Abstract Book

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION

Sao Pedro, Sao Paulo, Brazil

November, 9th to 11th, 2025

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Chair: Amauri Antônio Menegário

Co-chair: Marco Aurélio Zezzi Arruda

Organization

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Welcome Message

In 2025, the Brazilian Meeting on Chemical Speciation (EspeQBrasil) is once again held jointly with the Rio Symposium on Atomic Spectrometry (RSAS), organised, respectively, by the São Paulo State University (UNESP) and the University of Campinas (UNICAMP). Since its first edition, in 2008, inspired and chaired by Prof. Dr Marco Zezzi Arruda (UNICAMP, Brazil), with the support of Prof. Dr Anne-Hélène Fostier (UNICAMP, Brazil) and Prof. Dr Reinaldo Calixto de Campos (PUC-Rio, Brazil), EspeQBrasil has stood out as a distinguished forum for scientists, students and industry, fostering discussions on the state-of-the-art in chemical speciation, its emerging applications and the major challenges in this field. The national reach and scientific excellence of EspeQBrasil are evidenced by its history and its organising institutions. The first two editions were organised by UNICAMP in São Pedro (SP). The Meeting then moved to the south of Brazil: in 2012, the Federal University of Santa Maria hosted the event in Bento Gonçalves (RS), and in 2014, the Federal University of Paraná hosted it in Curitiba (PR). In 2017, EspeQBrasil returned to São Paulo State (Águas de Lindóia) under UNESP's organisation, and in 2019 it was held in Salvador (Bahia). After the interruption caused by the COVID-19 pandemic, the Meeting resumed in 2023 in Bento Gonçalves (RS), organised by the Federal University of Pelotas. Although originally conceived for the Brazilian scientific community, EspeQBrasil has progressively expanded its international scope, and has now consolidated the participation of speakers and attendees from Latin America, North America, Europe and China. The 8th EspeQBrasil aims to provide an environment in which academic, scientific, technological and innovation advances in chemical speciation may be critically discussed within a broad context involving environmental, ecotoxicological, nutritional, medical and regulatory dimensions, with scientific, social, political and economic relevance. With the aim of further strengthening the international dimension of EspeQBrasil, this edition includes two short courses (one national and one international), 13 keynote lectures (seven international and six national) and six plenary lectures (five international and one national), in addition to oral and poster presentations. Due to the multidisciplinary and interdisciplinary nature of the topics addressed, the number of student participants has consistently increased at each edition, enabling interaction across different academic levels, strengthening research and education activities, and promoting engagement across diverse thematic areas of chemical speciation. With great pride and enthusiasm, the Organising Committee welcomes all participants to the 8th EspeQBrasil and hopes that the pleasant city of São Pedro will provide an excellent experience, combining high-level science, hospitality, tourism and the renowned gastronomic tradition of the region. Welcome to the 8th Brazilian Meeting on Chemical Speciation.

Amauri Antonio Menegário
Chair of the 8th EspeQBrasil

Marco Aurélio Zézzi Arruda
Co-Chair of the 8th EspeQBrasil

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Summary

Plenary Speakers

Frank Vanhaecke (Ghent University – Belgium)

Jörg Feldmann (University of Graz – Austria)

Marco Tadeu Grassi (Federal University of Paraná – UFPR – PR, Brazil)

Montserrat Filella (University of Geneva – UNIGE – Switzerland)

Paul Williams (Queen's University Belfast – QUB – United Kingdom)

Thomas Prohaska (Technical University of Leoben – MUL – Austria)

Keynote Speakers

Brian Quinn (Queen's University Belfast – QUB – United Kingdom)

Cláudia Carvalhinho Windmöller (Federal University of Minas Gerais – UFMG – MG, Brazil)

Daniela Anunciação (Federal University of Alagoas – UFAL – AL, Brazil)

Hendryk Gemeiner (São Paulo State University – UNESP – SP, Brazil)

Johanna Irrgeher (Technical University of Leoben – MUL – Austria)

Josué Carinhanha Caldas dos Santos (Federal University of Alagoas – UFAL – AL, Brazil)

Letícia Malta Costa (Federal University of Minas Gerais – UFMG – MG, Brazil)

Martín Resano (University of Zaragoza – UNIZAR – Spain)

Michaela Galiová (Brno University of Technology – VUT – Czech Republic)

Paola de Azevedo Mello (Federal University of Santa Maria – UFSM – RS, Brazil)

Ran Bi (Shantou University – STU – China)

Stefan Wagner (Technical University of Leoben – MUL – Austria)

Viktoria Müller (James Hutton Institute, United Kingdom)

Oral Presenters

Henrique Petrovich (São Paulo State University – UNESP – SP, Brazil)

João Jou Fujiwara (University of São Paulo – USP – SP, Brazil)

Katarzyna Bierla (French National Centre for Scientific Research – CNRS – France)

Raimundo Gamela (University of Campinas – UNICAMP – SP, Brazil)

Thiago Castanho Pereira (Federal University of Santa Maria – UFSM – RS, Brazil)

Tomáš Matoušek (Czech Academy of Sciences – CAS – Czech Republic)

Vanessa Alves (Federal University of Catalão – UFCAT – GO, Brazil)

Shotgun Presenters

Geisamanda Athayde (Federal University of Espírito Santo – UFES – ES, Brazil)

Gilberto Coelho (Czech Academy of Sciences – CAS – Czech Republic)

Gregório Morais Saravia (Federal University of Minas Gerais – UFMG – MG, Brazil)

Kristýna Bilavčíková (São Paulo State University – UNESP – SP, Brazil)

Vinnícius Henrique Cerqueira da Silva (University of Campinas – UNICAMP – SP, Brazil)

Virgínia Oliveira (State University of Ceará – UECE – CE, Brazil)

Tributes

Prof. Dr. Anne-Hélène Fostier
University of Campinas – UNICAMP – SP, Brazil

In recognition of her pioneering research on mercury speciation in the Amazon and its impact on environmental chemistry.

Prof. Dr. Montserrat Filella
University of Geneva – UNIGE – Switzerland

In recognition of her pioneering work shaping the conceptual foundations of speciation science and inspiring the global community.

Prof. Dr. Josué Carinhanha Caldas dos Santos
Federal University of Alagoas – UFAL – AL, Brazil

In recognition of his significant contributions to biospeciation and its impact on environmental and biological sciences.

Prof. Dr. Frank Vanhaecke
Ghent University – Belgium

In recognition of his pioneering contributions to isotope ratio analysis and its impact on speciation science worldwide.

Plenary Lectures

Opening Plenary

FROM NATURAL WATERS TO PLASTIC PRODUCTS, NEW CHALLENGES IN THE SPECIATION OF ANTIMONY AND GERMANIUM

Montserrat Filella[a*], Takuji B.M. Adachi[b], Johanna Brazard[b], Tomáš Matoušek[c]
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In environmental and toxicological sciences, it has long been known that measuring total concentrations of chemical elements is not sufficient to fully understand how they behave in the environment. Instead, their chemical speciation must be determined, for example in aquatic or terrestrial systems. Although there are still many cases where current methodologies are inadequate, such as for certain elements considered critical from a technological point of view, significant progress has been made in this field.
However, one aspect that is currently almost completely overlooked is that a new category of pollutants, which is receiving a lot of attention, namely plastics and plastic waste, also introduces the need to assess the chemical speciation of elements present as additives or residues from manufacturing processes. This field is rarely addressed by the chemical speciation analytical community.
This paper presents the development of analytical methods and examines case studies related to antimony and germanium, providing new data on their chemical speciation in both natural systems and manufactured plastic materials. The determination of the speciation of these two elements continues to represent an analytical challenge in natural environments, where many aspects of their biogeochemical cycles remain unresolved due to these limitations. At the same time, although both elements are found in plastics, research into their chemical speciation in these materials is still at a very preliminary stage.

NOVEL APPLICATION TYPES OF ICP-MS IN THE LIFE SCIENCES

Frank Vanhaecke*, Lana Abou-Zeid, Iker Basabe-Mendizabal, Rinus Dejonghe, Ana Lores-Padin, Mina Nikolić, Thibaut Van Acker, Tom Van Helden

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While ICP-MS has become a routine tool in clinical labs for element quantification in several types of biofluids, the technique has much more to offer in a biomedical context.
When combined with laser ablation (LA) as a sample introduction tool, the distribution of elements across a tissue section can be revealed in a quantitative manner. An improved design of the ablation cell and transfer line has led to a single pulse response (transient signal as observed after a single firing of the laser) below 1 ms, such that LA-ICP-MS elemental mapping can be done at a pixel acquisition rate up to 1,000 Hz[1]. The use of ICP-MS instrumentation equipped with a time-of-flight (ToF) analyzer maximizes the information uncovered in this way as every pixel contains information on nearly all elements of the PSE. The high sensitivity of ICP-MS also enables quantitative determination of both exo- and endogenous elements in individual cells. This can be accomplished using either laser ablation[2] (for both adherent and non-adherent cells) or pneumatic nebulization of a cell suspension[2] as a means of sample introduction[3]. Despite the lower sensitivity offered by ToF-ICP-MS instrumentation than by quadrupole-based ICP-MS, the former approach provides higher reliability as it enables the use of a cell marker, offers the possibility to normalize the elemental contents based on the cell size and provides multi-element information, thus enabling potential correlations between elements to be revealed. Finally, next to their concentration, also the isotopic composition of essential mineral elements provides useful information. Multi-collector ICP-MS enables natural variation in the isotopic composition of such elements to be revealed and quantified. In many contexts, isotope ratios have been demonstrated to be more sensitive in picking up changes in biochemical processes accompanying the development of a disorder and/or provide complementary information not embedded in the concentration data.[4] All of the above tools are currently being developed, optimized, validated and used in practical applications in many research groups. Examples of such applications for which the corresponding methodology was developed at the Atomic and Mass Spectrometry – A&MS research group of Ghent University (Belgium) will be discussed to demonstrate their added value.

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The authors would like to thank many colleagues active in the area of the life sciences in various institutions in Belgium and abroad for their indispensable contributions to the work presented.

UNRAVELLING ENVIRONMENTAL SPECIATION: A MULTI-TECHNIQUE APPROACH TO MERCURY IN PIPELINE DECOMMISSIONING

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Speciation analysis lies at the heart of understanding elemental behaviour in real-world systems—especially when dealing with complex, reactive, and hazardous species like mercury in industrial infrastructures. In environmental trace element analysis, no single technique can deliver the full picture. This plenary lecture will explore how a synergistic, multi-technique approach is essential to reveal the true speciation landscape in challenging matrices. Focusing on the case study of pipeline decommissioning where mercury has accumulated over decades of industrial use, we will showcase how diverse analytical strategies converge to map speciation across physical and chemical dimensions. From morphological characterisation via AFM and Raman spectroscopy, to size- and composition-resolved analysis through AF4-MALS-ICP-MS, from bulk and surface imaging with XRF and XANES, to cutting-edge single-particle and single-cell techniques such as SP-ICP-TOF-MS and SC-ICP-MS/MS – each method provides a piece of the puzzle. Together, they offer unprecedented insights into the transformations, mobility, bioavailability and potential risks of mercury species during and after decommissioning processes. This talk will discuss the practical and conceptual challenges of integrating these techniques – sample preservation, cross-calibration, detection limits, and data fusion – and advocate for a more holistic mindset in environmental speciation analysis. As regulatory and sustainability demands grow, such comprehensive analytical workflows are not just academic exercises – they're essential tools for responsible environmental stewardship.

MULTI-ELEMENTAL IMAGING OF SOILS, SEDIMENTS AND RHIZOSPHERES

Paul N. Williams

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Our understanding of biogeochemical processes in soils and sediments is challenged by the significant spatial and temporal heterogeneity inherent in these systems (Williams *et al.* 2011). Interactions at solid-liquid interfaces, and their effects on chemical speciation and bioavailability, remain particularly difficult to investigate due to the limited availability of suitable analytical tools. This presentation explores the topic through the lens of recent advances in multi-modal chemical speciation and imaging technologies. The parallel development of complementary techniques, including high-resolution diffusive gradients in thin films (DGT) (Yin *et al.* 2020), functionalised mesoporous silica-based binders (Yang *et al.* 2002), laser ablation-QQQ ICP-MS, and multilayer planar optode sensors (Fang *et al.* 2021), will be examined. The application of these technologies will be illustrated through a series of case studies. One such study focuses on the Osamu Utsumi mine complex, Brazil's first industrial uranium (U) prospecting facility, now undergoing remediation and regeneration. At this site, solute chemistries and fluxes of U and Critical Technology Elements (CTEs) are linked to sub-100 µm microniche hotspots in chemically diverse treatment zones. Another case study investigates the Northern Irish Long-Term Slurry (LTS) experiment, a 50-year grassland trial assessing the effects of slurry amendments on soil health and plant growth (Jia *et al.* 2024). This site has been characterised for high-resolution spatial patterns using laser ablation-QQQ ICP-MS. Finally, a novel method for multi-elemental bioimaging of freshly exposed Oryza sativa (L.) rhizospheres grown in flooded soils will be presented.

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ANALYTE/MATRIX SEPARATION TECHNIQUES FOR THE ACCURATE DETERMINATION OF ISOTOPE AMOUNT RATIOS BY PLASMA BASED SPECTROSCOPY

Thomas Prohaska[a,b], Johanna Irrgeher[a,b], Kerri Miller[b], Daniel Proefrock[c], Anika Retzmann[b], Michael Schober[a], Antonia Siebenbrunner[a], Stefan Wagner[a], Dorothy Walls[b], Tristan Zimmermann[c], Michael Wieser[b]

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Accurate and precise isotope amount ratio measurements are critical for a wide range of applications in geochemistry, environmental science, life science, material science and nuclear forensics. A central challenge in isotope amount ratio analysis by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), are matrix-induced interferences that can compromise the accuracy of the results. This study addresses the essential role of analyte/matrix separation techniques in minimizing such effects, with a focus on achieving both quantitative recovery of the target element and elimination of interfering matrix components. Using zinc (Zn) and molybdenum (Mo) as illustrative examples, we demonstrate the impact of (incomplete) matrix separation on the instrumental isotopic fractionation (IIF) behavior and overall measurement quality. For Zn, even trace levels of blank and matrix elements lead to significant shifts and low repeatability in measured isotope amount ratios [1]. For Mo, the challenge is compounded by the presence of isobaric and polyatomic interferences, which demand particularly clean chemical separation. A comparative case study is presented on the analysis of calcium (Ca) and strontium (Sr) isotopes, where different separation approaches - manual off-line chromatography, on-line separation via chromatographic columns, and an automated separation system [2] - are critically evaluated. The comparison highlights the trade-offs between throughput, reproducibility, and contamination risks, providing guidance for selecting the most suitable approach for specific research needs. In addition, emerging separation methods such as diffusive gradients in thin films (DGT) and membrane-based separation techniques are introduced [3]. These offer novel pathways for *in situ* or passive sample preparation and preconcentration, with potential applications in environmental monitoring and remote isotope studies. The performance of these alternative techniques is evaluated in terms of selectivity, analyte recovery, and compatibility with downstream isotopic analysis. Overall, this contribution emphasizes the crucial importance of rigorous chemical separation in ensuring accuracy and robustness of isotope amount ratio determinations. Best practices and method development strategies are discussed in light of current technological advances and analytical demands.

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[2] Retzmann A, Zimmermann T, Pröfrock D, Prohaska T and Irrgeher J, Anal. Bioanal. Chem. 409 (2017) 5463-5480
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Closing Plenary

LEGACY OF THE DOCE RIVER DISASTER: ENVIRONMENTAL CONTAMINANTS, PERSISTENCE, AND BIOLOGICAL IMPACT

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The Doce River Basin (DRB) in southeastern Brazil has faced chronic contamination from decades of mining and industrial activities, further intensified by the catastrophic failure of a tailings dam occurred in 2015.[1] This presentation will discuss the results of a study that combines high-resolution chemical profiling with metabolomics to investigate the persistence, distribution, and biological impacts of complex contaminant mixtures in the DRB. Elevated levels of trace metals were linked to mining regions, while organic pollutants were associated with urban and industrial discharges. Seasonal dynamics influenced contaminant transport, with higher metal concentrations during the wet season.[2] To elucidate toxicological mechanisms, *Rhamdia quelen* embryos were exposed to environmental samples, and untargeted LC-HRMS metabolomics coupled with advanced chemometric methods revealed distinct metabolic disruptions, particularly under metal-dominant exposures.[3] We will present evidences that these findings provide new insights into the ecological risks posed by chronic exposure to mixed contaminants and underscore the importance of integrative approaches for environmental risk assessment in impacted freshwater systems.

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[3] Yamamoto FY et al., Sci. Total Environ. 974 (2025) 179158.

Keynote Lectures

THE EFFECTS OF SELENIUM NANOPARTICLES, SELENITE AND SELENATE IN HYDROPONIC CULTIVATION

Letícia Malta Costa

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Selenium (Se) is widely recognized as an essential trace element for humans and animals, though its essentiality for plants remains unconfirmed. Nevertheless, plants play a crucial role in mitigating Se deficiency in the environment by participating in its uptake and transformation. The bioavailability of Se in the environment depends on its chemical forms: selenite (Se^{4+}), selenate (Se^{6+}), and elemental selenium (Se^{0}) nanoparticles (SeNPs). The latter can be formed naturally through the reduction of selenite. Recently, Se^{0} nanoparticles have attracted growing interest due to their high biological activity and relatively low toxicity. However, to enable their application in hydroponic systems, it is essential to ensure the stability of these nanoparticles in the liquid phase. Despite the increasing attention, the mechanisms of bioaccumulation and transformation of various Se species in plants remain poorly understood. This lecture will present and discuss key findings from recent literature, along with experimental results from our research group, to shed light on these processes.

NANOFERTILIZATION STRATEGIES WITH SELENIUM SPECIES: TOWARD SUSTAINABLE FORTIFICATION IN VEGETAL MODELS

Daniela Santos Anunciação[a*], Isadora Rebeca Alves da Silva Santos[a], Laura Lira Facas[a], Marcos Felipe Miranda Ferreira[a], Vânia de Lourdes das Graças Teles[b]

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The record of 70 million Brazilians in a condition of moderate to severe food insecurity, the exponential growth of the world population and the decrease in arable land per capita reveal the need to utilize cultivated areas for food production[1]. To tackle this issue, scientists have intensified their research to develop strategies to increase the production of nutrient-rich foods. Thus, there is a demand for fertilizers of increased efficiency in order to enhance this production. This study conducted a laboratory-scale investigation to evaluate the potential of different selenium species, specifically ionic forms (Se(IV) and Se(VI)) and elemental selenium nanoparticles (SeNPs), as urease inhibitors from *Jack bean* (*Canavalia ensiformis*), followed by their application in an experimental model using lettuce (*Lactuca sativa*). Initially, anti-ureolytic assays were performed, and IC_{50} values were determined using the Berthelot method[2]. The effectiveness of the selenium species was assessed in comparison with conventional urease inhibitors, under varying concentrations and in the presence or absence of soil humic substances. Based on the *in vitro* data, an experimental model was developed using lettuce (*L. sativa*), enabling the optimization of micro-scale cultivation conditions and the evaluation of selenium exposure on seed germination and plant development. This model aims to establish a selenium fortification framework for lettuce with potential scalability to other crops, such as common beans (*Phaseolus vulgaris*). At the highest concentration tested (100 mg L^{-1}), the inhibitory potential of Se(IV) and Se(VI) was below 50%, and further reduced in the presence of humic substances. In contrast, SeNPs demonstrated a significantly higher inhibitory capacity, with an IC_{50} of 5.88 mg L^{-1}, highlighting their promise as a basis for the development of more efficient nanofertilizers that enhance nitrogen fixation and uptake in plants. The nanofertilization and biofortification model using lettuce was developed on a microscale in a controlled germination and growth chamber under 12-hour light cycles. Germination rates were satisfactory (approximately 80%) regardless of the selenium species applied. However, in the hydroponic cultivation stage, dose-dependent physiological responses were observed depending on the selenium species used. These effects will be further analyzed in terms of selenium translocation during the fortification assessment phase.

