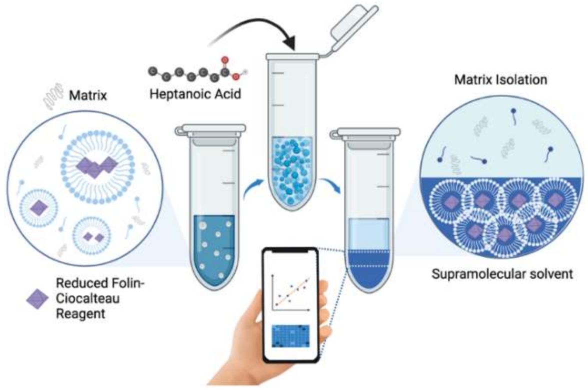

Figure 1. Rapid analysis of total phenolic content using smartphone

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# New polymer sorption materials for simultaneous separation and recovery of platinum group elements from waste

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Platinum Group Elements (PGE) are strategic metals for the economy, the supply of which is at high risk due to limited and rapidly depleting global resources, expensive mining processes, and wide use in many sectors of the economy [1]. Since 2011, they have been on the list of critical raw materials for the European Union.

Rhodium (Rh), palladium (Pd), and platinum (Pt), due to their good electrical conductivity, resistance to high temperatures and corrosion, and catalytic properties, are used in the automotive, chemical, and electronics industries. The most extensive amounts of Rh (91%), Pd (85%), and Pt (42%) are used in the automotive industry for the production of catalytic converters. Three-way ceramic catalytic converters are assumed to contain 0.8–1.5 g Rh, 1.5–5.0 g Pd, and 3–7 g Pt [1,2]. To meet the growing industrial demand for Rh, Pd, and Pt, they are recycled, mainly from spent catalytic converters.

The work proposes new polymer materials with advanced properties synthesized by copolymerization of thiosemicarbazide or 2-thiobarbituric acid with 1-vinylimidazole as a functional monomer and ethylene glycol dimethacrylate as a cross-linking agent in the presence of 2,2-azobisisobutyronitrile as an initiator. Using the batch extraction method, the conditions for simultaneous retention of Rh(III), Pd(II), and Pt(IV) ions on these sorbents (pH, contact time of the analyte with the sorbent, temperature) were optimized. Next, selectivity and the kinetic and equilibrium parameters of the sorption process were studied. Under optimal conditions, the retention efficiency of Pd(II) and Pt(IV) on new polymer materials was close to 100%, and the retention efficiency of Rh(III) ions was approximately 70%. The maximum sorption capacity was 3.24 mg/g for Rh, 45.3 mg/g for Pd, and 18 mg/g for Pt.

In order to monitor the concentration of PGE in spent catalysts and during the control of the metal recovery process from waste, a sequential method for the determination of Rh, Pd, and Pt using a high-resolution continuous source flame atomic absorption spectrometry (HR-CS FAAS) was developed. The usefulness of the developed materials was confirmed by using them for the separation and recovery of Rh(III), Pd(II), and Pt(IV) ions from samples of spent catalyst converters.

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# The analysis of small glass fragments from portable electronic device screens for forensic purposes

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Glass fragments are frequently found at numerous crime scenes, such as traffic accidents, burglaries, and street fights. The analysis of such microparticles provides a lot of crucial information, including details about the potential connection of the suspect with the crime scene. This is a result of the easy transfer of such micro-objects from broken glass objects to the clothing, shoes, or hair of people involved in the incident [1, 2]. Nowadays, forensic technicians increasingly often reveal micro-fragments of glass from the screens of mobile devices such as smartphones, laptops, tablets, and iPods at crime scenes. According to data collected by the World Bank Group, there were statistically 108 mobile numbers per 100 inhabitants of the world in 2022 [3]. These data confirm that nowadays, mobile devices have become an integral part of our lives. However, any appropriate research has not been carried out that would allow the development of a method for identifying the origin of glass fragments from smartphone screens and linking them to specific models of mobile devices. For this reason, such micro-fragments have no evidentiary value in cases related to traffic accidents or other crimes in which the screen of a portable electronic device was broken.

The examination of levels of O, Na, Mg, Al, Si, K, Ca, and Fe in each glass sample from smartphone screens (PED), glass containers (P), and float glass (CW - window sheets and vehicle windows) was carried out in 4 replicates with the usage of a Scanning Electron Microscopy Coupled with an Energy-dispersive X-ray Spectrometer (SEM-EDS, HITACHI S-4700, EDS Thermo NORAN). All obtained results were interpreted with the usage of statistical and chemometric tools. The gathered data prove that glass samples from specific layers of smartphone screens (PED) could be distinguished from glass fragments from other analyzed categories (CW+P) based on their elemental composition.