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[**Acknowledgments: CNPq, FAPEAL, CAPES, FINEP, UFAL**]

ARSENIC SPECIATION IN MARINE ECOSYSTEMS

Ran Bi [a*], Zhendong Lyu [ab], Jinying Xu [a], Stanislav Musil [b], Wenhua Liu [a], Yongfeng Jia [c], Jörg Feldmann[d]

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Arsenate (As^{V}), an oxyanion closely analogous to phosphate, is transported into algae via phosphate (Pi) transporters, particularly under phosphorus limitation [1, 2]. Despite typically low dissolved arsenic in seawater, marine algae can accumulate it to concentrations orders of magnitude higher than in seawater. Following uptake, arsenate is enzymatically reduced to arsenite (As^{III}) and subsequently methylated to monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA); in microalgae and marcoalgae, DMA is rapidly converted to arsenosugars, hence MMA is rarely detected and DMA typically remains minor [3]. The routes and extents of absorption, bioaccumulation, and transformation vary among algal taxa and with growth conditions, making arsenic speciation strongly dependent on algal physiology and environmental conditions [4, 5]. The four arsenosugars most commonly reported are glycerol (AsS-OH), phosphate (AsS-PO_4), sulfonate (AsS-SO_3), and sulfate (AsS-SO_4) [6-8]. These species are often interpreted as detoxification products of inorganic and methylated arsenic and/or as degradation products of arsenolipids [9- 12]. Marine biota exhibit large variability in As speciation due to the differences in species, trophic levels, habitats or life stages [13-15]. AsB is the predominant As species in marine animals; the pathway of AsB formation may vary significantly based on the different food chain characteristics and sulfur and nitrogen interactions [16]. Marine animals span multiple trophic levels; nevertheless, AsB predominates across taxa and shows no consistent biomagnification [17, 18]. Substantial knowledge gaps remain regarding the biotransformation of these As species in the marine food web. Hence, sufficient information on ecological effects, such as trophic levels, habitats, and environmental conditions on As concentration and speciation in the marine food web, shall be provided to understand the bioconversion of As in the marine food web.

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Acknowledgments
National Natural Science Foundation (41877379, 42377231)
Department of Agriculture and Rural Affairs of Guangdong Province, Research on Industrial Innovation Technology for Guangdong Modern Marine Ranching (2024-MRI-001)
National Key R&D Program of China (2025YFE0100600)

EXPLORING EXPERIMENTAL MODELS FOR ASSESSING THE TOXICITY OF MERCURY SPECIES

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Speciation analysis primarily aims to develop strategies in sample preparation and instrumental methodologies for the quantification of distinct chemical species.[1,2] Moreover, studies that assess parameters related to bioavailability and toxicity are frequently conducted. In this context, both the harmful and beneficial effects, along with the distribution of a specific chemical species, may vary significantly depending on the experimental model employed. This lecture will showcase a series of studies on mercury species within biological and environmental systems, utilizing both molecular and elemental techniques to generate quantitative data capable of producing (bio)chemical information. The biological models investigated included proteins and enzymes, cell cultures, and various animal models (rats, flies, and zebrafish), all of which were employed to help elucidate the mechanisms underlying effects or disorders associated with organic mercury species.[3-4] Additionally, findings from the analysis of biological samples (blood and urine) were examined in the context of mercury exposure, highlighting the effects of environmental contamination, specifically from estuarine waters, on the health of local fishermen.[9-11] Understanding the interconnections among models with varying levels of complexity is crucial for deciphering the chemical pathways that govern the behavior and impact of each mercury species. Lastly, the presentation will explore current advancements and future perspectives in cutting-edge technologies and novel experimental models in this field.

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[**Acknowledgments: UFAL, IQB, PPGQB, CAPES, CNPq, FAPEAL, and FINEP**]

QUANTIFICATION IN SINGLE-EVENT ICP-MS

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Single-event ICP mass spectrometry (SP-ICP-MS) has become a powerful method for characterizing different types of micro/nano-particles (MNPs), such as nanoparticles, cells, or microplastics. Despite the remarkable advancements in this technique over the past decade, most studies still rely on the most traditional methods first proposed for signal evaluation and quantification. These methods typically involve two main approaches: (1) using integrated intensity as the analytical signal, and (2) calculating a transport efficiency (TE) coefficient. However, the increasing availability of MNP standards, along with advancements in hardware and software, opens up new possibilities for MNP sizing, including the use of methodologies that do not require the calculation of any TE coefficient. This presentation will discuss alternative calibration and quantification approaches for single-event ICP-MS applications, highlighting the advantages and disadvantages of each methodology, as well as their preferred application areas.

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[Acknowledgments]

The authors are grateful to the European Regional Development Fund (“ERDF A way of making Europe”) for financial support through the Interreg POCTEFA Nanolyme EFA99/1, to project PID2021-122455NB-I00 (funded by MCIN/AEI/ 10.13039/501100011033 and by ERDF) and to the Aragon Government (Grupo E43_20R and grant PROY_E17_24). We also thank the I3A Impulso call, the Ibercaja Foundation and the University of Zaragoza. A.B. acknowledges the Department of Science, University and Knowledge Society from DGA for his predoctoral grant (2021 call). E.B.-F. acknowledges financial support from the Ramón y Cajal programme (RYC2021-031093-I) funded by MCIN/AEI/10.13039/501100011033 and the European Union (NextGenerationEU/PRTR). A.R.-I. thanks European Union’s Horizon 2020 research and innovation program under the Marie-Sklodowska-Curie grant agreement Nº 101034288.

CHALLENGES AND ADVANCES IN PREPARING SAMPLES FOR SPECIATION ANALYSIS OF NON-METALS

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In contrast to the speciation analysis of metals, non-metals are less investigated despite the well-known role that those elements can play. Depending on the context, they can have biological importance (as iodine, for example) or can be a matter of concern (as bromine, depending on the concentration, and sulfur, depending on the molecule). A variety of technological problems are related to the presence of non-metals and their species, as in the context of fuels and fossil fuels industry. In this context, by critically evaluating the literature, total element concentration can be considered a challenge for analytical chemists in the case of non-metals research and method developments. Sample preparation represents a critical issue for several reasons, such as species conversion, low-boiling point of some important molecules for some technological context, contamination (the case of chlorine, for example), that can be highlighted as some important aspects deserving attention. When analyzing detection possibilities, the limitations related to the determination of non-metals (as the low emission wavelength) and the low mass-to-charge ration for mass spectrometry (as e.g. Cl, Br, S, and P) affect method development, especially at low concentrations. Challenging aspects, literature overview and recent developments will be presented focusing on applications to fuels, biofuels and related samples.

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[**Acknowledgments: CNPq, CAPES, FAPERGS and PETROBRAS**]

ISOTOPE RATIOS AS A NEW PARADIGM IN MERCURY SPECIATION STUDIES

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Due to the high toxicity of mercury, there is significant interest in developing studies focused on its speciation. Over the past decade, advances in multiple-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) have enabled the use of isotope analysis for mercury speciation, allowing for much more detailed investigations of the processes affecting this metal in the environment. The fundamental principles of the technique, along with key analytical challenges – including the prevention of isotopic fractionation, optimization of sample preparation procedures, and control of Hg vapor generation – will be presented and critically discussed. Mercury has seven naturally occurring isotopes with different abundances. The magnitude of isotope ratio variations in Hg tends to be greater than in most other metals, providing a wider range of mass-dependent and mass-independent fractionation possibilities. These fractionations have been explored by several authors to gain important insights into the biogeochemistry of mercury, particularly in vulnerable regions such as the Amazon. Nevertheless, there remains a considerable gap in data and understanding regarding the full potential of this technique in environmental research. Several examples of the application of Hg isotope ratios in scientific studies will be presented, including: quantifying the contribution of different metal sources at specific points in Amazonian rivers; investigating methylation processes; examining oxidation – reduction dynamics; and studying photochemical transformations, among others. Artisanal and small-scale gold mining, which relies heavily on mercury, is one of the most pressing environmental challenges in the Amazon region. Isotope ratio analysis has proven to be a powerful tool already in use to investigate the problems associated with this activity in such a critical ecosystem. Selected studies on Hg isotopic signatures and their environmental impacts on tropical rivers will also be discussed.

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[**Acknowledgments: CNPq, FAPEMIG, PROJETO Brumadinho UFMG**]

SPECIATION OF PFAS IN ENVIRONMENTAL SYSTEMS: THE KNOWN, THE UNKNOWN, AND THE ENVIRONMENT IN BETWEEN

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Per- and polyfluoroalkyl substances (PFAS) have become notorious for their persistence, mobility, and global environmental presence. While targeted analysis has long been the cornerstone of PFAS monitoring, it tells only part of the story. In many cases, a significant proportion of organofluorine remains unaccounted for, suggesting that much of what exists in our water, soils, and biota is still unidentified or transformed in ways we don't fully understand.

As regulations tighten and analytical tools advance, it is essential to revisit targeted PFAS analysis and how can we expand the amount of identified PFAS ; not just for environmental chemists, but for anyone involved in water quality, public health, or sustainability.

USING ICP/MS COUPLED WITH ELEMENTOMIC MODELLING TO DETERMINE THE COUNTRY OF ORIGIN FOR DIFFERENT FOOD COMMODITIES

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Inductively coupled plasma mass spectrometry (ICP/MS) is a powerful analytical tool for detecting and quantifying elements. The most common type of ICP/MS analyses from food and feed matrices centre on elemental contamination, but this lecture will focus on data analyses using statistical models to determine the country of origin for different commodities. These studies are conducted, because food fraud is rampant, and analytical tools need to be developed to help combat this fraud. Important commodities like rice[1], salmon[2], and soya[3] have been studied to determine the country of origin using elementomic modelling. The analysis methods and elementomic model construction steps will be presented as examples for each of the three aforementioned commodities, including data fusion with the output of other MS platforms.

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[Acknowledgments]

Maria del Mar Aparicio-Muriana, Yunhe Hong, Cynthia A. Chilaka, Brian Quinn, Philip McCarron, and Nicholas Birse – all from Queen's University Belfast

SPECIES-SPECIFIC SULFUR ISOTOPE RATIO ANALYSIS

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Sulfur isotope ratios have emerged as powerful tracer in geochemical, environmental and biological systems providing insights in sulfur cycling, pollution sources and redox processes across diverse natural and anthropogenic settings. The sulfur isotope composition is altered by various chemical, physical, and biological processes. The most significant changes are caused by kinetic isotope fractionation associated with microbial redox reactions. Over geological timescales, such processes have resulted in large reservoirs of terrestrial sulfur with differing isotopic compositions, and thus different atomic weights (Ar). The currently known natural variability of sulfur isotope composition ranges between $\delta_{IAEA\text{-}VCDT}(^{34}S/^{32}S)$ = +135 ‰ ($x(^{34}S)$ = 0.0473 and $A_r(S)$ = 32.075) and $\delta_{IAEA\text{-}VCDT}(^{34}S/^{32}S)$ = -55 ‰ ($x(^{34}S)$ = 0.0398 and $A_r(S)$ = 32.059). Sulfur isotope abundance ratio measurements, typically reported relative to the internationally accepted 0-delta anchor reference material IAEA-VCDT (as $\delta_{IAEA\text{-}VCDT}(^{34}S/^{32}S)$ or $\delta_{IAEA\text{-}VCDT}(^{33}S/^{32}S)$), are used as tracers or indicators of environmental conditions or processes in various applications. In addition to classical gas source isotope ratio mass spectrometry (GS-IRMS), multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has become an emerging method for precise sulfur isotope ratio analysis. MC-ICP-MS offers the significant advantage of requiring smaller sulfur quantities for measurements. The main metrological challenges lie in controlling the blank value and molecular interferences (particularly from $^{32}(^{16}O\text{-}^{16}O)^+$ and $^{34}(^{17}O\text{-}^{17}O)^+$, as well as correcting for instrumental isotope fractionation (IIF). This presentation will address these metrological challenges and introduce new applications of sulfur isotope ratio measurements, especially in relation to species-specific sulfur isotope compositions. Recent developments in soil research using diffusive gradients in thin films (DGT) for stable isotope analysis enable targeted sampling of labile, plant-available fractions from the soil environment surrounding plant roots. The technique allows high spatial resolution speciation, pre-concentration of analytes, and matrix separation in a single step. These analytical advantages of the DGT technique are combined with precise isotope ratio determinations via MC-ICP-MS to analyze stable sulfate-sulfur composition alongside stable isotope compositions of lead and strontium in DGT-labile (i.e., reversibly adsorbed) soil element fractions. These techniques can be used as a geo-referenced proxy for food origin. Another application involves the development and optimization of a species-selective method for identifying the sulfur isotope composition of sulfur-containing amino acids cysteine and methionine in hair. Unlike total sulfur, the isotope composition of these key sulfur amino acids provides more detailed information on an individual's nutritional status and living conditions, as they originate from different sources and follow different metabolic pathways. Methionine cannot be synthesized by the human body and must be obtained through the diet, whereas cysteine is synthesized internally but requires a constant sulfur supply. Initial results are presented for the development of a sample preparation method (hair hydrolysis), separation of the sulfur-containing amino acids using high-performance liquid chromatography (HPLC), and sulfur isotope determination using MC-ICP-MS. The most recent development involves determining $\delta^{34}S/^{32}S$ and $\delta^{33}S/^{32}S$ isotope ratios from microgram and sub-microgram amounts of sulfur in sulfide and sulfate materials using an elemental analyzer coupled to an MC ICP-MS. Sulfur is converted into SO_2, and isotope compositions are determined from transient signals relative to reference pulses of SF_6 gas.

ELEMENTAL MAPPING AND ISOTOPIC ANALYSIS OF LABILE SOLUTE SPECIES USING DIFFUSIVE GRADIENTS IN THIN FILMS

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Solutes play a fundamental role in biogeochemical processes, but are often challenging to quantify due to their reactive and mobile (i.e., labile) characteristics. Historically, the lack of suitable methods to assess the spatial and temporal variations of labile solute species *in situ* has limited our understanding of solute dynamics. The integration of diffusive gradients in thin films (DGT) with inductively coupled plasma mass spectrometry (ICP-MS) and its related methods has initiated a transformative shift in solute analysis. Using selective binding phases within DGT devices together with the sensitivity and precision of modern ICP-MS instrumentation, this integrated approach emerged as a powerful tool to simultaneously quantify the spatiotemporal fluxes of multiple solute species whilst providing non-biased and high-precision (i.e., accurate) isotopic information, even at ultra-trace levels and microscale spatial resolution. This presentation will showcase recent advances in DGT-based elemental mapping and isotopic analysis of solutes through selected case studies. The first study focuses on a novel DGT technique in combination with multi-collector (MC-)ICP-MS, enabling simultaneous quantification of labile strontium (Sr) and lead (Pb) concentrations and isotope ratios in environmental waters.[1] Applied to natural freshwater and soil-plant systems, this method provides new insights into the mobility, bioavailability, and geological signatures of Sr and Pb in both aquatic and terrestrial ecosystems. The second case study addresses the assessment of localized solute dynamics at the soil-root interface (i.e., rhizosphere) of arsenic (As) hyperaccumulators grown in As-rich soil – a key challenge in understanding As hyperaccumulation phenomena in plants. By coupling species-specific solute sampling by DGT with spatially resolved elemental analysis by laser ablation (LA-)ICP-MS, this approach enables the *in situ* observation of root-induced As(III)/As(V) redox cycling and associated speciation changes, enhancing our understanding of As uptake mechanisms in hyperaccumulating plants.[2] Finally, the development of DGT as an innovative diagnostic tool for medical applications will be presented. Specifically, skin patches based on selective DGT binding layers have been designed to determine a range of trace elements and copper (Cu) isotope ratios in sweat on human skin. This non-invasive approach enables the assessment of metabolic and disease-related biomarkers, potentially opening new ways towards early disease detection in personalized medicine. Overall, these examples highlight the versatility and expanding applicability of integrated DGT ICP-MS techniques across environmental and biomedical sciences. By enabling species-specific, high-resolution, and isotopic analyses under *in situ* conditions, these advancements not only deepen our understanding of solute behavior in complex dynamic systems, but also pave the way for novel diagnostic and monitoring tools in both natural and clinical settings.

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TRACING THE ORIGINS OF CO_2 AND HELIUM IN MINERAL SPRING WATERS OF THE WATER CIRCUIT OF MINAS GERAIS USING NOBLE GAS GEOCHEMISTRY

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The Water Circuit of Minas Gerais, in southeastern Brazil, has attracted attention since the 19th century for its numerous mineral springs, characterized by elevated mineral content and high CO_2 levels. Despite decades of research, the origin of CO_2 enrichment in these springs remains unresolved.[1] Here, we present the first noble gas isotope data from these spring waters combined with hydrochemical data. Gas samples for total dissolved gas analysis were obtained using a custom-built extraction device equipped with a membrane contactor separating the water and gas flow lines, and subsequently analyzed with a quadrupole mass spectrometer (Omnistar GSD 350, Pfeiffer Vacuum).[2] Water samples for dissolved noble gas isotope analysis were collected in copper tubes[3] and analysed using a Nu Noblesse HR mass spectrometer interfaced to a noble gas processing and purification inlet system.[4] All samples exhibited high He concentrations and elevated $^4He/^{20}Ne$ values with respect to atmospheric values, indicating a deep origin and the gradual accumulation of radiogenic ^4He in the waters. Spring samples showed air-corrected $^3He/^4He$ (R_c/R_a) values between 0.55 and 3.39 R_a, suggesting an admixture of crustal and mantle volatile contributions. A consistent $^3He/^4He$ decrease with increasing distance from the Caxambu shear zone was observed, indicating that the release of deep fluids is fault controlled. It is suggested that major fault segments within the Caxambu shear zone serve as continuous pathways for the ascent of mantle derived CO_2 and He, enriching the springs of the Water Circuit region. $CO_2/^3He$ and $\delta^{13}C$ (CO_2) signatures point to a significant crustal-carbonate contribution for the CO_2 although no carbonate lithologies have been confirmed in the region to date.

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[**Funding was provided by FUNDUNESP (3446/2023) and CNPq. PHB acknowledges NSF awards 2121637, 2151120, 2152551, 2232531, 2321494, and 2319897. The authors thank the Agency for Development of the State of Minas Gerais (Companhia de Desenvolvimento de Minas Gerais – CODEMGE) for giving access to the field sites and all given support during sampling.**]

HIGHLY EFFECTIVE CHEMOTHERAPY ENABLED BY LA-ICP-MS: IN SITU TRACING AND BIOIMAGING OF ORGANOMETALLIC AGENTS

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The generic term 'cancer' represents a diverse group of diseases characterised by uncontrollable and abnormal cell growth in any tissue or organ of the body. To date, over 100 forms of the disease have been identified, with approximately 19 million new cases diagnosed worldwide in 2020. Medical treatment generally involves the use of platinum-based anticancer agents. However, cisplatin and other platinum-based derivatives often have side effects relating to Pt toxicity and are less effective due to the acquired chemoresistance of tumour cells (1, 2). Efforts to improve drug efficiency are linked to the synthesis of metal-based compounds that replace platinum with other metals and incorporate specifically designed ligands. In this context, metallocene derivatives containing various metals (Fe, Ti, V, Zr, Ru, Os, Ir etc.) have been tested (3–5). Current research efforts are increasingly directed toward developing targeted therapies that reduce tumour viability or metastatic potential. Among the actively investigated molecular targets are galectins (6). Galectins are multifunctional proteins with complex roles in various pathologies. Their dysregulation is implicated in numerous diseases, particularly cancer and fibrosis. Among them, galectin-1 (Gal-1) and galectin-3 (Gal-3) stand out for their consistently strong protumoral activity. (7). Our research focuses on the tracking and two-dimensional imaging of newly synthesised cytotoxic Ru-tetrazene complexes and novel organometallic Gal-1 inhibitors, using the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The laser beam introduction system (LA) is an attractive sampling strategy for ablating extremely low masses, down to picograms, with high spatial resolution at the cellular level. Furthermore, when combined with high-resolution inductively coupled plasma mass spectrometry (ICP-MS), this method becomes an effective tool for ultra-trace multielement analysis in the biomedical sciences. This lecture will demonstrate the potential of the LA-ICP-MS method for single-cell analysis, with the aim of determining the effectiveness of tested substances, studying kinetic mechanisms and clarifying chemoresistance in cancer cell lines. In addition to in vitro experiments, the lecture will also cover in vivo experiments.