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# Alterations in elemental distribution in rats' brains with autism spectrum disorder - comparative analysis of LA-ICP-MS images

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Autism Spectrum Disorder (ASD) is a neurodevelopmental disorder characterized by persistent difficulties in initiating and maintaining social communication and limited, repetitive and inflexible behaviour patterns. The exact etiology of ASD is unknown, however the potential causes may be genetic, epigenetic and/or environmental [1]. In people with ASD, compared to healthy people, differences were observed in the content of selected elements (including Al, As, Cd, Cr, Mn, Pb, Se) in body fluids and tissues. In addition to the total content of elements, only their distribution in tissues can change [2,3], which can be analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). This method was used in comparative studies on the content and distribution of a panel of elements necessary for the functioning of the body, as well as potential environmental toxins, in three areas of the rat brain (forebrain, hippocampus and cerebellum). The study included the control group and the experimental group (1-month-old) of animals. Autism was induced by a single administration of teratogenic agents (thalidomide or sodium valproate) to their mothers on the 11th day of pregnancy. The sample preparation procedure and calibration method based on in-house gelatin standards were optimized. Statistical data treatment based on Principal Component Analysis and Analysis of Variance was performed. Statistically significant differences were observed in Zn distribution in selected parts of the brain between control and experimental group. The obtained results indicate the need for elemental analysis not only of the total content, but also of its distribution in the tissue.

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# Separation of inorganic forms of tellurium using on-site SPE followed by ICP-MS or ICP-OES – the right solution for Te monitoring in water

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Tellurium is one the technology-critical elements, for which the demand has increased due to their application in the emerging technologies. With solar panel production accounting for 60% of the annual Te consumption, an often raised issue are the potential risks to human health and the environment associated with exploitation of large quantities of CdTe photovoltaic panels (PVs). Especially, there is rising concern about Te species leaching from landfills after inadequate disposal of PVs. In water, tellurium mostly occurs as Te(IV) and Te(VI) oxyanions. Both are considered toxic, and their toxicity depends on speciation – tellurites(IV) are about 10 times more harmful than tellurates(VI). Both anions are also highly soluble and mobile in the environment. Therefore, the study of Te, including speciation analysis, should be considered in modern monitoring of water reservoirs as part of the sustainable development of new technologies. The most tricky part of speciation analysis is sampling and sample pretreatment, because the equilibrium between speciation forms is fragile, and the primary speciation can be easily disturbed. Metalloids oxyanions could be oxidized in the presence of Fe/MnOx (suspended particles in water) as a result of photocatalysis occurring under UV-Vis exposure. Oxygenation of the water system may cause changes in the ratio of Te oxyanions. Therefore, maintaining the stability of the studied species is quite challenging, and chemical fixation is not always a good solution as it may trigger an answer of the speciation system aimed to maintain the redox equilibrium. Therefore, separation of chemical forms immediately after sampling, without prior interfering with the primary speciation, seems to be a better option. Solid phase extraction (SPE) can be used on-site due to its simplicity and transportable equipment. A commercially available anion exchange SPE column was proposed to retain anionic Te(IV) and separate it from Te(VI). Separation is based on differences in protonation of both anions, which depends on pH of the solution. The proposed procedure could be applied on a large scale in routine environmental monitoring of water to determine Te forms with elemental techniques such as ICP-OES and/or ICP-MS, after on-site sample pretreatment. Separation of the species just after sample collection allows off-line determination and long-term storage.

# Ensuring the Validity of Proteomic Results: A Case Study in Monitoring Fluorine-Containing Drug Therapies

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Proteomic analysis using advanced high-resolution mass spectrometry technology is a multi-step process that includes sample preparation, mass spectrometry measurements, data analysis and interpretation of the results using appropriate databases as well as bioinformatics tools. The results of such studies are crucial for a comprehensive understanding of the mechanisms of biological processes, thereby confirming the safety of administered drugs. However, to draw conclusive insights from proteomic studies, the reliability and reproducibility of the results must be ensured. The validity of results in proteomic research requires consideration of multiple factors at each stage of the analytical process. The preparation of clinical tissues must be meticulously performed according to validated protocols to ensure that protein extraction, digestion, and sample preparation for LC-MS/MS do not introduce changes or contaminants that could affect the results. Additionally, proper calibration of measurement equipment is essential for obtaining reliable data, particularly in quantitative label-free proteomic analysis.

This presentation discusses the implementation of ISO/IEC 17025 "General requirements for the competence of testing and calibration laboratories" and ISO 15189 "Medical laboratories – Requirements for quality and competence" standards in the validation process of proteomic studies [1]. Within the context of these standards, it outlines procedures for developing a universal protocol for conducting proteomic research, including the calibration of high-resolution mass spectrometers and monitoring the stability of chromatographic conditions. The proposed protocol for the validity of proteomic results has been applied in our laboratory to monitor the safety of administered fluorinated drugs [2,3].

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The study was carried out in laboratories of the University of Warsaw, accredited in accordance with ISO/IEC 17025:2017 "General requirements for the competence of testing and calibration laboratories" (accreditation number: AB 1525) by the Polish Centre for Accreditation, and the medical laboratory of the University of Warsaw, with implemented requirements in accordance with ISO 15189:2022 "Medical Laboratories– Requirements for Quality and Competence" (laboratory in accreditation process).

# Xanthine oxidase activity levels correlation with molybdenum concentration in the livers of the donors and recipients of liver allografts

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Liver parenchyma, including bile duct epithelial cells, are rich in xanthine oxidase (XO). This rate-limiting enzyme catalyzes the final steps in purine catabolism, converting hypoxanthine and xanthine into uric acid. It exists under normal conditions in the dehydrogenase form, which does not generate superoxide, and in the oxidase form, which does. During ischemia or proteolysis, the dehydrogenase form prevalent in most cells can transform into an oxidative form. This transformation produces reactive oxygen species, which can induce oxidative stress and organ dysfunction by causing protein fragmentation, lipid peroxidation, and direct tissue damage. XO's significance extends to various liver pathologies.

Studies on chronic liver diseases have shown significantly higher serum XO levels compared to healthy controls with the greatest increases in some cholestatic disorders. In addition, non-alcoholic fatty liver disease (NAFLD) shows an indirect connection with XO activity, as NAFLD patients often exhibit high serum uric acid levels. Researchers have linked NAFLD with hyperuricemia onset, suggesting that XO plays a crucial role in NAFLD progression and may serve as a promising therapeutic target for patients.

In this study, we examined XO activity levels in the liver tissue of the 40 patients who participated in liver transplantation (as a donor or recipient). Participants were divided into 2 groups and 6 subgroups: 10 donors (control group) and 30 recipients (study group). The latter is further divided into 5 categories by primary liver pathology: 6 Alcohol liver disease (ALD), 9 viral infection (HBV or HCV), 4 primary biliary cholangitis (PBC), 6 Primary sclerosing cholangitis (PSC), 5 Wilsons Disease (WD). The XO activity levels were compared between control group and each study group separately. The statistically significant differences were noted in groups with liver failure induced by viral infection ALD, PSC and PBC. Every study group showed reduced XO activity comparing to the control. Moreover, the content of molybdenum (Mo), a vital cofactor for the proper function of XO, was determined by inductively coupled plasma mass spectrometry. The content between the Mo and XO activity was established (Fig. 1).

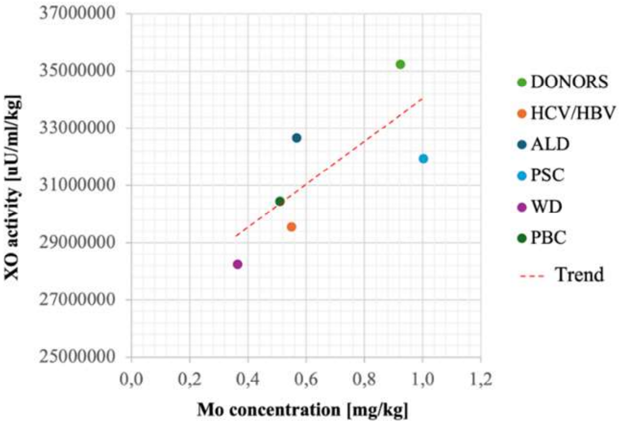

*Figure 1. XO activity and Mo concentration correlation*

# Application of multicollector mass spectrometry and laser ablation in the study of magnesium isotopes fractionation phenomenon during transport through an ion-selective membrane

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The development of muliticollector inductively coupled plasma mass spectrometry (MC-ICP-MS) has enabled highly precise isotopic analysis of magnesium in previously unexplored areas of knowledge. A good example is the study of the division of Mg isotopes between two coexisting phases in samples of plant, animal, and even human origin. Such fractionation phenomena have been discovered during the observation of different directions of Mg isotope fractionation in plants with different carbon bonding mechanisms (C3 and C4) [1]. So far, it has been assumed that the intracellular isotopic composition of Mg depends on the rate of Mg binding in intracellular compartments and on the ratio of the rate of magnesium transport inside and outside the cell. However, to gain expanded knowledge about the mechanisms of Mg ion transport through the cell membrane, it is first necessary to conduct more advanced studies on the fractionation of Mg isotopes during passage through a membrane built of synthetic compounds, replicating the ability of a biological membrane to transport Mg.