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Poster and oral presentations

Section: Speciation and Fractionation in the Environment

SPECIATION OF SUB-PPT OF GERMANIUM IN NATURAL WATERS BY HYDRIDE GENERATION-CRYOTRAPPING-ICP MS/MS

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Monitoring of Ge species at the very low concentrations found in natural systems is not straightforward even with modern instrumentation. The properties of Ge for ICP MS analysis are not favourable: the element is not easily ionized in plasma and is distributed among several isotopes that are susceptible to isobaric interference from other elements and molecular ions. This is a reason why the geochemical cycling and the presence of Ge in the environment remain understudied.

The speciation of Ge is quite different in freshwater and seawater. In both, inorganic Ge, iGe, is present in concentrations ranging from tenths to low ng L–1. Conversely, methylated germanium species are found in seawater at concentrations of about 20–24 ng L–1 Ge as methylgermanium, MGe, and 6–8 ng L–1 Ge as dimethylgermanium, DMGe, whereas only traces of these species are found in freshwater. Inorganic Ge participates in natural processes and in Ge cycling, but MGe and DMGe appear to be conservative and inert. Speciation analysis is therefore essential.

A possible solution to this analytical challenge is to employ modern versions of relatively old hydride generation (HG) principles together along with volatile species preconcentration and separation by cryotrapping (CT), as well as modern ultrasensitive detection by ICP MS/MS. This presentation focuses mainly on the analytical aspects of the method. HG converts Ge species to the corresponding volatile (methylated) germanes, which are released into the gas phase, leaving behind most of the potential interferents in the residual solution. The volatile analytes from a relatively high sample volume are then collected in a cold trap. Upon heating of the trap, the germanes corresponding to each species are then released according to their boiling points in the form of very narrow peaks.

A semi-automated setup for HG-CT will be presented. One version allows the simultaneous speciation analysis of Ge along with As and Sb species in natural waters using the same selective HG conditions. Modifications to the method and a blank reduction strategy then allow to achieve 5–10 times better detection limits, down to 0.015, 0.005, and 0.003 ng L–1 for iGe, MMGe, and DMGe, respectively, using a Ge-specific method1. Sample conservation with respect to Ge species will be discussed. Results of Ge speciation from the Lake Geneva study2 and examples from recent studies of other hydrochemical systems will also be shown.

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[The authors acknowledge the Czech Science Foundation (23-06530S) as well as the institutional support of the Czech Academy of Sciences (RVO: 68081715) and Strategy AV21 (VP20 – Water for life) for valuable support.]

DETERMINATION OF TOTAL MERCURY AND QUANTIFICATION OF THE ORGANIC FRACTION IN ANTARCTIC SEAWEEDS

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Seaweeds are important environmental organisms that serve as biomonitors of water quality for various contaminants, as their sulfur-containing structures can bind mercury[1]. Quantifying mercury in seaweeds indicates environmental contamination. Among determination techniques, Thermal Decomposition Amalgamation Atomic Absorption Spectrometry (TDA-AAS) using a Direct Mercury Analyzer (DMA) is notable for eliminating sample preparation and, when combined with appropriate organic extraction, this technique also allows the quantification of the organic fraction of the element in the form of methylmercury (MeHg)[2]. This study aimed to optimize the EPA Methods 7473 and 3200 to determine total mercury (T-Hg) and MeHg in Antarctic seaweed, respectively, and to evaluate green analytical metrics by comparison with conventional methods for determination of T-Hg and MeHg. Seaweed samples were collected in 2017–2018 on Deception Island, South Shetland Islands, Antarctica, known for its active volcano, a natural source of Hg contamination through geogenic processes. To preserve the samples, they were refrigerated and frozen until pre treatment for analysis. Thus, the stability of Hg in frozen samples has been demonstrated for at least four years[3]. The T-Hg concentration in the samples was determined according to Ribeiro (2024) using EPA Method 7473, while mercury speciation was performed following Maggi (2009) and EPA Method 3200, which employs a DMA-80 EVO (Milestone, Italy). Samples were pretreated by washing with ultrapure water, dried at 50 °C for ~24 h, and ground to complete homogenization. The sample mass for T-Hg analysis was optimized to 50 mg, sufficient for reliable determination. MeHg speciation method was optimized reducing sample mass and reagent volumes. The procedure included hydrolysis (100 mg sample with 1 mL HCl, 5 min vortex), extraction (2 mL organic solvent, centrifugation at 2400 rpm for 20 min, repeated), and back-extraction (0.6 mL L-cysteine, 1%, centrifugation), with 200 µL of extract transferred to quartz trays for DMA analysis. With this extraction process, only the organic fraction was removed. When analyzed by DMA, the entire mercury content was converted to elemental mercury (Hg^0) for quantification. To validate results for T-Hg and MeHg, limits of detection (LOD) and limits of quantification (LOQ), standard addition studies, and certified reference material (CRM) analyses were performed, along with a comparative evaluation using AGREE (Analytical GREEnness Metric Approach and Software) green analytical metrics. The methods optimized to apply in this study (EPA 7473 and 3200) were assessed against conventional approaches (EPA 245.1 and 1630) for determining T-Hg and MeHg speciation, with values closer to 1 indicating greater greenness. The conventional EPA Method 7473 (T-Hg) scored 0.76, compared to 0.38 for EPA Method 245.1, which involves acid digestion for sample preparation followed by determination using Cold Vapor Atomic Absorption Spectrometry (CV-AAS). EPA Method 3200 (MeHg) scored 0.60, compared to 0.43 for EPA Method 1630. These differences reflect the extensive sample preparation and use of strong acids. The T-Hg concentrations in the Antarctic seaweed samples were determined as follows: 15.2 ± 0.1 µg kg^{-1} in *Adenocystis utricularis*; 21.8 ± 0.2 µg kg^{-1} in *Kallymenia antarctica*; 17.1 ± 0.4 µg kg^{-1} in *Notophycus fimbriatus*; 14.7 ± 0.6 µg kg^{-1} in *Palmaria decipiens*; and 16.8 ± 0.7 µg kg^{-1} in *Spongomorpha arcta*. The LOD for T-Hg was 0.06 µg kg^{-1}, with a LOQ of 0.16 µg kg^{-1}. CRM BCR-060 analysis showed 103 ± 2% agreement, and spike-and-recovery tests yielded 105 ± 3%. MeHg speciation analyses are ongoing. In conclusion, the optimized methods effectively quantified Hg and MeHg speciation in Antarctic seaweeds, providing unprecedented results with greener approaches than classical methods.

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Acknowledgments: CNPq, CAPES, INCTBio, FAPERGS, ANALÍTICA, and UFPel

INFLUENCE OF Se^{4+}, Se^{6+}, AND SE-NANOPARTICLES ON EARLY GROWTH OF GOLDEN FLAXSEED IN HYDROPONIC CULTIVATION

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Selenium (Se) is an essential micronutrient for human health, yet it is estimated that approximately one billion people worldwide have an insufficient dietary intake of Se. To combat this deficiency, various strategies have been explored, including plant biofortification using ionic Se and, more recently, selenium nanoparticles (SeNPs). Golden flaxseed (*Linum usitatissimum* L.) presents several agronomic advantages, such as rapid growth, high yield, and ease of cultivation, making it a promising model for metal(loid) uptake studies[1]. Its popularity as a functional food is also growing, as it is considered a rich source of omega-3 fatty, dietary fiber, and protein[2]. In this work, golden flaxseed was germinated and transferred to 200 mL plastic pots (n = 2) for hydroponic cultivation using 7,5% Hoagland solution. Seedlings were exposed to sodium selenate (Se^{6+}, Na_2SeO_3), sodium selenite (Se^{4+}, Na_2SeO_3) or selenium nanoparticles stabilized with chitosan (SeNPs) in a controlled growth room (29 ± 2 ºC, 12 h dark/12 h light, 830 lux, and 52% humidity) for 15 days. The concentrations ranged from 0 to 100 µM for Se^{6+} and Se^{4+} and from 0 to 50 µM for SeNP.[3,4] The nutrient solution with different Se species was changed every 3 days. After 15 days of cultivation, root (R), stem (S), and leaf (L) biomasses and R and S lengths were measured. The plant organs were washed with water and a cold 10 mM K_2HPO_4 solution. Afterwards, R, S and L were separated, dried, and weighed, and elemental analysis for B, Cu, Fe, Mn, Mo, Se, and Zn was performed by ICP-MS after microwave digestion with distilled HNO_3, H_2O, and H_2O_2[3]. Sample preparation was evaluated for precision in replicates of spiked samples (2 levels), limits of detection (LOD) and quantification (LOQ). Results indicated that root length inhibition was similar for Se^{4+} and SeNPs, while for Se^{6+} exposure was about five times more toxic. Selenium reduced plant biomass, with SeNPs having a reduced effect, resulting in the following toxicity order: Se6+ >> Se4+ > SeNPs. Recovery in spiked samples ranged from 85–117%, except for the low-level of Mn (138%) and Fe (128%). LOD and LOQ varied from 0.1 µg L^{-1} (Mo) to 3 µg L^{-1} (Zn) and from 0.3 µg L^{-1} (Mo) to 11 µg L^{-1} (Zn), respectively. An uptake mechanism by the roots was observed, leading to increased Se accumulation in plants exposed to higher concentrations of SeNPs in the nutrient solution, around 10 to 20 times higher than that observed with Se^{6+} or Se^{4+}. A correlation was observed between SeNPs concentration in the nutrient solution and total Se in roots (R^2 = 0.99, ICP-MS), a trend not evident with Se^{6+} (R^2 = 0.81) or Se^{4+} (R^2 = 0.68). Supplementation with the three Se species resulted in antagonistic and synergistic effects on micronutrient concentrations across flaxseed plant organs. Antagonistic effects were observed for Mn and Mo in roots, stems and leaves for all Se treatments, as well as for B in leaves of plants exposed to Se^{4+} and SeNPs. In contrast, synergistic effects were noted for all Se species with Zn and Fe in the R, S, and L. Additionally, synergistic effects were observed to B and Cu across all organs in Se^{4+}-treated plants and for Cu in all organs after Se^{6+} supplementation. These findings highlight the distinct influence of Se species on the translocation and uptake of essential micronutrients in flaxseed under hydroponic cultivation. A passive uptake mechanism of SeNPs by flax roots appears to be involved. Overall, SeNPs demonstrate potential as a less toxic Se source for the agronomic biofortification of flaxseed.

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FAPEMIG (APQ-04528-23), CNPQ (406109/2023-0), CAPES for financial support.

DETERMINATION AND SPECIATION OF METHYLMERCURY IN HEPATIC TISSUES OF MARINE VERTEBRATES BY HPLC-AFS

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The Santos Basin is one of the most important sedimentary basins in Brazil, an area rich in biodiversity, with endemic and endangered species. With the discovery of vast hydrocarbon reserves in the pre-salt layer, the basin has played a crucial role in the development of the oil and natural gas industry in the country. Such activities can have significant impacts on the marine environment and coastal ecosystems, releasing metallic contaminants into the environment. Among these is mercury (Hg), which is highly toxic and can cause damage to the nervous, immune and cardiovascular systems, in addition to affecting the reproduction and development of organisms. In the environment, Hg can undergo chemical and biological transformations, forming different species with varying degrees of toxicity. Therefore, the determination of total Hg is not sufficient to characterize the degree of contamination by the element. Organic species such as methylmercury (MeHg) are considered more toxic than inorganic Hg and can undergo bioaccumulation and biomagnification throughout the trophic levels, mainly affecting animals at higher levels in the chain. In this study, the liver of marine tetrapods will be analyzed in order to determine and quantify the presence of MeHg in these organisms and, if there is contamination, discuss the possible causes of this and its relationship with oil production in the basin. The species studied are: *Sotalia guianensis*, *Pontoporia blainvillei*, *Chelonia mydas*, *Spheniscus magellanicus* and *Larus dominicanus*. The analysis method uses High Performance Liquid Chromatography (HPLC) coupled to Atomic Fluorescence Spectrometry (AFS), already widely used for Hg speciation, having proven to be a sensitive and low cost method. The main hypothesis of the study is that different Hg species vary in concentration among tetrapod species, where a greater presence of MeHg would indicate a compromise to marine life forms and their entire trophic web. Furthermore, it is expected to observe potential patterns between the ratios of total mercury (THg) and methylmercury in animals with different trophic levels, gender, age and location. Finally, it is expected to infer the consequences of oil activities on the biota of the region, especially in the case of the presence of MeHg, which may indicate the need to take measures in this regard. So far, MeHg concentrations varied significantly among the species, indicating differences in bioaccumulation, which are more common in mammals (*S. guianensis* and *P. blainvillei*), but with a high level found in turtles (*C. mydas*) and penguins (*S. magellanicus*), which is not commonly found in literature. In some animals, such as the turtle, it represents a significant part of the total amount of Hg. Some samples exceeded food safety reference values, suggesting a potential health risk to predators and humans. Intraspecies distribution also varied, indicating the influence of factors such as diet, age, or habitat. The data reinforce the importance of continuous environmental monitoring in marine and coastal ecosystems. This research may contribute to issues of environmental impact, public health, improvement in extraction and analysis methods, contamination monitoring, adaptation to complex matrices, among other extremely relevant issues.

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[**Acknowledgments: PRH-ANP, FAPESP, CEA, UNESP**]

FLUORESCENT PROBE BASED ON N,S-DOPED CARBON QUANTUM DOTS FOR INORGANIC ARSENIC SENSING

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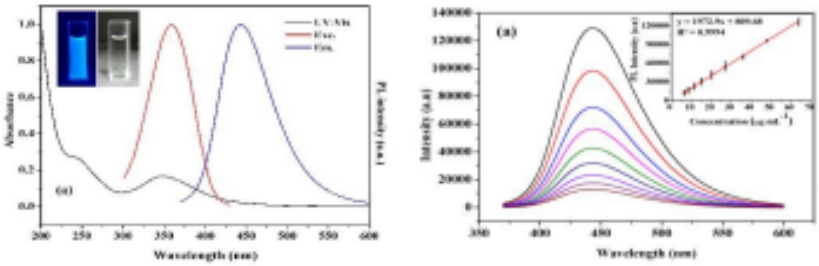
The inorganic arsenic species (iAs), As (III) and As (V), are the most toxic arsenic (As) chemical forms, considered carcinogenic. The main sources of As exposure for humans are water and food[1]. Thus, it is crucial monitoring iAs in these matrices. In general, iAs analysis is performed by high performance liquid chromatography coupled with inductively coupled plasma mass spectrometry (HPLC-ICP-MS) which is relatively expensive and difficult to operate[2]. In this study, a dual fluorescent probe based on carbon quantum dots (CQDs) with high sensitivity toward iAs was developed. Nitrogen- and sulfur-doped carbon quantum dots (N,S-CDs) were synthesized via a hydrothermal method using citric acid, ethylenediamine, and mercaptosuccinic acid. The synthesis was optimized through a full factorial experimental design with a central point, in which the effects of temperature, reaction time, and ethylenediamine volume on the quantum yield (QY) were systematically evaluated. The optimal conditions — 200 °C, 3 h of reaction, and 1.0 mL of ethylenediamine — resulted in N,S-CDs with a QY of 32.22% ± 1.27. Atomic Force Microscopy (AFM) analysis confirmed the formation of nanoparticles smaller than 7.0 nm, while Fourier Transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) identified amine and thiol functional groups on their surface. These features were directly related to the high sensitivity and selectivity of the proposed chemical sensor. The material was used to analyze inorganic As in tap water and seaweed samples. For seaweed samples, 1.0 mL of the sample was extracted with 5.0 mL of water with overnight agitation. Afterward, the sample was centrifuged, and the extract was used for determination. For iAs quantification, 1.0 mL of the sample or extract was mixed with 1.0 mL of carbon dots and immediately analyzed by molecular fluorescence. The method showed detection limits (LOD) below 0.92 μg L^{-1} in environmental water and seaweed samples, with recovery rates from 90.62% to 104.48%, excellent selectivity, and precision (RSD < 8.58%). The iAs content in the water samples varied between 3.0 and 6.0 μg kg^{-1}, being within the acceptable limit (10 μg kg^{-1}). In the algae samples, the iAs content was 2.30 ± 0.02 mg kg^{-1}, a value higher than the tolerable limit for food in Brazil. Finally, the method's environmental sustainability was assessed using AGREE software, confirming its greener profile compared to conventional analytical approaches.

Figure 1: Profile of emission and absorption of CQD and Calibration curve



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[CNPq, FUNCAP, CAPES]

ASSESSING THE LABILITY OF RARE EARTH ELEMENTS IN DARK COLORED SANDS FROM THE ILHABELA ARCHIPELAGO (SP), BRAZIL

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Rare earth elements (REE) are a group of 17 elements, including the lanthanides (La–Lu), scandium (Sc), and yttrium (Y). These elements are classified into two subgroups: light (La–Eu) and heavy (Gd–Lu). Widely used in technologies such as lasers, electronics, permanent magnets, and medical devices, REE also plays a significant role in environmental research such as chemical tracers[1,2]. Monazite, rich in uranium (U), thorium (Th), and REE, represents a key geological material, with radiogenic heavy mineral deposits found in coastal environments[3]. Ilhabela is located off the coast of the state of São Paulo, in southeastern Brazil. It is characterized by a mountainous terrain predominantly composed of igneous and metamorphic rocks, with approximately 80% of its area covered by Atlantic Forest. Dynamic processes of weathering and erosion, along with fluctuations in sea level, contribute to the formation of beaches and recent sedimentary deposits[4]. These beaches include dark-colored sandy areas like Veloso and Enchovas, which may contain monazite and associated mineral assemblages that could influence local geochemical signatures. However, these sites have been the subject of few investigations. This study quantifies and characterizes the distribution of REE (La–Lu) in sand samples from selected beaches in Ilhabela, focusing on dark colored sandy areas, with comparison to a non-monazitic beach impacted by human activities. The total REE content was assessed through acid digestion, following standardized US EPA methods. Approximately 0.175 g of each sample was processed using microwave-assisted digestion (Ethos Easy, Milestone) with 9 mL of concentrated HNO_3 (65% v/v) and 3 mL of concentrated HCl (35% v/v). The resulting solution was diluted with ultrapure water (18.2 MΩ cm, Milli-Q® system) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS). To evaluate the REE dynamics, the Diffusive Gradients in Thin Films (DGT) technique was employed. This passive sampling method allows pre-concentration of analytes over a defined period, facilitating the assessment of their lability. The DGT devices consist of a cellulose acetate membrane for protection, an agarose diffusion layer, and carminic acid immobilized in agarose gel as the binding phase to adsorb REE[5]. Sand samples were dried to constant weight, homogenized, and sieved to 2 mm. Samples were conditioned at controlled moisture levels and allowed to reach a stabilized state prior to DGT deployment. Following this period, the devices were positioned in contact with the samples and maintained for a defined duration to allow REE uptake. Afterward, the binding gels were removed, transferred to centrifuge tubes, and eluted with 2 mL of 1 M HNO_3 for element recovery. Porewater was extracted from sand samples using centrifugation followed by filtration through PTFE filters with a pore size of 0.45 µm[6]. The REE content of DGT eluates and porewater samples was measured using ICP-MS. This study contributes to a better understanding of the distribution and dynamics of REE in coastal areas, providing relevant information for regional environmental management and for evaluating the role of these elements in coastal ecosystem processes.

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[**Acknowledgments: CAPES, CNPq, FAPESP**]

MICROWAVE-ASSISTED EXTRACTION FOR ORGANOFLUORINE DETERMINATION IN SOIL: A PROOF-OF-CONCEPT STUDY

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The widespread use of organofluorine compounds based on per- and polyfluoroalkyl substances (PFAS) has led to the introduction of those chemicals into environmental compartments, such as surface waters and soil[1]. PFAS, which are highly persistent, bioaccumulative, and toxic, are typically found in soil at concentrations ranging from ng g^{-1} up to µg g^{-1}. While liquid chromatography-tandem mass spectrometry (LC-MS/MS) is commonly used for the targeted analysis of specific PFAS, this approach is limited to compounds for which analytical standards are available. To get a broader estimate of the total organofluorine compound content in a soil sample, sum parameter analysis can be used, with extractable organic fluorine (EOF) being the most common measurement. Most sample preparation methods for the determination of EOF in soils are based on the ultrasound assisted extraction (UAE) using methanol as extracting solvent[2]. Another common method for organic compounds extraction from soil samples is the microwave-assisted extraction (MAE). This approach uses efficient microwave heating in closed, pressurized vessels, allowing the rapid extraction of target analytes with minimal losses due to volatilization. However, there are no reports in the literature demonstrating the applicability of MAE for EOF extraction in soils. Therefore, the aim of the present work was to present a proof-of-concept study, showing the possibilities of using MAE for EOF extraction from soil samples. The MAE procedure was carried out in an Ethos 1600 microwave oven (MLS Mikrowellen-Labor-Systeme, Germany) equipped with an HPR-1000/10 segmented rotor and ten 100 mL HPV-100 tetrafluoroethylene modified (TFM) vessels and 40 mL quartz inserts. For the EOF quantification a high-resolution continuum source graphite furnace atomic absorption spectrometer (HR-CS-GFMAS) (ContrAA 800 G, Analytik Jena, Germany) was used. The determination procedure was based on the formation of gallium monofluoride (GaF) molecule, which was monitored at 211.2488 nm, according to a previously optimized method[3]. Furthermore, complementary analytical techniques such as Ion Chromatography (IC) and LC MS/MS were used to quantify inorganic fluorine and target PFAS, respectively. MAE parameters such as extraction temperature (from 50 up to 90 °C), heating time (from 10 up to 20 min), extracting solution (MeOH, MeOH + 0.5% HAc, and MeOH:MTBE (1:1) + 0.5% HAc) were studied using 1 g of soil sample and 20 mL of extracting solution. A previously optimized UAE method for EOF extraction on soils was used as reference method[2]. According to the reference method, the EOF concentration on soil sample was 0.468 ± 0.027 µg g^{-1}. In experiments using 80 °C of extraction temperature and heating time of 15 min (5 min ramp + 10 min hold) and 20 mL of MeOH as extraction solution, agreements of 78 ± 7% with the reference method were observed. With the use of MeOH + 0.5% HAc as extraction solution, an agreement of 150 ± 10%, possibly due to the extraction of fluorine from the TFM vessel. To overcome this issue, a quartz insert was used inside the TFM vessel. By using the quartz insert with MeOH + 0.5% HAc as extraction solution, an agreement of 98 ± 6% with reference method was observed, with blank values lower than MAE method LQ (10 µg L^{-1}). Spiking experiments were carried out with the fortification of EOF on the sample using perfluorooctanoic acid (PFOA) in levels of 50 and 100%, resulting in recoveries of 80 and 86%, respectively. The concentration of inorganic fluorine in the MAE extracts was below 10 µg L^{-1}(IC method LQ), demonstrating the selectivity of the method for EOF extraction. The LQ of the proposed MAE method was 0.18 µg g^{-1}. The targeted PFAS analysis by LC-MS/MS revealed no significant difference in extraction efficiency between the MAE and UAE reference method. Therefore, the proposed method was suitable for EOF extraction from soil samples, presenting a new alternative for sample preparation on PFAS sum parameter analysis.

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[**The authors would like to thank BAM, CNPq, FAPERGS, and CAPES**]

ESTABLISHMENT OF AGAROSE AS A DIFFUSIVE GEL FOR IN SITU MEASUREMENT OF RARE EARTH ELEMENTS IN THE ENVIRONMENT THROUGH THE DIFFUSIVE GRADIENTS IN THIN FILMS (DGT) TECHNIQUE

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Introduction: Rare earth elements (REEs), widely used in high-technology, are considered emerging contaminants [2, 1]. The DGT technique is a promising tool for monitoring them; however, the traditional polyacrylamide gel presents limitations. Agarose emerges as a safer and little-explored alternative. This work aims to evaluate its use as a diffusive gel in DGT, considering pH, ionic strength, agarose concentrations, and filter membranes on the diffusion coefficients of REEs. The DGT technique allows in situ speciation measurements with lower disturbance to natural waters, avoiding changes due to sampling and storage [3], and components such as the diffusive gel, filter membrane, and binding gel are known to influence the measured labile species and diffusion behavior [4].
Material and methods: The diffusion coefficients of REEs were obtained by ICP-MS in diffusion cells, testing agarose gels (1.5%, 2.0%, and 2.5%) to balance resistance and reliability. Cellulose Nitrate (NC) and Polyethersulfone (PES) membranes were also evaluated for their influence on diffusion [6]. Future experiments will expose gels to different pH values (4, 6, and 8) and ionic strengths (1–100 mM) to simulate environmental conditions and verify their effects.
Results and discussion: Experiments on agarose concentration revealed that increasing agarose concentration decreases REE diffusion coefficients. Increasing agarose concentration reduces gel porosity and increases the density of the polymeric network, leading to a lower diffusion rate of REEs and greater mechanical strength of the gel. The 2% gel showed the best performance regarding both resistance and diffusion rate of REEs. Furthermore, the results of the filter membranes, NC and PES, revealed that the membrane allowing the highest REE diffusion in agarose is PES. The Cellulose Nitrate (NC) membrane reduced diffusion coefficients compared to Polyethersulfone (PES), due to higher tortuosity and surface interactions of NC, which hinder ion transport. In contrast, PES presents a more hydrophobic and uniform structure, imposing less additional resistance to diffusion [6].
Conclusions: For the first time, diffusion coefficients of REEs in agarose gels were determined, data not currently available in the literature [5]. The 2% agarose gel presented the best balance between mechanical strength and diffusion rate, standing out as an alternative to APA in the DGT technique, both in solutions and in sediments.

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We thank FAPESP (2024/18362-0) for funding the project and UNESP for the infrastructure and qualified professionals for project guidance and conduction of this Scientific Initiation.

UNRAVELING THE POTENTIAL OF LC-ESI-HRMS-ICP-MS/MS IN THE SPECIOMICS ANALYSIS OF SOYBEAN CALLUS UNDER COPPER NANOPARTICLES EXPOSURE

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The cultivation of soybean callus represents a promising strategy to investigate physiological and metabolic responses under controlled stress conditions [1]. In this study, callus derived from transgenic soybean varieties Roundup Ready (carrying the *cp4-epsps* gene, obtained via *Agrobacterium* sp.) and Intacta (carrying the *Cry1Ac* gene) were exposed to different concentrations (10, 50 or 100 µg/L) of copper nanoparticles (CuNPs). The objective was to assess the impact of these metallic NPs on metabolic profiles. For this purpose, a speciomics analysis approach, which consist on the study of the chemical species in the sample through omics-based [2] employing high performance liquid chromatography coupled to high-resolution electrospray ionization with inductively coupled plasma tandem mass spectrometry (LC-ESI-HRMS-ICP-MS/MS) [3], as demonstrated in Figure 1. This integration enabled the identification of metallobiomolocules (containing Cu, Fe, Mn, Mg, S, P and Zn) and other secondary metabolites, already totalizing 399 compounds. The results showed differences between the two transgenic varieties, with both known and unknown metabolites being identified. These metabolites are biomarkers associated with tolerance or sensitivity to nanoparticle-induced stress. This works contributes to advancing the understanding of metallic nanoparticle effects in plant systems, providing insights both for environmental risk assessment, development of safe biotechnological applications, as well as for identification of possible new metabolites.

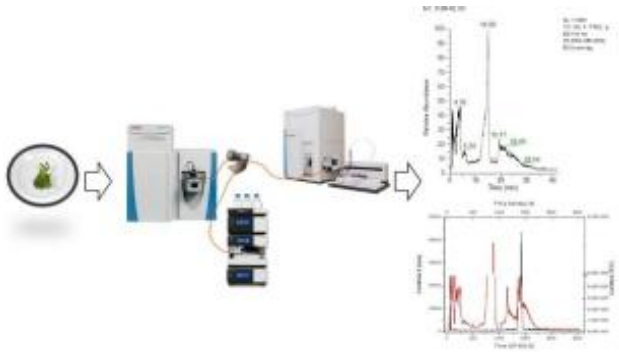

Figure 1. Chromatograms obtained simultaneously in HILIC-LC-ESI-HRMS-ICP-MS/MS (upper part, m/z chromatogram of organic compounds) and (bottom part, Sulphur chromatogram from elemental analysis, showing the possibility of having this element linked to organic compounds at different RT) of soybean callus sample with 10 µg/L of CuNPs.

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[FAPESP, CNPq, CAPES]

SPECIATION AND QUANTIFICATION OF Cr (VI) AND Cr (III) IN WATER BY IC-ICP-MS: TRACKING TOXIC AND ESSENTIAL CHROMIUM

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Chromium enters the environment through both natural processes and industrial activities, with the latter being the primary source of Cr (III) and Cr (VI). Cr (III) is essential for human metabolism and exhibits low toxicity and mobility due to its association with minerals and organic matter. In contrast, Cr (VI) is highly toxic and carcinogenic, as chromate ions readily cross biological membranes. Since chromium toxicity is dependent on its oxidation state, accurate speciation is essential, as total chromium concentration alone cannot reliably reflect its toxicological effects[1]. Brazilian legislation, such as CONAMA Resolutions No. 357/2005 and 430/2010, and Ordinance GM/MS No. 888/2021, establish maximum limits for different types of water, ranging from 0.05 mg L^{-1} for freshwater and drinking water to 1 mg L^{-1}.10 mg L^{-1} for saline, brackish, and effluent waters. In this work, the concentration of Cr (III) and Cr (VI) in water were determined using the Thermo Scientifi Inuvion Ion Chromatography system coupled with the Thermo Scientific iCA RQPlus ICP-MS. An isocratic separation was achieved with 0.3 mol·L^{-1} nitric acid at a flow rate of 0.40 mL·min^{-1} employing a Thermo Scientifi Dione IonPa AG7 anion-exchange guard column (50.0 × 4.0 mm) with an injection volume of 25.0 µL. Detection was performed by ICP-MS equipped with a PFA-LC nebulizer, a quartz spray chamber, and an injector center tube (ID 2.50 mm), connected to a sampling and skimmer cone interface. Plasma power was set at 1550 W, with nebulizer and auxiliary gas flow rates of 1.02 and 0.80 L·min^{-1}, respectively[2]. Data acquisition was performed with a dwell time of 0.1 s and a total analysis time of 200 s. The calibration curve ranged from 0.05 to 10.0 µg L^{-1} for Cr^{3+} and Cr^{6+} (Figure 1). The species of Cr were determined for drinking water, seawater and mineral water, which were analyzed in triplicate. The concentration the Cr (III) for all samples was below the limit of detection (LOD). Cr (VI) concentrations varied from 0.020 to 0.31 ppb in drinking water, 0.09 to 0.14 µg L^{-1} in seawater, and 0.25 to 0.95 µg L^{-1} in mineral water. Different water samples were analyzed before and after spiking with 1 µg L^{-1} Cr (VI), with recoveries of 90.0 ± 2.0% (drinking water), 100.2 ± 1.1% (seawater), and 76.5 ± 4.0% (mineral water). No spiking was performed for Cr(III). Method accuracy was evaluated using the reference material Ground Water (ES-L), which yielded 0.05 ppb for Cr (III) and 7.34 ppb for Cr (VI), in good agreement with the certified total chromium value of 8.01 ppb.

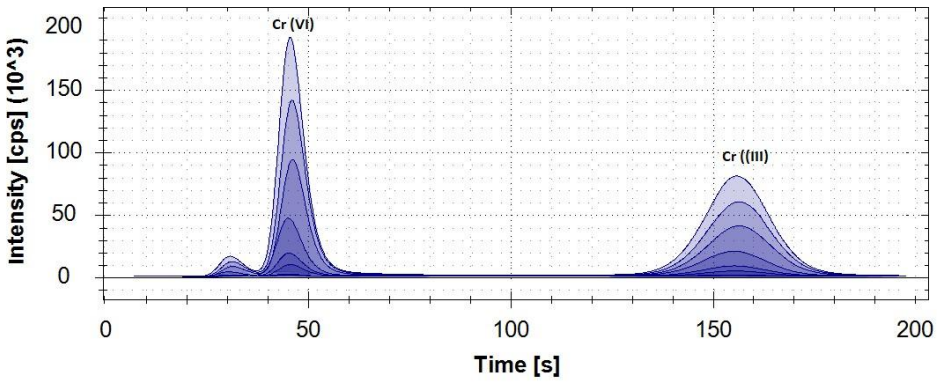

Figure 1: Chromatogram showing the injection of the calibration curve containing 0 – 10 ppb of both species Cr.

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FRACTIONATION OF RARE EARTH ELEMENTS IN MARINE SEDIMENT

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Rare earth elements (REEs) are associated with geological processes and have the potential to be a tool for studying anthropogenic environmental inputs. Therefore, the aim of this study was to perform the geochemical fractionation of REEs in marine sediments. For this purpose, the sequential extraction technique[1] was employed, followed by analysis by inductively coupled plasma mass spectrometry (ICP-MS) with collision cell. All sediment samples were prepared to determine the distribution of REEs in the geochemical fractions: exchangeable (EXCH), carbonate-bound (CARB), associated with iron and manganese oxides and hydroxides (OXI-HYD), organic matter (OM), and residual (RES).

The limits of detection (LOD) and quantification (LOQ) obtained were adequate for the determination of elements in the fractions, except for the EXCH fraction, which required high dilution to reduce the salinity of the solution, compromising the sensitivity of the analysis. To evaluate the accuracy of the sequential extraction procedure, the certified reference material CRM BCR 667 was used. Accuracy was verified by comparing the sum of REEs concentrations in the fractions with the total concentration determined after complete sample decomposition. Satisfactory results were obtained for La, Ce, Pr, Sm, Gd, Tb, and Yb, with recoveries ranging from 80% to 100%.

On the other hand, Eu, Dy, Ho, and Er showed lower recoveries (60% to 80%), possibly due to their low concentrations, which hindered quantification. Sc and Y, however, showed recoveries greater than 150% at all stations, indicating possible analytical interference during ICP-MS determination, even with the use of the collision cell.

Samples analysis indicated that the highest concentrations of REEs were associated with the OXI HYD and RES fractions. The significant presence of REEs in the OXI-HYD fraction may be related to anthropogenic sources, such as agricultural, metallurgical, and mining activities, as well as the presence of urban centers along the river basins that flow into the studied area, directly influencing the sedimentary characteristics of the coastal region.

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[FEST/RENOVA-PMBA FAPES, CAPES, CNPq, LabPetro/UFES and PPGQUI/CCE/UFES]

CHEMICAL FRACTIONATION OF RARE EARTH ELEMENTS IN THE AMAZON BASIN: AN ULTRAFILTRATION PERSPECTIVE

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The Amazon River's particle-borne flows, originating from its main tributaries, play a fundamental role in the biogeochemical cycling of nutrients and trace elements. Overall, these flows act as essential vectors in the transport of matter from land to the marine environment. The lanthanide series, also known as rare earth elements (REEs), has unique geochemical significance due to their similar chemical properties[1]. Therefore, the abundance patterns of these elements in aquatic systems can be used as tools to understand key weathering and river transport processes. Ultrafiltration is widely employed in research to assess how dissolved organic matter (DOM) affects both the concentration and speciation of rare earth elements (REEs) across various natural water systems. DOM plays a crucial role in elements dynamics, either by adsorbing pollutants or by forming stable complexes with metals, including REEs[2,3]. The goal of this study was to perform chemical fractionation of REEs in the Amazon basin and, consequently, improve understanding of natural biogeochemical processes and potential contamination risks of these elements in the region. The study focused on different river systems, including the Negro and Solimões. Additionally, the potential effects of industrial activities in the city of Manaus on the Rio Negro were also assessed. The investigation was conducted using water samples obtained from rivers during the unprecedented drought that affected the region in November 2024. Sampling sites included tributaries of the Negro River—specifically Tarumã Mirim and Tarumã Açu—as well as the main channels of both the Negro and Solimões Rivers, and the confluence zones where their waters merge into the Amazon River. The total REE content was determined after microwave digestion of the samples following the adapted EPA 3015A protocol. The filtered content was obtained using a PVDF syringe filter with a pore size of 0.45 µm. For the ultrafiltrated content, membranes with sizes of 3, 10, 30, and 300 kDa were used. After filtration, all samples were acidified with HNO_3 (Merck) 2 % (v/v). All measurements were performed on an ICP-MS (Thermo Fisher, Germany), using APEX system to reduce possible interference during analysis. Results showed that among the samples evaluated, those collected in the Tarumã-mirin River presented the highest concentrations of REE (ranging from 6.75 ng/L to 5354, of Lu and Ce, respectively), and our results showed that 30% of the REE are in filtrated fraction (0.45 µm). Regarding the ultrafiltered fraction, in general, the concentrations followed the order 300 kDa > 30 kDa > 10 kDa > 3 kDa, and in addition, samples from the Solimões River showed concentrations lower than the LD of the method. Since rare earth elements (REEs) tend to bind to high-molecular-weight humic substances or microbiological exudates, our results corroborate this trend. We observed that the fraction with the highest concentration (300 kDa) allows the passage of these species through the membrane, unlike the other fractions, which likely represent free ions or smaller complexes, such as carbonates, phosphates, and fulvic acids. These findings highlight the predominance of REEs associated with larger organic or colloidal structures in the aquatic environment, reinforcing the role of high molecular-weight compounds in their transport and bioavailability. This molecular partitioning has important implications for understanding REE mobility, potential ecological effects, and their behavior in natural waters, especially in regions influenced by varying geochemical and biological conditions such as the Amazon basin.

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[FAPESP, CAPES, CNPq]

MERCURY IN EVAPORATIVELY WEATHERED OILS: DIFFERENCES BETWEEN LIGHT, MEDIUM, AND HEAVY OILS

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Weathering alters the behavior of oil slicks, making them more persistent when spilled in marine environments by modifying their chemical and physical composition, thus prolonging their environmental impact and durability in the aquatic ecosystem[1]. This proposal aims to analyze the behavior of mercury in crude oils (light, medium, and heavy) both original and subjected to evaporative weathering. In the laboratory, the samples were subjected to distillation at top temperatures of 150 °C+, 200 °C+, and 250 °C+, simulating different evaporative weathering of oil slicks in a marine environment. These temperatures correspond to exposure times of approximately 0.5-1 h, 0.5-1 day, and 0.5-1 week, respectively[2,3]. Total mercury was determined directly without any pretreatment. The samples were heated in a water bath at 50°C for 10 min and shaken manually before being introduced into the Direct Mercury Analyzer. (DMA-80). The analytical curve was prepared from the masses of the solutions, since the DMA-80 operates with mass. A priori, an intermediate standard of 10 $mg.L^{-1}$ Hg was prepared by diluting 100-fold the 1000 $mg.L^{-1}$ stock standard solution. Appropriate volumes of the intermediate solution were pipetted to prepare solutions of 0.5, 1.0, and 10 $\mu g.L^{-1}$, and aliquots of these three solutions were weighed to analyze the masses of 0.0-14.0 ng Hg. 500 mg of additive (Milestone P/N 8603) was weighed into a boat; approximately 30 mg of sample was added; the boat was introduced into the sample tray, and the temperature program was run in three stages: first , for 1 min at 200 °C; followed by 2 min at 650 °C; and finally, the temperature was maintained at 650 °C for an additional 1 min , with a 1 min purge. The DMA-80 uses a low-pressure mercury lamp as its light source, designed to operate at a wavelength of 253.65 nm, with UV photonic detectors. The determination of physicochemical parameters in crude oil and residual fuels is recommended by the American Society of Testing Materials (ASTM). Sulfur contents ($m.m^{-1}$) were determined using ASTM D4294 and asphaltenes ($m.m^{-1}$) using ASTM D6560. In the initial heating stages (150 °C+), there is a reduction in Hg concentration in light and medium crude oils, attributed to the volatilization of organometallic compounds and the release of species such as Hg^0 and possibly $HgCl_2$ associated with saturated fractions[4]. This process highlights the role of volatile compounds in metal mobilization in the first hours after oil spills. There is a subsequent increase in mercury concentration up to 200 °C+, indicating that the metal may redistribute into less volatile fractions. Oils with low asphaltene content (<1% $m.m^{-1}$) exhibit greater ease in mobilizing Hg, while low sulfur levels favor the mobility and persistence of volatile forms of Hg, especially Hg^0 and HCl_2 prolonging their potential for dispersion in the environment[5,6]. In heavy oil, the Hg concentration increases at 150 °C+ but then decreases after 200 °C+, associated with the high asphaltene content (>3% $m.m^{-1}$). These oils promote Hg complexation, favoring the formation of inorganic species such as complexed Hg^{2+} and HgS [5]At 250°C+, it is observed that most of the Hg tends to stabilize in more polar compounds, reducing the metal's environmental mobility. Environmental risk assessment and post-spill monitoring should be considered, considering that the specification and distribution of Hg varies depending on the type of oil and the length of exposure of the spill to the sea.