The aim of the study was to investigate the process of magnesium transport through a selective membrane for Mg ions synthesized *in vitro*. A system with an ion-selective membrane containing a magnesium ionophore (ETH 5220), a lipophilic salt (potassium tetra-p-chlorophenylborate), plasticizers (chloroparaffin, o-NPPE), and a polymeric matrix (PVC), which separated the magnesium salt solution from the solution containing calcium salt, was constructed. Elemental and isotopic analysis of solutions on both sides of the membrane, as well as the membrane surface itself, was carried out. Changes in magnesium and calcium concentrations in solutions on both sides of the membrane were investigated to verify whether ions of these metals are transported from one side of the membrane to the other. MC-ICP-MS technique was applied to measure the isotopic ratio of Mg in this solution to indicate possible isotopic fractionation of Mg during transport through the membrane. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to compare the calcium and magnesium composition on the membrane surface before and after the experiment and the distribution of theseelements in the membrane at selected points.

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# Development of multifunctional reference materials for environmental and food safety applications

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Two innovative projects, the MPWN (Multifunctional Polish Natural Waters) and the MultiBio CRM (Multifunctional Biological Reference Material), are currently being developed at the University of Warsaw's Faculty of Chemistry in collaboration with GUM (Central Office of Measures) and Jan Kochanowski University in Kielce. These projects aim to produce robust reference materials crucial for environmental and food safety analyses in Poland.

The MPWN project involves selecting sampling sites such as Lake Roś for water collection, followed by rigorous preparation steps including filtration, acidification, and the admixture of selected elements to achieve desired analyte concentrations. The MultiBio CRM project focuses on the leaves and fruits of strawberries, with the latter being particularly difficult as a reference material due to their moisture content and clumping properties.

A key innovative feature of both projects is the incorporation of microplastic analysis. Identifying and quantifying microplastics in environmental and biological matrices is challenging due to the limited analytical techniques available. The projects aim to develop and validate methods for analysing microplastics in complex matrices like fruits and leaves. This aspect will be one of the major difficulties, requiring precise analytical procedures to ensure accurate and reliable results.

Both projects emphasise the need for inter-laboratory studies to validate measurement consistency and reliability across different testing facilities. Collaboration with external laboratories is encouraged to facilitate these studies. Interested parties are invited to contact us to participate in these inter-laboratory tests by providing contact details for sample submission.

These initiatives underline Poland's commitment to advancing metrological standards, ensuring compliance with regulatory requirements, and enhancing accessibility to locally produced certified reference materials. The MPWN and the MultiBio CRM represent a significant step forward in promoting health, safety, and environmental sustainability through robust metrological practices.

# Comparative analysis of text underlining and marginalia written in iron-gall inks in the Nieśwież Bible using X-Ray Fluorescence Spectroscopy.

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The Nieśwież Bible, a landmark in Polish biblical translation history, printed in 1572, holds unique features: underlined words and phrases alongside marginal notes inscribed in Latin and Arabic using iron-gall inks. This study aims to establish a chemical correlation between these underlines and marginal annotations based on the application of X-Ray Fluorescence Spectroscopy (XRF).

Hand written prayer book from a private collection was selected as the test object to perform optimization of working conditions. The aim of the optimisation was to obtain a readable XRF spectrum with clear signals for both major (Fe) and minor (Cu, Mn, Zn) elements, using the shortest possible measurement time. It was also necessary to block the possibility of excitation of fluorescence signals from the pages in the book block underneath the one which was investigated.

The measurements were conducted using the ELIO (Bruker) and Tracer SD-III (Bruker) XRF spectrometers. Optimization of instrumental parameters included the time of spectra collection (t = 30-300s) and materials employed as radiation shields between individual pages. Both organic (e.g., parafilm, paper, acrylic tile) and inorganic (e.g., palladium, aluminium foil, gold leaf sheet, pure Si wafers, Rh plate, graphite) materials were tested. Rhodium was selected as the most effective radiation shield, efficiently attenuating signals from other pages without interfering spectra registered for inked areas of the manuscript. The suitable acquisition time was determined to be 210 s for ELIO, while no significant variance in spectra intensity was observed for Tracer spectrometer.

This study can be used as an example demonstrating the potential of non-invasive comparative XRF analysis of historical manuscripts.

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