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FRACTIONATION OF GERMANIUM (IV) IN FRESHWATER MICROCOSMS

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Technologically Critical Elements (TCE) are essential for the development of emerging technologies and renewable energy. The combination of high demand, intensive exploitation, and low natural abundance of certain critical elements has caused global imbalances between supply and demand, justifying their classification as TCE. This situation highlights the need to assess the associated environmental impacts, since their exploitation promotes the remobilization of these elements across different environmental compartments. Among TCEs, germanium (Ge) stands out as it remains poorly studied regarding its behavior and distribution in the environment. This study investigated the most prevalent Ge(IV) oxyanions in freshwater systems (H_4GeO_4 and $H_3GeO_4^-$) using laboratory microcosms constructed with water and sediment collected from Parque das Águas (Pinhais, PR). The analyte was added to the systems and monitored over 30 days, with periodic water sampling to determine the total, dissolved, and particulate-bound fractions. The labile fraction was assessed using the DGT device with a ferrihydrite (FeOOH) binding phase, and Ge quantification was performed by ICP OES (LOD 0.20±0.01 µg L^{-1}, RSD 14%; LOQ 2.1±0.2 µg L^{-1}, RSD 11%). Environmental parameters (dissolved oxygen, pH, and conductivity) were also monitored. Results indicated strong interactions of Ge(IV) oxyanions with sediment and suspended particulate matter, reflected by decreased concentrations in the water column, likely due to the presence of Fe and Al oxyhydroxides in these matrices. However, part of the species remained dissolved, as evidenced by stable concentrations throughout the monitoring period, possibly due to complexation with dissolved substances and solids via cation-mediated electrostatic interactions. The labile fraction correlated with total dissolved solids, suggesting that the presence of this material contributes to the persistence of the species in the dissolved phase. These results contribute to the understanding of Ge(IV) environmental behavior in aquatic ecosystems and highlight the importance of studying the mobility and bioavailability of TCE.

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Acknowledgments:

UFPR, CME-UFPR, Tecpar, Capes, Petrobras, INCTAA, Fest, Finep e PPGQ-UFPR.

USING NOBLE GAS GEOCHEMISTRY AND WATER ISOTOPES TO CHARACTERIZE THE GROUNDWATER FLOW OF THE GUARANI AQUIFER SYSTEM AT THE BRAZIL-URUGUAY BORDER REGION

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Tracing the movement of groundwater is essential for reliable conceptual models to support its sustainable management. Noble gas analysis in groundwater provides critical insights into various hydrological processes, contributing valuable information for understanding aquifer dynamics. Since noble gases (e.g., helium, neon, argon, krypton, xenon) are chemically inert and not influenced by biological or chemical reactions, they serve as excellent tracers for interpreting groundwater systems[1]. The Guarani Aquifer System (GAS), among the largest aquifers on Earth, serves as an essential transboundary water resource for Brazil, Argentina, Paraguay, and Uruguay. The hydrochemical variability within the GAS, reflecting the diverse processes influencing groundwater as it flows from recharge zones toward the basin center, has been highlighted in previous studies (e.g., Teramoto et al., 2020[2]). On this poster we will present data on dissolved gases obtained from a total of 27 groundwater wells, encompassing both the confined and unconfined sections of the southern Guarani Aquifer System (GAS), along with its overlying and underlying aquifers, in the western border region of Brazil and Uruguay. Dissolved gases from groundwater were collected using a newly developed in-situ extraction device and subsequently analyzed in the laboratory with a benchtop gas mass spectrometer (Omnistar GSD 350, Pfeiffer Vacuum). From the measured dissolved noble gas concentrations, we derived noble gas temperatures, representing the soil temperature at the time of aquifer recharge, and excess air values, expressed as ΔNe. Excess air was relatively low and comparable between the unconfined and confined portion of the GAS, with values of 7.7 ± 6.1 % and 7.8 ± 6.7 %, respectively. Mean NGT for the confined portion of the GAS was slightly higher (22.6 ± 4.9°C) than that of the unconfined portion (17.9 ± 2.0°C), which is in conformity with the mean annual air temperature (MAAT) of the region. Elevated He concentrations and higher noble gas temperatures (NGTs) in wells from the confined portions of the GAS, located far from the recharge area, indicate that recharge likely occurred prior to the Last Glacial Maximum (LGM). The pronounced variability in NGTs, together with existing water isotope evidence from the confined GAS, further suggests possible mixing with groundwater from adjacent underlying or overlying aquifer systems. The study presented was published in STOTEN 966 (2025), https://doi.org/10.1016/j.scitotenv.2025.178690.

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[**The authors deeply thank the PEDECIBA Geociencias – Universidad de la República for support of this postdoctoral research. The authors gratefully acknowledge the National Administration of State Sanitary Works of Uruguay (Administraci´on Nacional de las Obras Sanitarias del Estado – OSE) and Cooperativa Agroindustrial Alegrete LTDA (CAAL) for giving access to the field sites and all given support during sampling.**]

Hg STABLE ISOTOPE ANALYSIS IN AMAZON SEDIMENTS: SOURCES AND FRACTIONATIONS

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The Amazon, the largest tropical biome on Earth, is one of the most important regulators of global biogeochemical cycles [1]. Mercury (Hg), due to its toxicity and mobility, is particularly relevant in this region, where both natural sources (lateritic soils, vegetation) [2] and anthropogenic inputs (artisanal small-scale gold mining [3], biomass burning [4]) coexist. Nevertheless, studies on Hg stable isotope in Amazon sediments remain scarce, limiting the understanding of its biogeochemical cycle in this area. This study applied Hg stable isotope analysis to assess sources and fractionation processes in sediments from the Rio Negro basin (Manaus and Anavilhanas). The samples were collected at four sites: three in the Anavilhanas Archipelago (two banks of Negro River and Lake Cabeçudo) and one near Manaus (3 km upstream from the confluence of the Negro and Solimões rivers) during the extreme drought of November 2023. Total mercury (THg) was determined by direct mercury analyses (AMA 254, Altec). For mercury isotopic analyses samples were digested with HNO_3 and H_2O_2 according Nitschke et al. (2024) and determined by MC-ICP-MS (Nu Instrument) with cold vapor generation, using NIST 3133 and an UM-Almaden standards following Guédron et. al., (2018). Isotope ratios and fractionations were calculated following Bergquist & Blum (2007). THg in Rio Negro sediments ranged from 0.03 to 0.19 µg/kg. Comparing with Araújo and coworkers (2018) publication data, THg in sediments ranged from 0.07 to 1.02 µg/kg, and the higher concentrations were observed in samples collected close to ASGM, in Xingu and Para rivers. The samples of both studies exhibited negative δ^{202}Hg values, from -2.24 to -0.89 ‰, indicating that the sedimentary Hg is isotopically light, a signature of natural processes like adsorption or microbial methylation. The Rio Negro samples showed more negative δ^{202}Hg (mean: -1.90 ± 0.18 ‰), with the negative MIF ranging from -0.72 to -0.20 ‰ (mean: -0.47 ± 0.16), and a Δ^{201}Hg/Δ^{199}Hg slope of ≈0.86, suggesting that the photoreduction of Hg^{2+}, complexation and/or adsorption were more relevant processes. The sediments described by Araújo and coworkers (2018) showed also negative δ^{202}Hg values (−0.89 to −2.14‰) together with variable MIF ranging from negligible to moderately negative (Δ^{199}Hg from −0.05 to −0.51‰). This isotopic composition indicates that Negro River sediments were more fractionated in light isotopes and have a signature of photochemical processing in the presence of organic matter. In contrast, samples from the Xingu and Pará rivers (Araújo et al., 2018) showed a positive shift in both δ^{202}Hg and Δ^{199}Hg values, along with higher THg concentrations, this suggests the influence of recent atmospheric mercury inputs with minimal fractionation, potentially associated with artisanal small-scale gold mining. The fractionationso observed were similar with the data presented in Nitschke and coworkers (2024). These findings demonstrate the effectiveness of Hg stable isotope ratios as tracers of photochemical and biogeochemical transformations, providing insight into the sources, pathways, and environmental fate of mercury across the Amazon, particularly in distinguishing recent anthropogenic inputs from background natural signatures.

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Acknowledgments: We thank the Fluvius Anavilhanas, Projeto Brumadinho UFMG, CAPES, FAPEMIG and IPREM for financial supports

Poster and oral presentations

Section: Speciation and Fractionation in Nutrition and Food Sciences

SELENIUM SPECIATION AND NUTRITIONAL ASSESSMENT OF RICE GRAINS CULTIVATED WITH NANOPARTICLES

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A significant portion of the global population lacks access to a balanced diet, leading to widespread micronutrient deficiencies.[1] Selenium (Se) is an essential element for humans. However, its deficiency affects approximately 1 billion people worldwide.[1] Agronomic biofortification of food crops using Se nanoparticles (SeNPs) has emerged as a potential solution.[2,3]It is known that organic Se compounds exhibit greater bioavailability and low toxicity compared to inorganic forms. Therefore, to ensure food safety, it is critical to assess whether non-bioavailable or toxic Se species are formed when SeNPs are introduced into plants. Considering the essential role of Se in human nutrition and the widespread consumption of rice, it is hypothesized that SeNPs could be a safe and effective nano-fertilizer for rice biofortification. The main objectives of this study were: (1) to utilize nanotechnology to produce Se-enriched rice grains; (2) to evaluate the accumulation and speciation of SeNPs; (3) to estimate the contribution of the consumption of enriched rice on selenium intake. Pot experiments with rice plants (*Oryza sativa* L.) were conducted under greenhouse conditions with foliar application of SeNPs at 0.5 mg L^{-1}. Selenium accumulation in grains was determined by inductively coupled plasma mass spectrometry (ICP-MS) following acid digestion, while speciation was determined by high-performance liquid chromatography coupled with ICP-MS (HPLC-ICP-MS) following enzymatic extraction with α-amylase and Protease XIV (Sigma-Aldrich, St. Louis, MO, USA). The application of SeNPs significantly ($p < 0.05$) increased Se concentrations in rice grains by 103% compared to the control group. From a nutritional perspective, grains biofortified with SeNPs had the potential to meet 110% of the recommended daily Se intake established by the Institute of Medicine for adults (55 µg day^{-1})[4], while the Se content in control plants was insufficient to meet its daily requirements. Four Se compounds (SeMet: seleno-DL-methionine, $SeCys_2$: seleno L-cystine, Se^{4+}: selenite, and Se^{6+}: selenate) were identified in both control and Se-enriched grains, with retention times of 4.1, 6.2, 12.1, and 16.8 min, respectively. SeMet was the predominant species, followed by $SeCys_2$. The proportion of organic Se increased from 85% in the control group to 94% in the Se-biofortified group. For inorganic Se, the proportion of Se^{6+} decreased from 10% in the control group to 3% in biofortified grains, while Se^{4+} showed a slight reduction from 5% to 3%. The increase in organic Se proportions, taken together with the decrease in inorganic Se, suggest that SeNPs biotransform to organic Se in rice tissues, demonstrating their bioavailability. The foliar application of SeNPs enabled the production of Se-enriched rice with Se levels controlled within a safe range for human consumption. This approach offers a viable strategy for addressing Se deficiency through nanotechnology in agriculture.

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[**Acknowledgments**]

This work was supported by the São Paulo Research Foundation (FAPESP, grants 2014/05151-0, 2016/10060-9, 2020/00284-2, 2022/14645-2, and 2022/04254-6), National Council for Scientific and Technological Development - CNPq and National Fund for Scientific and Technological Development – FNDCT (CNPq/MCTI/FNDCT grants 305175/2022-0, 446189/2024-3, and 315044/2025-0), and financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) - Finance Code 001.

NOVEL SELENIUM METABOLITES IN EDIBLE MUSHROOMS: IMPLICATIONS FOR FUNCTIONAL FOOD DEVELOPMENT

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Mushrooms are consumed worldwide and their popularity continues to grow, owing not only to their nutritional value and their recognized functional properties but also to taste assets. A distinctive feature of these organisms is their ability to accumulate elements, including selenium, from the growth substrate and metabolize them into a variety of organic compounds. Within this context, selenium is of particular interest because of its essential role in human and animal health and its unique biochemical overlap with sulfur metabolism. Edible mushrooms can take up inorganic selenium and transform it into bioavailable organic species, making them a possibly important natural dietary source. However, the efficiency of assimilation is strongly influenced by the chemical form supplied, and systematic studies directly comparing the metabolic fate of selenite (Se(IV)) and selenate (Se(VI)) in fungi are still scarce. In this study, the selenium-metabolizing capacity of four mushroom species- *Pleurotus pulmonarius*, *P. ostreatus*, *P. djamor*, and *Hericium coralloides*- was systematically investigated. The experimental design aimed to (i) evaluate the uptake and distribution of selenium supplied as Se(IV) or Se(VI), (ii) characterize known and novel Se-containing metabolites, and (iii) assess the presence of sulfur analogues to better understand the interplay between Se and S metabolism. Additionally, an alternative source of Se in form of nanoparticles (SeNPs) was tested on *P. pulmonaris*. Total selenium concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS), showing that SeNPs were more efficiently accumulated then both Se(IV) and Se(VI). Sequential extraction revealed that up to 60% of selenium was localized in the water-soluble fraction, highlighting its potential bioavailability. Anion-exchange chromatography coupled with ICP-MS enabled detection of major species, including selenomethionine (SeMet), residual Se(IV), and Se(VI). To further explore the diversity of metabolites, hydrophilic interaction liquid chromatography (HILIC) combined with high-resolution electrospray ionization mass spectrometry (HR-ESI-MS) was employed, leading to the identification of novel compounds such as selenoneine and ergothioneine derivatives. The discovery of these metabolites indicates that mushrooms can channel selenium into previously unrecognized metabolic pathways, expanding our understanding of fungal selenium biochemistry. These findings have important implications for the development of selenium-enriched mushrooms as functional foods and for optimizing biofortification strategies aimed at improving human selenium intake.

BIOACCESSIBILITY OF BROMINE AND IODINE IN PLANT FOOD SUPPLEMENTS

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Plant food supplements (PFS) have gained popularity, mostly due to the numerous reports on health benefits associated with their use, such as weight management, sports performance enhancement, and other specific aids. However, the widespread use of PFS give rise to concerns regarding their quality and safety. Inadequate quality control and the lack of authoritarian regulation or labelling information, as well as reported adulteration practices, are of concern.[1]In this regard, quality control of both raw botanical materials and the final PFS is essential to ensure consumer safety. Although some research has demonstrated the presence of contaminants in these samples (*e.g.*, heavy metals and pesticides)[2], the bromine and iodine presence are few addressed. These elements, which can occur in soil due to weathering or by the addition of pesticides (*e.g.*, methyl bromide), play an important role in the metabolism. The excess or deficiency of iodine and, in less extension, bromine, can result in health problems to humans and their determination of the content in food and related samples is necessary. Nevertheless, despite the information about the total content is essential, it is insufficient to understand their effects in the organism, being necessary to assess the bioaccessible fraction.[3]In this sense, this study aimed to report on the total content and bioaccessible fraction of bromine and iodine in PFS samples. An *in-vitro* INFOGEST 2.0 digestion protocol was used to assess bioaccessibility.[4] Three PFS samples that have gained significant popularity were used (one sample per type): maca (*Lepidium meyenii Walp.*), ora-pro-nobis (*Pereskia aculeata Miller*) and fenugreek (*Trigonella foenum-graecum L.*). The total concentration, bioaccessible and residual (non accessible) fractions of Br and I in PFS samples were successfully determined by inductively coupled plasma mass spectrometry (ICP-MS). Microwave-induced combustion was used to digest the samples, for determining total concentration and residual (non-acessible) concentration by ICP-MS. Bromine exhibited comparable bioaccessibility among the samples (from 50 to 67%), with a very low intake level (< 1 μg kg^{-1} *bw*). A high concentration of iodine (*ca.* 3,000 μg g^{-1}) was found in a sample derived from fenugreek, which can be associated with the sample matrix components. Bioaccessible iodine fraction was found to be 57% for this sample, which would result in an iodine intake of about 1700 μg day^{-1}, 10-fold higher than the recommended daily intake. These findings highlight the importance of conducting studies on the total concentration and the bioaccessibility of bromine and iodine in PFS, to assess the potential risks associated with contaminants in these supplements.

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[**CAPES, CNPq, FAPERGS, CAS and C&EN and UFSM**]

FOO-04

EVALUATION OF THE BIOACCESSIBLE CONTENT OF MUSHROOMS PRODUCED IN THE STATE OF CEARÁ

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Mushrooms are excellent alternatives to animal proteins due to their antioxidant and antitumor properties, as well as their richness in essential minerals. This research aimed to evaluate the bioaccessible levels of micronutrients in mushroom samples produced in Ceará State. The samples were purchased from supermarket chains in Fortaleza, Ceará, Brazil, and the selected species were Paris, Portobello, Shimeji, and Shitake. Samples were frozen, freeze-dried, and milled before analysis. For total analysis, approximately 0.250 g of sample was decomposed in a microwave-cavity oven with 2 mL of 65% m m^{-1} HNO_3 and 1 mL of 30% m m^{-1} H_2O_2. The mixture was then diluted and analyzed by ICP-OES. A procedure for bioaccessibility analysis was adapted from Santos et al. (2022). In this procedure, 9.0 mL of ultrapure water was added to 0.300 g of sample. After 15 min, 0.2 mL of gastric solution (pepsin at 10% w v^{-1} dissolved in 0.1 M HCl) was added, the pH was adjusted to 2.5, and the mixture was incubated in a thermostatic bath at 37 °C for 2 h. For intestinal digestion, simulated by the addition of 2.5 mL of an intestinal solution of pancreatin and bile salts in a carbonate buffer, after this, the pH was adjusted to 7.4, and the mixture was incubated in a thermostatic bath at 37 °C for 2 h. The sample was then centrifuged, and the supernatant was considered bioaccessible and analyzed by ICP OES. As shown in Figure 1, the percentage of bioaccessibility ranged from 14.9% to 77.5%, with selenium (Se) showing the highest values, particularly in Shimeji and Shitake, consistent with the high Se concentration in Ceará soils (~599 ng/g). Phosphorus (P) was also highly bioaccessible across all species, likely influenced by soil traits and the use of vermicompost and fertilizers. P contributes to the mobilization of toxic elements in contaminated soils. Based on daily nutrient recommendations, these mushrooms qualify as sources of B, Cu, Mn, P, and Zn.

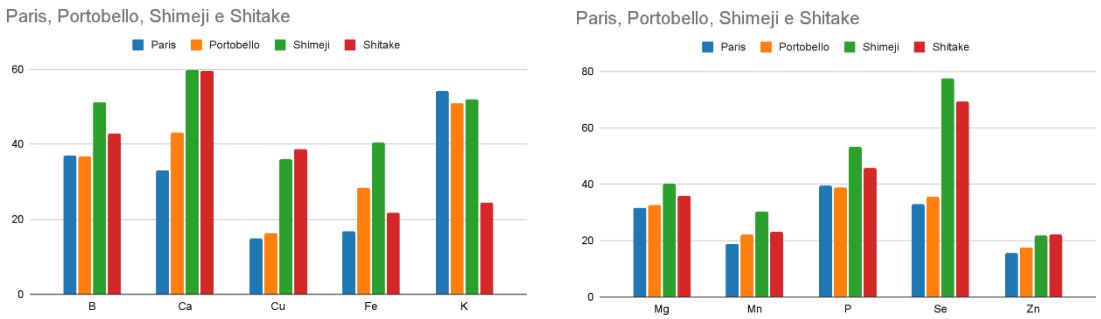

Figure 1. Bioaccessible fraction of trace elements in mushrooms

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Acknowledgments: NUTEC, CNPq, FUNCAP

SERUM FRACTIONATION OF COPPER, MANGANESE, AND ZINC IN ADOLESCENTS WITH OBESITY AFTER CASHEW NUT INTAKE

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Obesity is associated with alterations in serum copper (Cu), manganese (Mn), and zinc (Zn) levels, which are linked to oxidative stress and inflammation[1]. Depending on the specific blood subfraction analyzed, the concentrations of these elements may reflect distinct metabolic responses. The inclusion of cashew nuts within an adequate diet may provide health benefits. The study aimed to evaluate the effects of cashew nut consumption on the fractionation of Cu, Mn, and Zn in blood samples of adolescents with obesity. The study is a randomized controlled trial conducted among students diagnosed with obesity in schools in Fortaleza, Ceará, Brazil. The inclusion criteria were adolescents aged 10 to 16 years, of both sexes. The participants were divided into a control group (CON) and a cashew nut group (CASN). The CASN group received 30 g day^{-1} of roasted cashew nuts for 12 weeks, and both groups received nutritional counselling during the study. Trace elements in cashew nut were determined by ICP OES and the content was18.9 ± 1.0, 14.7± 0.7, and 43.9 ± 2.0 mg kg^{-1} for Cu, Mn and Zn, respectively. The content of trace elements and superoxide dismutase (SOD) were assessed at the beginning and end of the study. The elements were determined in plasma and erythrocyte samples by inductively coupled plasma–mass spectrometry with a reaction cell (DRC-ICP-MS) using He as reacting gas. The analysis differences were compared, after logarithmic correction, by ANOVA for repeated measures with Bonferroni post hoc correction.

Table 1. Characterization of variables in the Control (CON) and the cashew nut group (CASN), according to intervention time in weeks.

Elements	CON (n=27)		CASN (n=49)		p (T0)	p (time/ group)
	T0	T12	T0	T12		
SOD, U g Hb^{-1}	4258 (906)	4484 (728)	4449 (872)	4863 (905) *	0.381	0.605
Plasm, *mg L^{-1}*						
Cu	1.17 (0.20)	1.21 (0.29)	1.07 (0.23)	1.00 (0.24) *	0.075	**0.040**
Mn	2.26 (2.98)	1.79 (0.54)	1.87 (1.33)	4.50 (16.98)	0.669	0.561
Zn	0.76 (0.36)	1.48 (1.02) *	0.66 (0.12)	1.30 (0.89) *	0.101	0.667
Erythrocyte, *mg L^{-1}*						
Cu	0.77 (0.18)	0.70 (0.27) *	0.62 (0.15)	0.82 (0.14) *	**0.012**	**<0.001**
Mn	0.03 (0.01)	0.28 (0.01)	0.24 (0.01)	0.32 (0.01) *	**0.002**	**<0.001**
Zn	10.1(1.9)	10.0 (2.9)	8.45 (1.73)	10.8 (2.0) *	**<0.001**	**<0.001**

Abbreviations: Hb, Hemoglobin; T0, initial time; T12, final time. *Intragroup analysis showed a p-value of less than 5%.

After 12 weeks of intervention, cashew nut consumption reduced plasma Cu levels, which may be associated with decreased inflammation and lower levels of ceruloplasmin, the primary plasma Cu transporter. In contrast, cashew nut consumption increased erythrocyte Cu, Mn, and Zn, suggesting an improvement in intracellular levels that may have contributed to enhanced activity of superoxide dismutase, an enzyme for which these elements serve as cofactors. There were no drastic changes in the students' diets between the groups, other than the addition of nuts. Furthermore, nutritional counselling was provided to both groups which could have improved food choices.

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Acknowledgments: USIBRAS, CNPq MAI/DAI, CAPES, FUNCAP

SELENIUM ORGANIC COMPOUND FOR ALFALFA BIOFORTIFICATION – Se UPTAKE AND CHEMICAL SPECIATION

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Selenium is an important oligoelement for humans, with plant-based foods being one of its sources[1]. The uneven distribution of the mineral in the earth crust may cause deficit of the nutrient in certain population around the globe, making it important to find and study ways of increasing the content of Se in plants. Through addition of Se compounds in the growing medium of plants, it is possible to increase the concentration of the element in the edible parts of the plant, in a process called biofortification. Se biofortification in plants is widely studied, and although the application of inorganic Se salts and Se nanoparticles are reviewed,[2,3] the use of organic selenium compounds is not yet well reported. For human diet, the chemical species of the element is of utmost importance, as it directly impacts the absorption and the toxicity of the nutrient in the human organism.[4] In this sense, this work aims to evaluate the use of an organic selenium compound (Se-Org) to biofortify alfalfa plants by hydroponic process, evaluating the uptake of the element by the plant as well as the Se species in which the element is present in the biofortified plant. The experiment consisted of treating the plant with increasing amounts of the Se-Org: 0 (control), 10, 20 and 40 µmol Se per Liter. The alfalfa seed was initially germinated in wet filter paper for 2 days, and then transferred to a hydroponic deep-water culture system (60 seeds per treatment). The plants were initially grown for 2 weeks in a 50% Hoagland solution of nutrients in the absence of Se. After the initial growing stage, 100% Hoagland solution was applied with the addition of the Se-Org in the respective treatment
concentration. The solution was completely replenished every 4 days with addition of Se-Org. After two weeks, the plants were collected and separated in roots and shoots, freeze-dryed and cryogenically milled. For total elemental determination, 200 mg of the powdered material was digested in a convective heated digestion oven (Vert Technologies) with 2 mL of HNO_3 and 1 mL of H_2O_2, for 20 minutes, at 240 ºC. The digested material was analysed by triple quadropole ICP-MS system, equipped with O_2 reaction cell (iCAP TQ, Thermo Fisher Scientific). It was seen that the plants effectively absorbed the Se in the nutrient solution, achieving root content of 87.52, 132.9 and 230.0 mg kg^{-1}; and shoot content of 35.1, 76.5 and 101.3 mg kg^{-1} with the treatment with 10, 20 and 40 µmol Se per Liter, respectively. These results show the increment of Se in Se-Org treated alfalfa in relation to control treatment, which the nutrient could not be found. For the chemical speciation analysis, the powdered dry samples (100 mg) were extracted with tris-HCl buffer (5 mL, pH=7.5) and Pronase E enzyme (10 mg) for protein lysis. Extracts were analysed via GF-AAS for selenium quantification, and HPLC-ICP-MS was used for speciation. The efficiency of Se extraction using only tris-HCl buffer was 103% and using tris-HCl plus enzyme was 98%. Results showed that Se-Org is a possible additive in nutrient solutions to biofortify alfalfa hydroponically, achieving higher content of Se in the different parts of the plant proportionally to the quantity of Se-Org added. Also, chemical speciation results show that the compound was effectively absorbed and bio-converted into seleno amino acids.

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[**João Jou Fujiwara wants to thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the scholarship**]

NUTRITIONAL INVESTIGATION OF HOW SELENIUM CHEMICAL SPECIES BEHAVE IN SEVERAL COOKED MEATS

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Selenium (Se) is an essential micronutrient with key roles in antioxidant defense, metabolism, and immune regulation, mainly through selenoproteins and amino acids such as selenocysteine and selenomethionine[1]. Its bioavailability, the fraction absorbed and utilized by the body, depends on chemical form and dietary conditions[1,2]. Cooking can alter Se species, increasing or decreasing bioavailability[1]. Although meats often contain high Se concentrations, not all is bioavailable, being influenced by species and cooking method[1]. Therefore, understanding the Se species present in meats and their behavior after preparation is essential for nutritional assessment[2,3]. This study analyzed Se behavior in chicken, beef, and fish through three approaches: (i) total Se quantification by microwave-assisted digestion and Inductively coupled plasma mass spectrometry (ICP-MS); (ii) Se bioavailability via simulated human digestion; and (iii) Se speciation in raw and cooked meat by high performance liquid chromatography coupled with ICP-MS. Total Se quantification showed a recovery of 90.4%. Bioavailability assays indicated higher values in raw samples: 59% (raw chicken) vs. 51% (cooked), 98% (raw fish) vs. 61% (cooked), and 90% (raw beef) vs. 29% (cooked). Speciation revealed that cooking reduced inorganic Se: selenite (Se(IV)) decreased in fish and beef, while selenate (Se(VI)) decreased in chicken. Thermal processing thus affects Se species differently, lowering the bioavailability of inorganic forms, which are more toxic, while preserving organic species. Integrating quantification, bioavailability, and speciation provides a comprehensive view of cooking's impact on Se in meats. This work establishes a foundation for strategies to optimize Se absorption through diet and improve food safety.

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[**Acknowledgments**]

This work was supported by the São Paulo Research Foundation (FAPESP, grants #2014/05151-0, 2016/10060-9, and 2024/21690-0), Brazilian National Council for Scientific and Technological Development (CNPq grant 141134/2024-0), and financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

EVALUATION OF BIOACCESSIBILITY OF MINERALS IN SPIRULINA SAMPLES

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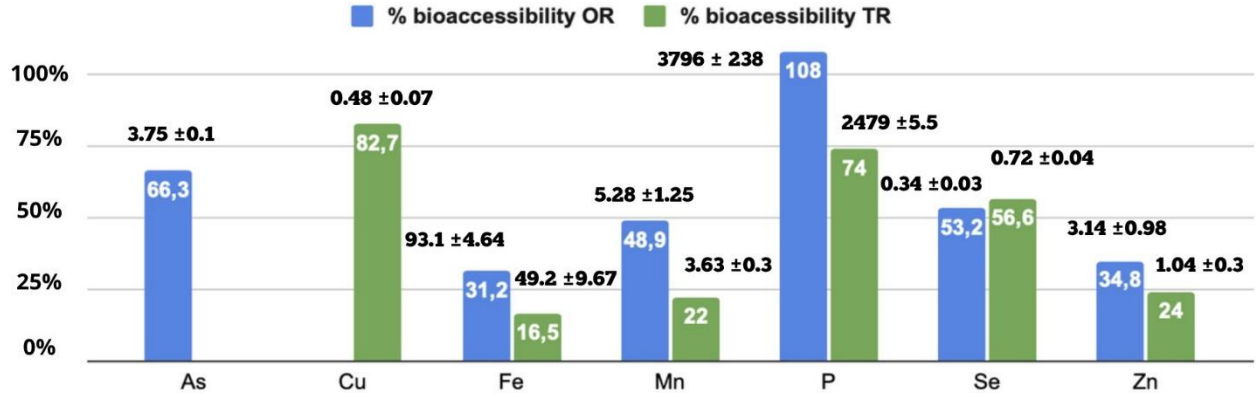
Spirulina is a dietary supplement produced from blue-green algae, also known as cyanobacteria from *Arthrospira platensis* and *Arthrospira maxima* species, which is an excellent source of many important nutrients, such as minerals.[1,2] However, not every nutrient ingested is completely absorbed; therefore, studies of bioaccessibility factors are essential to understand the absorption of not only nutrients but also potentially toxic elements into the human body. This work aimed to determine the bioaccessible fractions of minerals in two different Spirulina samples, organic and non-organic. This experimental trial submitted spirulina samples to an *in vitro* test. The simulated digestion for bioaccessibility analysis was carried out using the methods of Menezes and collaborators.[3] After the digestion, the samples were centrifuged, and the supernatant was analyzed. Also, the samples were decomposed using nitric acid (HNO_3) in a digestion block for 3 h at 120ºC for elemental analysis. The samples were analysed by ICP OES, and the bioaccessible content was calculated using the formula: Percentage of bioaccessibility = (Bioaccessible mass fraction / Total content) x 100. The results are represented in Figure 1:

Figure 1 - Bioaccessible percentage of microminerals in spirulina samples (OR - organic, TR - non-organic);



Legend: The bioaccessible content (mg kg^{-1}) is represented above the bars (mean SD, n=3).

The bioaccessible levels of Fe were significantly higher on the organic sample, even though both samples showed statistically equivalent total Fe content. The same profile was observed for Mn, P, and Zn. On the other hand, As levels were only relevant in the organic sample, showing the capacity of these microalgae to absorb different inorganic substances from the environment. However, the presence of additives in the non-organic sample, such as microcrystalline cellulose (anti-caking agent) and carnauba wax (coating agent), could have influenced the bioaccessibility, as the organic sample is made up entirely of Spirulina. These findings highlight the importance of follow-up bioavailability essays to better understand how the different ways of production and the presence of toxic elements in the environment might affect Spirulina composition.

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[**Acknowledgments: FUNCAP, CAPES, NUTEC, CNPq**]

OPTIMIZATION AND VALIDATION OF ULTRASOUND-ASSISTED EXTRACTION COMBINED WITH HPLC-ICP-MS FOR ARSENIC SPECIATION IN RICE GRAINS

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Rice is a staple crop crucial for food security in many countries, including Argentina, one of the leading producers in Latin America, with an annual output of approximately 1.3 million tons. The Corrientes province stands out as the country's main rice-producing region [1]. However, rice is recognized as a primary dietary source of arsenic (As), since the plant can accumulate this element in its grains. Arsenic is a toxic element naturally present in the Earth's crust and is associated with mutagenic, teratogenic, genotoxic, and neurotoxic effects [2].

In this study, a high-frequency ultrasound-assisted extraction (HUAE) method coupled with high-performance liquid chromatography–inductively coupled plasma mass spectrometry (HPLC-ICP- MS) was optimized to evaluate arsenic (As) in husked rice from northeastern Argentina. The optimal conditions were identified as 0.05 mol L^{-1} HNO_3, 5 minutes of sonication at maximum power (100 W), using a Box-Behnken design. Under these conditions, the recovery of total As (t-As) reached 98%. The limit of detection (LOD) was 0.39 µg kg^{-1} and the limit of quantification (LOQ) was 1.29 µg kg^{-1}.

The optimized method was applied to 64 samples collected from local farmers. Results showed comparable t-As concentrations across most samples, with some exceeding the maximum permissible limit of 300 µg kg^{-1} established by the Brazilian Health Regulatory Agency (ANVISA), Codex Alimentarius, and the World Health Organization (WHO). Figure 1 presents the t-As concentrations along with arsenic speciation, identifying monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and As(V).

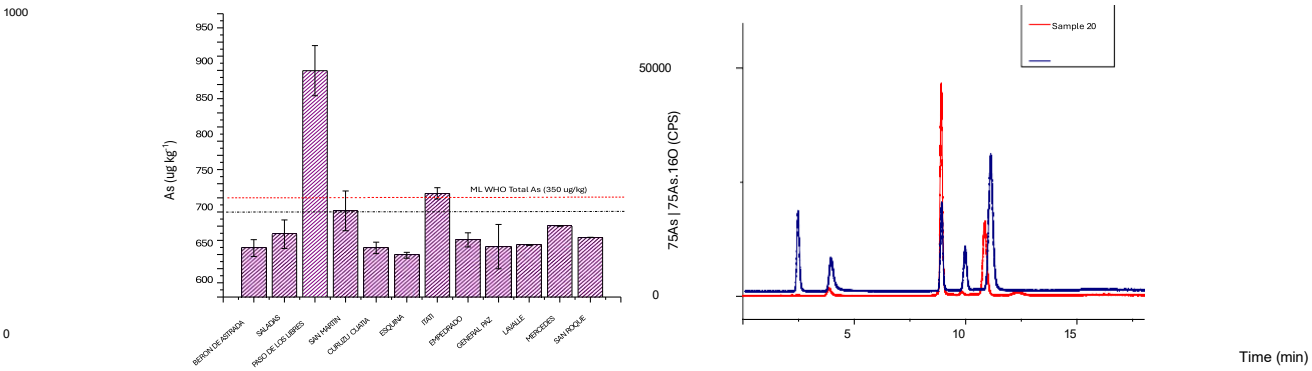

Fig 1. Total As in Argentina husked rice from Corrientes (left) and Chromatograms of sample 20 and Standards (right).

The speciation analysis revealed a predominance of DMA, with all samples showing inorganic arsenic concentrations well below the recommended limits. Moreover, the procedure preserved the integrity of the native As species—As(III), As(V), MMA, and DMA. In conclusion, the developed method, based on high-frequency ultrasound and diluted HNO_3, proved efficient for both total arsenic determination and speciation in husked rice, offering advantages such as simplicity, rapid analysis, and low cost.

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Acknowledgements: FAPESP, CAPES and CNPq for financial support

SELENIUM SPECIATION AND EVALUATION OF MINERAL BIOACCESSIBILITY IN SAPUCAIA NUTS USING ENZYMATIC EXTRACTION AND IN VITRO DIGESTION

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Chemical speciation is an essential tool for understanding the bioavailability and toxicity of elements in foods, as the chemical form can influence their absorption in the body. Selenium (Se) stands out as an essential micronutrient, involved in antioxidant processes, with higher bioavailability when present in organic species, such as selenomethionine. Sapucaia nut (*Lecythis pisonis Cambess*) is considered an important source of minerals and Se, but there are still few studies on its characterization and the release of these elements in the body. In this context vitro digestion is an important tool to simulate human gastrointestinal conditions and assess the fraction of elements that are effectively released and potentially absorbed (bioaccessible). Thus, the present study aimed to perform chemical speciation of Se through enzymatic extraction and to evaluate the bioaccessibility of elements via in vitro digestion. For this purpose, sapucaia nut samples (0.40 g) were subjected to enzymatic extraction using protease XIV or protease XIV + lipase solutions, incubated in an orbital shaker at 37 °C for 16 h. After filtration through PVDF membranes (0.45 µm), Se speciation was carried out by HPLC-ICP-MS using selenite, selenate, and selenomethionine standards using PRPX-100 column, with a mobile phase of $(NH_4)_2HPO_4$ 60 mmol L^{-1} (pH 6)[1]. To simulate the digestive steps (salivary, gastric, and intestinal), synthetic fluids were used: initially, 1.5 mL of salivary fluid was added to the sample, followed by 3 mL of gastric fluid (2 h incubation), and subsequently 3 mL of intestinal fluid, 3 mL of bile fluid, and 0.5 mL of 1 mol L^{-1} $NaHCO_3$ solution (2 h). At the end, samples were cooled on ice and centrifuged at 2000 rpm for 30 min, and the soluble fraction was analyzed by ICP OES[2,3]. Chromatographic results revealed a predominance of selenomethionine, the most bioavailable species compared to inorganic forms. A second, not yet characterized, peak was also observed, possibly resulting from selenomethionine oxidation. In bioaccessibility studies, only iron (Fe), nickel (Ni), and selenium (Se) showed relevant concentrations. Iron was completely released in the salivary and gastric phases, while Ni and Se were released throughout all digestive steps: about 40% of Ni and 48% of Se were released in the initial phases, and 60% of Ni and 52% of Se in the intestinal phase. This study demonstrated that sapucaia nut is a relevant source of selenium, predominantly in the form of selenomethionine, the most bioavailable organic species, reinforcing its potential as a functional food. In vitro digestion proved to be an efficient tool to simulate human gastrointestinal conditions and assess the bioaccessibility of minerals, showing that iron, nickel, and selenium are released at different stages of the digestive process. These results highlight the importance of in vitro digestion as a complementary method to chemical speciation, allowing a better understanding of the fraction of nutrients effectively available for absorption and contributing to the evaluation of the nutritional value of sapucaia nut.

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[CAPES, CNPq, FAPERJ]

Poster and oral presentations

Section: Emerging Topics in Chemical Speciation and Isotope Analysis

HYPHENATED TECHNIQUES WITH PLASMA BASED HYDRIDE ATOMIZERS FOR SPECIATION ANALYSIS

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Volatile species generation (VSG) has been widely applied for more than fifty years to determine trace levels of metals by atomic spectrometry. Besides efficient analyte introduction and matrix separation, VSG also enables speciation analysis, which has become one of the most dynamic areas of trace element research in the last two decades. Since atomic spectrometric detectors are inherently destructive, speciation requires coupling VSG with separation techniques. Three principal approaches are possible: selective generation, post-column generation, and generation of substituted species.
The aim of this work was to apply all of the above-mentioned strategies to develop two competitive hyphenated methods for the separation of arsenic species, based on either HPLC or GC. Detection was performed by atomic absorption spectrometry (AAS) using a multiple-microflame quartz tube atomizer or newly developed plasma atomizers based on dielectric barrier discharge (DBD) or atmospheric pressure discharge (APD). The atomization mechanisms in these plasma atomizers were also investigated. In addition, cryogenic trapping or in-atomizer trapping of arsenic species was employed to achieve significant improvements in detection limits.
The HPLC-based method combined post-column hydride generation with atomization in a DBD plasma. An in-situ trapping step inside the atomizer enabled focusing of arsenic species into sharp peaks, providing enhanced detection limits. Quantitative retention and controlled release were achieved by oxygen addition into the carrier gas, controlled by a lab-made gas control unit synchronizing HPLC, oxygen switching, and AAS.
The GC-based method relied on VSG of substituted species followed by cryogenic trapping in a quartz U-capillary immersed in liquid nitrogen. Trapped species were released, separated by GC, and detected using multiple-microflame quartz tube atomizer, DBD or APD.
VSG techniques are compatible with a wide range of spectrometric detectors, including AAS, atomic fluorescence spectrometry, inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectrometry, as well as certain chromatographic detectors. The developed hyphenated techniques with AAS detection were compared with ICP-MS and flame ionization detection (FID) in terms of achievable detection limits. Results demonstrate that VSG-based hyphenated approaches coupled with AAS offer competitive performance and provide a robust alternative for arsenic speciation analysis.

Acknowledgments

This research has been supported by the Czech Science Foundation under contract 23-05974K and by the Institute of Analytical Chemistry of the Czech Academy of Sciences (Institutional Research Plan no. RVO: 68081715).

INTERACTIONS OF CeO_2 NANOPARTICLES WITH HUMIC SUBSTANCES FROM THE RIO NEGRO

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The Rio Negro, one of the largest tributaries of the Amazon River, is characterized by high concentrations of humic substances (HS) derived from decaying vegetation, which give the water its dark color. Naturally occurring CeO_2 nanoparticles (nano-CeO_2) have been detected in this riverine environment and may interact with humic substances, affecting nanoparticle stability, aggregation, and bioavailability. Understanding these interactions is essential to assess the environmental fate and potential impacts of nano-CeO_2 in Amazonian waters. The aim of this work was to evaluate (i) the effect of humic substances from the Rio Negro in wet (HS_W) and dry (HS_D) seasons on nano CeO_2 stability over time at different HS concentrations, and (ii) the influence of humic substances on the availability of Ce to the water. Two separate experiments were conducted. In the first, triplicate solutions containing nano-CeO_2 and humic substances at 1, 5, and 10 ppm were prepared, with additional suspensions of nano-CeO_2 and humic substances alone as controls. These solutions were analysed by single-particle ICP-MS (spICP-MS) immediately after preparation (T_0), and at 24 h (T_{24}) and 96 h (T_{96}) to assess nanoparticle stabilization over time. A suspension of AgNP (NanoXact Silver Nanospheres, Citrate, 80 nm, NanoComposix) was diluted about 10^5times and used to calculate transport efficiency of spICP-MS analysis. The dwell time of ICP-MS was set to 5 ms and the acquisition time was 60s. Sample flow rate was determined by gravimetry. Data was analysed using spCal[1] software (v. 1.4.2). In the second experiment, the effect of humic substances on nano-CeO2 stability and labile Ce availability was evaluated using DGT devices. Solutions contained 10 ppm of HSW or HS_D with 250 µg/L nano-CeO_2, and nano-CeO_2 suspensions without HS were included as controls. Ce concentrations in solution (C_{sol}) and in DGT eluates (C_{DGT}) were measured by ICP-MS. Results from the DGT experiment showed that in the absence of humic substances, only 33.2 ± 1.5 µg/L of Ce remained in suspension. HSW increased C_{sol} to 61.7 ± 16.7 µg/L (HS_W/nano-CeO_2 ratio = 1.9), while HS_D promoted greater stabilization, with 128.0 ± 6.0 µg/L (HS_D/nano-CeO_2 ratio = 3.9). Measurements of DGT eluates revealed a strong reduction in the labile fraction: C_{DGT}/C_{sol} = 0.014 ± 0.004 for HS_W and 0.005 ± 0.001 for HS_D, compared to 0.081 ± 0.007 in the control. spICP-MS results from the first experiment confirmed that humic substances strongly stabilized nano-CeO2 over 96 h. In the absence of HS, suspensions lost 88-95% of the initial particle numbers, indicating rapid sedimentation or aggregation. In contrast, particle losses in HS_W solutions were much lower, with 13-31% lost at T_0, 22-30% at T_{24}, and 18-28% at T96. HS_D solutions showed slightly higher losses initially (20-26% at T_0 and 21-28% at T_{24}) but decreased overtime, with only 11-20% lost by T_{96}. The slightly lower losses observed in HS_W may suggest that seasonal differences in humic composition, likely related to higher molecular weight or more aromatic components during the flood season, enhance nanoparticle persistence in solutions. In conclusion, these experiments demonstrate that humic substances from the Rio Negro significantly stabilize nano-CeO_2 and increase Ce concentrations in suspension, yet strongly limit labile Ce availability, with seasonal variability modulating nanoparticle persistence and bioavailability. Additional analyses on humic substance composition, nanoparticle size, and mass are ongoing, and this work is still in progress to further support the presented findings.

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[**We thank FAPESP for the financial support (Processes #23/11694-5 and #23/15970-7)**]

SPECIATION ANALYSIS OF METHYLMERCURY VIA SPECIES SPECIFIC ISOTOPE DILUTION GC-ICP-MS - TECHNICAL NOTE 30465

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Mercury is known as a highly toxic element with ubiquitous occurrence due to its global cycle.[1,2] The toxicity, metabolism, and pathways depend on the mercury species. [2,3] When mercury is methylated by bacteria, its toxicity and environmental persistence are increased: methylmercury (MeHg+) is bioaccumulated and biomagnified within the food chain and can have severe impacts on biota and human beings.[2] Hence, knowing the molecular species of mercury in the environment is crucial. The determination of MeHg+ with species-specific isotope dilution gas chromatography-inductively coupled plasma mass spectrometry (GC-ICP-MS) has evolved to be the gold standard in speciation analysis of mercury due to its accuracy, precision, and additional isotope information.[4,5] The strength of this technique is in the ability to account for non-quantitative recoveries and monitoring of Hg side products (methylation, demethylation) during sample preparation, which would not be recognized with GC-atomic fluorescence spectrometry (GC-AFS) where no isotope information is acquired.[4,6]

The setup comprising a Trace 1310 GC coupled to the Element 2 HR-ICP-MS via the new GCI 200 Interface was applied successfully for the determination of methylmercury. A good analytical result depends on the accurate determination of the peak area, which is not given at very small peaks because the background noise has an influence on the peak area. The results for DORM-2 (fish muscle) and ERM-CC580 (estuarine sediment) showed good precision and accuracy in a short chromatography time of 3.8 min. Provided a suitable preparation and extraction method, this technique can be applied for most environmental samples spanning from plant material to sediment samples and different water samples covering most applications for compound-specific Hg ultra-trace quantification.

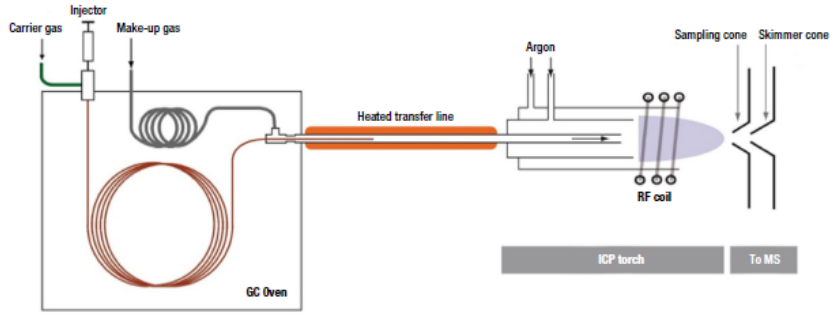

Figure 1. Scheme of the setup of the gas chromatograph (GC) coupled to a high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) via a heated transfer line

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Poster and oral presentations

Section: Speciation and Fractionation Analysis in Life and Pharmaceutical Sciences

PHA-01

EXPLORING BEHAVIOUR OF UNIQUE COMPOUNDS BY LA-ICP-MS: ANTICANCER *IN VIVO* AND *IN VITRO* EXPERIMENTS

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Prevention, diagnosis and early treatment are important in the fight against cancer that counting more than 100 diseases [1]. Many types of cancers have a high chance of cure if diagnosed early and treated appropriately, the most frequently via chemotherapy.
In the last decades, many researchers have focused on the synthesis of metal-based compounds replacing platinum with different metals [2], and additionally on the binding the individual ligands. Recently was also found, potential compounds may exhibit tumour tissue inhibitory properties based on ability to bind to galectins. Galectins are a family of β-galactoside-specific lectins that are involved in multivarious physiological and pathological processes, and are secreted at low levels in healthy tissues, whereas their expression is increased in cancer tissue [3]. The importance of galectin-1 (gal-1) and galectin-3 (gal-3) in tumour development is well documented when playing crucial roles in proliferation, metastasis, angiogenesis, immune evasion and drug resistance.
The main goal of this project was to incorporate high-end advanced analytical imaging technique, specifically Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), into oncological research for localization and quantification of a completely novel class of organometallic substances (242 and 298) with ruthenium central atom. These complexes are highly selective gal-1 inhibitors, and their structure is designed to interact with intercellular or extracellular gal-1. In *in vitro* single-cell experiment, the interaction of Ru-compounds 242 and 298 was investigated in three human breast cancer cell lines differing in gal-1 and gal-3 expression. To approximate behaviour in the human body, LA-ICP-MS was used to investigate substances in mice cancer tissue and to monitor possible metastasis via 2D imaging. The working settings of quadrupole-based ICP-MS and excimer laser ablation system was optimized to achieve highresolution 2D imaging. Inkjet standards were also developed to quantify the results obtained. LA-ICP-MS clearly demonstrated the increased cell permeability to complex 298 containing butyl group, compared to complex 242 interacting with extracellular gal-1. However, specific interaction of the Ru-complexes with gal-1 was not clearly demonstrated, as the cancer cell line with gal-3 showed higher levels of 298 compared to the cancer cell line expressing gal-1. This result is probably due to interaction with other substances in the cells. Ruthenium was also identified in mouse tissue sections.

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The work was supported by the project FCH-S-25-8807 of Ministry of Education, Youth and Sports of the Czech Republic. We also thank Czech Science Foundation for financial support (grant number 23-06115S) and MH CZ – DRO (MMCI, 00209805). Supported by the project National Institute for Cancer

Research (Programme EXCELES, ID Project No. LX22NPO5102) – Funded by the Eur – Next Generation EU.

PHA-02

(BIO)EFFECTS OF MERCURY DERIVATIVES ON HUMAN ERYTHROCYTES: A COMPARATIVE STUDY

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Exposure to mercury (Hg) and its derivatives is a global concern due to their significant risks to human health[1]. Among these derivatives, thimerosal (TM) is widely used as a preservative in vaccines and dermocosmetics[2]; phenylmercury (PM) has been employed as a fungicide but remains poorly investigated regarding its toxicity; and mercuric chloride ($HgCl_2$) is primarily used in laboratory applications. Erythrocytes (Ery), cells rich in hemoglobin (Hb), have the primary function of transporting oxygen. This study aimed to evaluate and compare the effects of these mercury species on human erythrocytes. Blood samples from volunteers (n = 8) were exposed to different concentrations and incubation times: TM (1.25 and 2.5 µM; 2 and 5 min), PM (0.125–1 µM; 3 min), and $HgCl_2$ (1.25 and 2.5 µM; 2 and 5 min) (CAAE 02840318.2.0000.5013). Oxygen uptake by Hb was significantly reduced in all conditions, in a concentration- and time-dependent manner. With TM, reductions of 49% and 69% were observed at 1.25 and 2.5 µM after 2 min, respectively, reaching 75% and 80% after 5 min. PM induced reductions of 34% (0.125 µM), 39% (0.25 µM), 46% (0.5 µM), and 48% (1.0 µM) compared to controls. $HgCl_2$ also showed concentration- and time-dependent effects: 1.25 µM led to reductions of 33.4% (2 min) and 54.5% (5 min), whereas 2.5 µM caused 68% (2 min) and 81% (5 min) loss of Hb functionality. In addition, the well-known O_2 uptake inhibitor sodium cyanide (NaCN) was tested, producing decreases of 32% and 42% at 1.25 and 2.5 µM after 2 min, and 66% and 72% at the same concentrations after 5 min. Thus, mercury species exert marked toxic effects on erythrocytes. Atomic force microscopy (AFM) revealed that PM induced morphological deformations, with a 52% reduction in cell height, an increase in diameter, and altered erythrocyte elasticity. Similarly, TM promoted an increase in diameter, reduced height, greater membrane roughness, and a decrease in Young's modulus. In the osmotic fragility assay, only PM compromised membrane integrity, whereas TM did not alter this property under the tested conditions. Both compounds reduced total sulfhydryl content, confirming their affinity for free cysteine residues in Hb and erythrocytes. Reactive oxygen species (ROS) production was significantly increased by PM, with rises of 11% (0.125 µM), 41% (0.25 µM), and 47% (0.5 µM), whereas TM did not cause relevant changes compared to controls. In conclusion, this study demonstrates that although both TM and PM interact with thiol groups and induce morphological alterations in erythrocytes, PM exerts more severe effects, including membrane damage and substantial ROS generation, rendering it more toxic than TM and comparable to $HgCl_2$ under specific conditions.

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CAPES, CNPq, FAPEAL, and FINEP.

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION
Sao Pedro, Sao Paulo, Brazil
November, 9th to 11th, 2025
PHA-03

ASSESSMENT OF MERCURY FRACTIONATION IN PERNA PERNA MUSSELS USING THERMAL DESORPTION ATOMIC ABSORPTION SPECTROMETRY (TD AAS)

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Mussels have significant economic and social importance in various countries due to high commercial sales and considerable human consumption. In Brazil, among the cultivated species, the brown mussel Perna perna represents approximately 19% of the country's mariculture production.[1] As filter-feeding bivalve organisms, mussels obtain their food by filtering water, removing suspended particles such as phytoplankton, zooplankton, and other microorganisms.[2] However, this feeding process also exposes them to the absorption and accumulation of chemical contaminants, including toxic metals such as mercury. Due to biological processes, the excretion of this contaminant is slow, leading to its accumulation in the organism's tissues. Thus, assessing mercury content in mussels is essential for understanding the environmental impacts of pollution and evaluating the toxicological risks associated with their consumption.[3] Furthermore, mercury accumulation in mussels can affect higher trophic levels in the food chain, intensifying the effects of biomagnification and increasing the exposure of marine predators and humans to this toxic metal. Typically, mercury quantification in mussels is based on the determination of total concentration. However, this approach does not provide detailed information on the different chemical forms of mercury and their bioavailability in the environment. Therefore, in addition to total mercury quantification, fractionation of this metal in mussel tissues is essential to understand its mobility and potential toxicity. This study aimed to develop a method for fractionating mercury species in five stages using a direct mercury analyzer in a simple and efficient manner. A total of 20 Perna perna mussel specimens were collected from each sampling site along the Espírito Santo coast. Mercury species were characterized according to the temperature range at which they were released and detected. The limit of quantification (LOQ) was established at 0.076 μg kg^{-1}, and method accuracy was assessed using the certified reference material ERM-CE278k Mussel Tissue, in addition to comparing the values obtained from total mercury determination with the sum of the fractionated species. The total mercury concentrations in fresh weight ranged from 0.0235 to 0.0489 μg g^{-1} in males and from 0.0236 to 0.0415 μg g^{-1} in females. A comparison between the mean total mercury concentration and the sum of mercury concentrations obtained through five-step fractionation revealed no statistically significant difference. The largest portion of mercury was released in the second fractionation stage at 230 ºC, which is characterized by the release of Hg bound to organic matter.The results indicate that five-step thermal mercury fractionation is effectively applicable to mussel samples. Although it does not allow for the individual quantification of each mercury species, such as methylmercury, the method is a valuable tool for understanding mercury transfer across different trophic levels in the food chain. Additionally, it stands out for eliminating the need for prior sample digestion and the use of toxic reagents, making it a more environmentally friendly and practical approach.

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[CAPES; FAPES; CNPq; UFES; UVV; NCQP; LEA]

Poster and oral Presentations

Section: Advances in Analytical Techniques and Sample Preparation for Chemical Speciation and Fractionation

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION
Sao Pedro, Sao Paulo, Brazil
November, 9th to 11th, 2025
ADV-01

SEQUENTIAL INJECTION ANALYSIS (SIA) METHOD FOR DETERMINATION OF PHOSPHORUS SPECIES IN FERTILIZERS

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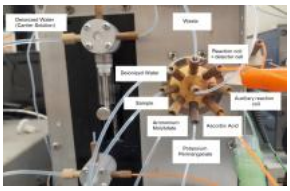
Fertilizers are considered essential for agricultural production; however, indiscriminate use causes contamination of food, soil, and water. Phosphorus, a contributing agent to the eutrophication of water bodies, can be determined by the molybdenum blue method[1]. The official methods of the Ministry of Agriculture and Livestock (MAPA) are still performed in batch or by gravimetric analysis[2], generating significant waste and taking longer when compared to flow analysis[3]. This project aims to study the speciation of phosphite and phosphate, using an automated Sequential Injection Analysis (SIA) method, oxidizing phosphite to phosphate with potassium permanganate.

Figure 1: SIA system utilized in the method.



The analyzer was configured based on adaptations from phosphate methods in SIA[1] and phosphite methods in FIA[3]. The setup had deionized water at port 2, phosphorus-containing sample at port 3, 5% (w/v) ammonium molybdate with 0.25% oxalic acid in 1 mol L^{-1} sulfuric acid at port 4, 0.001 mol L^{-1} potassium permanganate in 1 mol L^{-1} sulfuric acid at port 5, and 1% ascorbic acid in water at port 6. Ports 7 and 8 were connected to coils, with port 7 containing an auxiliary reaction coil and port 8 connected to the main reaction coil and the spectrophotometer detection cell. Port 1 was the waste disposal. Before each new determination, the sampling channel was cleaned. Then, the sample solution and deionized water from port 2 were sequentially aspirated, forming a “sandwich” into the holding coil, and sent to the auxiliary coil. The initial section of the auxiliary coil solution was discarded. Then, ammonium molybdate solution, the auxiliary coil solution, and ascorbic acid solution were aspirated back to the holding coil, at a flow rate of 200 µL s^{-1}, and pumped through the reaction coil to the detector at port 8, overlapping them before the absorbance measurements. The method is then repeated, changing only the deionized water aspirated from port 2 to potassium permanganate in the auxiliary coil step, which will give the total phosphorus content.
Calibration curve solutions varying from 1 to 10 mg L^{-1} of P-phosphate and from 500 to 2000 mg L^{-1} of P-phosphite were measured in the presence and absence of permanganate, and interference was observed for phosphate in the presence of permanganate. Three calibration curves were then constructed. Utilizing various solutions with random concentrations, phosphate content was measured, adjusted for the interference of permanganate, and phosphite content was calculated by subtraction of the corresponding signal. Deviations varied from 2,3 to 19% in phosphate analysis and from 2.2 to 17% for phosphite. Fertilizer samples were dissolved and boiled in deionized water, following MAPA procedures[2], then recovery tests were performed. Phosphate readings varied between 108% and 110%, but phosphite readings had higher percentages when adding phosphate (between 107% to 142%) and lower phosphite percentages (60% to 94%).

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[**CNPq 126605/2023-8, 126095/2024-8**]

EVALUATION OF EXTRACTION METHODS FOR SUBSEQUENT ARSENIC SPECIATION IN FOOD BY LC-ICP-MS

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Arsenic is a toxic element with carcinogenic and mutagenic properties. However, the toxicity of these substances changes according to the species. Therefore, speciation analysis is necessary to understand the availability of As and its effects on different organisms. The most common inorganic As species are As(III) and As(V), and the most common organic species are methylated derivatives like dimethylarsenic acid (DMA) and monomethylarsenic acid (MMA).[1] To ensure the species preservation during speciation analysis, it is essential a careful investigation regarding the aspects of the analytical sequence from the sample preparation to the detection technique. Sample preparation is one of the most critical steps in the analytical process, considering factors that may affect species stability. In general, extraction methods are used for speciation analysis, since they involve milder conditions concerning temperature and reagent concentration. Conventional extraction (conductive heating and mechanical stirring), microwave-assisted extraction (MAE), and ultrasonic-assisted extraction (UAE) are a few of the many extraction procedures that can be used.[2] This study critically evaluated the main factors that could influence of stability and extraction efficiency of As species. Given the variety of As species in different matrices, samples of algae, rice, and fish were selected for this study to cover as many As species as possible. The extraction efficiency was evaluated based on parameters such as the type and concentration of extraction solution, as well as the time and temperature of the extraction. The stability of As species was evaluated based on the concentration of the extraction solution, as well as the addition of ions capable of accelerating redox reactions within the medium, such as Cu, Fe and Zn. It was observed that the energy source used in the extraction method did not affect the stability or extraction efficiency of the As species. However, the temperature and extraction time influenced the extraction efficiency. The HNO_3 concentration in the extraction solution was also found to influence the extraction efficiency, resulting in the conversion of the unknown As species (named UK1) present in the algae. It was observed that adding Fe^{3+} in algae the UK1 species was converted into As(III) and As(V), while in rice, As(III) and DMA was converted into As(V). Additionally, As species in the samples were quantified using optimized extraction conditions for each matrix, without species conversion. Due to their composition, the optimized conditions were different for each sample. The extraction procedure for algae and rice involved mixing 200 mg of each sample with 10 mL of 0.01 mol L^{-1} HNO_3. The extraction procedure for fish involved mixing 200 mg of sample with 10 mL of ultrapure water. The extraction temperature and time were 75 °C and 2.5 minutes, respectively, for all samples analized. At the end of the extraction process, extracts were collected and filled up to 25 mL with ultrapure water for the subsequent determination of As species by LC-ICP-MS. The limit of quantification of the proposed method was 0.06 µg g^{-1}. The range of the agreement between the speciation analysis considering all heating processes and the extraction of total arsenic concentration was from 97 to 104% for algae, from 100 to 107% for rice and from 92 to 105% for fish. This study allowed the As speciation in algae, rice and fish samples. It was possible to demonstrate that the heating process used for extraction did not affect the results. However, the efficiency and stability of As species during extraction are significantly impacted by factors such as temperature, extraction time, and the concentration of the extraction solution. In conclusion, this study emphasises the importance of carefully selecting extraction parameters to ensure the accurate speciation analysis of arsenic in diverse biological matrices.

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[**UFSM, CNPq, FAPERGS and CAPES**]

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION
Sao Pedro, Sao Paulo, Brazil
November, 9th to 11th, 2025
ADV-03

HIGHLY SENSITIVE OSMIUM DETERMINATION USING A PLASMA-MEDIATED VAPOR GENERATION COUPLED WITH ICP-MS

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A novel and fully automated method for ultrasensitive determination of osmium was developed as a more efficient alternative of sample introduction technique for ICP-MS. It was based on plasma mediated vapor generation (PMVG) where the plasma generator was constructed using a tubular configuration of a dielectric barrier discharge (DBD). A MicroMist nebulizer was used for liquid sample introduction into the PMVG reactor and a lab-made high-voltage power supply was used for plasma generation. Agilent 8900 ICP-MS/MS was utilized as a detector and the PMVG system was coupled with the autosampler through the Integrated Samples Introduction System (ISIS), resulting in an automatic flow-injection setup. The early development of the PMVG technique was focused on the proper and robust construction of the PMVG reactor, different configuration of inner and outer Cu electrodes and the voltage modulation to obtain a stable plasma. After establishing a robust operation, systematic studies were performed to identify the main factors influencing PMVG efficiency of Os. Oxidative conditions of PMVG (using HNO_3, H_2SO_4, or H_2O_2 in the liquid medium) were found to be significantly more effective then reductive conditions (formic acid and acetic acid). Other experimental parameters affecting the PMVG efficiency, transport of generated volatiles and sample throughput were evaluated. Cesium, which is assumed to produce no volatile species during the PMVG, was used as the element to track the effects of those parameters on the physical transport of the spray. The response originating from the spray transfer enhancement caused by the PMVG seems to be negligible in comparison to that originating from PMVG. ICP-MS/MS instrumental conditions were also thoughtfully studied, and interference-free detection of ^{189}Os spectral was achieved with He in the collision cell. Under optimal conditions, employing HNO_3 in the liquid medium, the PMVG efficiency achieved was > 95%, which was reflected in a detection limit at the pg L^{-1} level. Interferences from potential coexisting metals, inorganic acids, and their anions were investigated and accuracy was verified by analysis of a certified reference material OREAS 684 (platinum group element ore) following peroxide fusion for sample preparation. In order to elucidate the nature of the volatile Os species formed in the PMVG process, direct analysis in real time high-resolution mass spectrometry (DART-HRMS) with an Orbitrap analyzer was employed[1]. The measurements confirmed for the first time the generation of osmium tetroxide (OsO_4) as the volatile compound, providing strong evidence that the PMVG signal enhancement originates from true vapor-phase formation rather than aerosol transport. The developed PMVG-ICP-MS/MS method provides a highly selective and reproducible determination of Os with an extremely low detection limit. This highlights the potential of PMVG as an alternative sample introduction approach for determining trace amounts of Os in various environmental samples.

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

SPECIATION ANALYSIS OF ZINC PYRITHIONE, ZIRAM AND ZINEB ANTIFOULING BIOCIDES

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The optimization of analytical methods to quantify the antifouling (AF) biocides (e.g. Zinc Pyrithione - ZnPT, Ziram and Zineb) contribute to the knowledge of the distribution of these compounds in areas of nautical activities (e.g. seaports, marinas and docks) and associated with this are the difficulties of detection and analysis, for example, in seawater.[1] The coupling of high performance liquid chromatography (HPLC) with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) allows combining the separation power of the former with the high selectivity and sensitivity of the latter, making it the most widely used technique for the analysis speciation. The aim of this study was to perform tests using coupling HPLC, ultrasonic nebulizer (USN) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) as a preliminary phase for subsequent development of an analytical method using HPLC, USN and Inductively Coupled Plasma Mass Spectrometry (ICP MS) for the determination of the AF biocides ZnPT, Zineb and Ziram in seawater samples. Tests were performed with different methanol concentrations using the HPLC-USN-ICP OES coupling to verify the plasma response caused by the cooling of the central channel upon introduction of methanol. The best conditions for continuing the tests were using a mobile phase with 30% (v v^{-1}) methanol and the ICP OES radiofrequency power of 1,250 W. For the HPLC-USN-ICP OES coupling, the USN (model UAT6000+, CETAC) was set at temperatures of 140 °C and - 3 °C and a SpectraSYSTEM™ chromatographic pump and Gemini C18 chromatographic column (250 x 4.6 mm, 5 µm, Phenomenex) was used. The mobile phase 1[2] methanol:water (30:70, v v^{-1}) containing 0.175% (v v^{-1}) formic acid in the aqueous portion (pH = 2.96) in isocratic mode in reversed phase with a flow rate of 1 mL min^{-1} and mobile phase 2 containing methanol:water (30:70, v v^{-1}) and 0.02 mol L^{-1} ammonium acetate was adapted[3]. The volume of biocides used in HPLC was 200 µL of 10 µg L^{-1} of ZnPT, Zineb, Ziram and Zn^{2+}. Zn counts were measured at the wavelength of 206.2 nm (axial) of the ICP OES. In all separations, the highest Zn count was detected at 1 min 57 s, precluding speciation analysis during the chromatographic separation of ZnPT, Zineb, Ziram, and Zn^{2+} in a single injection using mobile phase 1. ZnPT was separated in 17.55 min (retention time, tr) and the Zn counts determined were 1,478 cts s^{-1} using mobile phase 2 and t_0 was determined at 5.85 min and the t'_r at 11.7 min. The Zn peak related to the Zineb injection was observed at 9.75 min (9 min 45 s, 570 cts s^{-1}) with t_0 = 5.2 min and t'_r = 4.55 min and the chromatographic separation of Zn^{2+} was observed in 30.55 min (30 min 33 s, 2,246 cts s^{-1}) with t_0 = 5.2 min and t'_r = 25.35 min. No peak formation occurred after Ziram injection. The result obtained of W_b (baseline) through the Gaussian curve of Zn^{2+} demonstrated a lower value of W_b (0.5350 ± 0.0410) and area 1.2356 ± 0.0617 indicating excellent symmetry of the chromatographic peak using the mobile phase 2. The W_b obtained through the Gaussian curve of ZnPT was 0.6466 ± 0.0948 and area of 1.2592 ± 0.0290 indicating excellent symmetry of the chromatographic peak. However, the W_b obtained through the Gaussian curve of Zineb presented the value of 4.9921 ± 0.3114 and area 0.7951 ± 0.0489 indicating broadening of the chromatographic peak. Comparing the chromatographic separations of ZnPT and Zn^{2+}, it can be concluded that it is possible to perform speciation analysis using mobile phase 2, the Gemini C18 column and the HPLC-USN-ICP-MS coupling.

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[CNPQ, FAPESP, UNESP]

CARBON QUANTUM DOTS: FLUORESCENT PROBES FOR ARSENIC SPECIATION

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Carbon Quantum Dots (CQDs) are carbon-based nanomaterials that exhibit intense fluorescence, standing out for their excellent optical properties, chemical stability, and ease of synthesis[1]. These particles show great potential for use as analytical probes in the detection of toxic metal ions, since their fluorescence intensity can vary proportionally to the analyte concentration. Furthermore, the incorporation of nitrogen atoms into the CQD structure enhances their interaction with metal cations, either through coordination or through electrostatic interaction, resulting in increased sensitivity of the analytical probe[2]. In this work, nitrogen-doped CQDs (N-CQDs) were synthesized and applied for the detection of toxic metal ions. The particles were obtained through a hydrothermal microwave assisted (HTMW) method and exhibited intense blue emission at 440 nm under excitation at 347 nm. Using 0.05 % (v/v) N-CQDs in aqueous solution and inorganic arsenic species at 1 mg L^{-1}, only As(III) induced fluorescence quenching of approximately 67%, whereas other ions such as As(V), didn´t significantly affect the emission of the nanoparticles. To verify the behavior of the fluorescent probe when the species are simultaneously present in the same solution, solutions containing As(III) and As(V) were prepared at a concentration of 1 mg L^{-1} each. The solutions were brought into contact with the N-CQDs solution and taken for analysis in the fluorimeter. The selectivity of N CQDs to the trivalent arsenic species is proven by observing that even with the simultaneous presence of As(V), the fluorescence quenching remains close to 60%. These results show that the synthesized material exhibits great potential to act as an on/off probe in the development of alternative devices for arsenic speciation analysis in various samples.

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The authors acknowledge the support of UFCAT, CNPQ, FAPEG, CAPES and FUNAPE.

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION
EspeQBrasil 2025
Sao Pedro, Sao Paulo, Brazil
November, 9th to 11th, 2025

ADV-06

DETERMINATION OF TECHNOLOGICAL CRITICAL ELEMENTS BY USING DIFFUSIVE GRADIENT IN THIN FILMS, HYDRIDE GENERATION, AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY TECHNIQUES

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Technologically critical elements (TCEs) such as tellurium (Te), germanium (Ge), gallium (Ga), indium (In), niobium (Nb), and tantalum (Ta) are essential for modern technologies but remain poorly studied regarding their environmental mobility and bioavailability. Their increasing release into aquatic systems through industrial and mining activities highlights the need for advanced analytical approaches capable of monitoring these elements at ultra-trace levels.

This study explores the application of Diffusive Gradients in Thin Films (DGT) for the determination of TCEs, combined with inductively coupled plasma mass spectrometry (ICP-MS). The main focus is the development of new binding phases based on cellulose functionalized with selective ligands, aiming to improve the retention and pre-concentration of these elements. Laboratory tests demonstrated successful immobilization of the ligands on the cellulose matrix, ensuring stability for DGT applications.

Immersion curve experiments were carried out using citric acid as the elution agent over a 48-hour period. The results showed linear responses for all elements tested (R^2=0,98), confirming Fick's Law for the DGT. Also, we were able to obtain for the first time the diffusion coefficients for Germanium, table 1. These findings demonstrate the feasibility of cellulose-based binding phases and provide an essential step toward accurate determination of TCEs in environmental samples.

Overall, the outcomes of this work contribute to advancing DGT methodologies for TCEs, establishing a foundation for future applications in freshwater systems impacted by industrial and mining activities. The development of reliable analytical tools for these emerging contaminants is crucial for understanding their environmental behavior and supporting sustainable monitoring strategies.

	Ge	In	La	Ce	Nd	Sm	Ga
D (cm^2/s)	2,99.10^{-07}	4,44.10^{-07}	5,65.10^{-07}	6,17.10^{-07}	6,88.10^{-07}	7,3.10^{-07}	9,7.10^{-08}

Table 1: Difusion Coeficient for Ge, In, La, Ce, Nd, Sm and Ga.

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[CAPES, Fapesp, CNPq]

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION
EspeQBrasil 2025
Sao Pedro, Sao Paulo, Brazil
November, 9th to 11th, 2025
ADV-07

BIOGENIC SYNTHESIS OF IRON NANOPARTICLES USING SOYBEAN SEEDS: COMPARATIVE EVALUATION OF Fe(II) AND Fe(III) PRECURSORS

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Metal nanoparticles are particularly notable for their applications in agriculture, with iron nanoparticles (FeNPs) standing out for their ability to enhance iron bioavailability, stimulate root growth, and improve water stress tolerance in soybean crops.[1] An important aspect to consider, however, is the replacement of conventional chemical reducing agents with biogenic synthesis approaches, which are more environmentally sustainable and cost-effective.[2]In this context, the use of soybean seeds (*Glycine max L.*) as a biogenic reducing agent has shown great promise.[3] This study investigates the synthesis of FeNPs using two different iron precursors, Fe(II) and Fe(III), by varying soybean grain concentration, iron concentration, as well as time and amplitude in a Cup Horn sonicator. Chemometric analyses were applied to establish the influence of these parameters, allowing the identification of optimal synthesis conditions. The results showed that syntheses involving Fe(II) were more efficient, particularly the 15th experiment, compared to those with Fe(III), which exhibited low yields under the same conditions. It was therefore concluded that higher energy input would be required to achieve FeNP synthesis from Fe(III).

a)

Synthesis Number	Time (min)	[Fe] (mM)	[Soybean] (g/100 mL)	Amplitude (%)	Lowest Peak Fe (II) - (nm)	Lowest Peak Fe (III) - (nm)
1	6	6	0,1	90	164,6	332,6
2	6	2	0,1	90	400,9	57,67
3	6	6	0,5	50	1326	294,4
4	3	2	0,5	90	3,638	183,4
5	6	2	0,5	50	3,153	65,3
6	3	6	0,1	50	98,8	245,3
7	3	6	0,5	90	3,973	4,904
8	3	2	0,1	50	97,8	277,9
9	1	4	0,25	70	3,743	129,4
10	6	4	0,25	70	4,378	56,49
11	4	4	0,25	30	2,989	172,3
12	4	4	0,25	90	4,362	226,2
13	4	1	0,25	70	4,583	237,1
14	4	7	0,25	70	9,055	232,3
15	4	4	0,5	70	2,757	248,7
16	4	4	0,5	70	2,785	128,9
17	4	4	0,25	70	3,209	236,7
18	4	4	0,25	70	3,889	128,6

b)

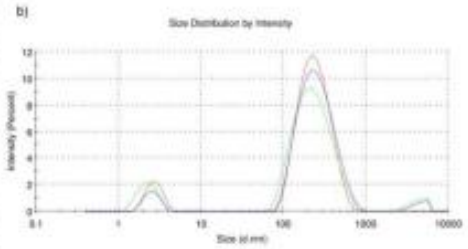

Figure 1 - a) Table of parameter variation; b) DLS spectra of synthesis number 15 for Fe(II).

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[Acknowledgments: FAPESP, CAPES and CNPq]

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION
Sao Pedro, Sao Paulo, Brazil
November, 9th to 11th, 2025
ADV-08

A Comprehensive Analysis of Chromium (III) and Chromium (VI) in Various Water Sources: ISO Standard 24384:2024

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This study details the development of a novel HPLC-ICPMS method for the rapid and accurate measurement of chromium species (Chromium (III) and Chromium (VI)) in various water sources. The method achieves detection limits of 10 ppt within an analysis time of less than 8 minutes, meeting stringent regulations for drinking water quality worldwide. Key issues related to the interconversion of chromium species during sampling, extraction, storage, and analysis are thoroughly addressed. The extraction efficiency is significantly influenced by the matrix type, presenting challenges that are critical to the methodology. The innovative coupling of HPLC with ICP-MS facilitates lower limits of detection (LODs) for multiple chromium species, demonstrating its effectiveness for regulated products. The importance of method validation is emphasized, as it is essential for ensuring the accuracy and reliability of results. Adherence to ISO Standard 24384:2024 enhances data traceability and validity, thereby reinforcing the credibility of the findings. Accurate speciation analysis is vital for assessing the potential risks associated with chromium in water, which has significant implications for environmental and public health. In summary, this study presents a reliable, efficient, and standardized method for chromium speciation analysis, contributing to regulatory compliance and environmental monitoring efforts.

8th BRAZILIAN MEETING ON CHEMICAL SPECIATION
Sao Pedro, Sao Paulo, Brazil
November, 9th to 11th, 2025
ADV-09

Closed vessel conductively heated digestion system: A reliable sample preparation alternative for EPA 3015A and 3051A official methods

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EPA 3015A and 3051A official methods have been extensively used for decades for the preparation of environmental samples (aqueous and soil/sediments samples, respectively) aiming at trace elements analysis. Both the methods were designed to perform microwave-assisted extraction with HNO3, or alternatively, HNO3 and HCl mixtures. Therefore, they are not intended to accomplish total decomposition of the sample, and the extracted analyte concentrations may not reflect the total content in the sample. In the last decade, the feasibility of closed vessels conductively heated digestion system (CHDS) has been demonstrated for the preparation of organic and inorganic samples aiming at elemental analysis by ICP-based methods. This work proposes a new method for the extraction of metals from aqueous, soil and sediment samples using a closed vessels CHDS. It was used a CHDS equipment model Simplify (Vert Technologies, Sao Paulo, Brazil) which allows the simultaneous digestion of 24 samples. The digestion vessels (Pmax = 30 bar) comprise a polytetrafluorethylene (PTFE) lid, 45 mL quartz tubes, and a polyvinyl chloride fixture that connects the lid to the tube. The PTFE lid features a top valve to relieve the residual pressure after digestion and a sided rupture membrane with a maximum pressure of 30 bar. A 9.5 mL test portion of aqueous samples (groundwater and wastewater) was digested with 0.5 mL of HNO 65% v v−1, and a 250 mg test portion of soil and sediment was digested with 2.25 mL of HNO3 65 % v v−1 and 0.75 mL of HCl 37 % v v−1 for 10 min, at 210 ºC. Temperature program consists of (i) 18 min ramp to 210 °C, (ii) 10 min plateau at 210 °C, (iii) 07 min cooling down (total time = 35 min). For soil and sediment samples, the final volumes were made to 25 mL with ultra-pure water. Aqueous samples were not diluted. A Thermo Scientific iCAP 6500 Duo inductively coupled plasma optical emission spectrometer (Waltham, USA) was used for elemental quantification. For aqueous samples, the results obtained by the proposed method were compared with those from EPA 3015A official method based on microwave-assisted extraction, and no significant differences were observed at 95% confidence level. In addition, standard addition experiments indicated that recoveries for Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, V and Zn ranged from 88 to 106 % for spiked groundwater and from 83 to 105 % for spiked wastewater. The concentrations of Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn determined in the SRM 2706 New Jersey Soil (NIST, USA) prepared by closed vessels CHDS were between the minimum and maximum concentration range from multi-laboratory testing of SRM 2706 using EPA 3051A official method.2 In the case of marine sediment, a candidate reference material, the concentrations of Ba, Co, Cu, Zn, Fe, Mg and Mn were also in the minimum and maximum range from the interlaboratorial trail using EPA 3051A official method. It can be concluded that the proposed closed vessels CHDS extraction method is a reliable alternative to EPA 3015A and EPA 3051A official methods aiming at environmental trace analysis. In addition, both methods can be simultaneously performed at the same batch in the Simplify Digestor.

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