RSAS 2025

BOOK OF ABSTRACTS

17th Rio Symposium

ON ATOMIC SPECTROMETRY

Sao Pedro, Sao Paulo, Brazil

November,12th to 14th, 2025

RSAS 2025

17th Rio Symposium

ON ATOMIC SPECTROMETRY

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Chair: Marco Aurélio Zezzi Arruda

Co-chair: Amauri Antônio Menegário

Organization

UNICAMP

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Welcome Message

It is with great pleasure that we welcome you to the 17th Rio Symposium on Atomic Spectrometry (RSAS). Since its first edition in 1988, the RSAS has become a unique forum for scientists, students, and professionals from academia, industry, and research institutes to share knowledge, discuss recent advances, and foster collaborations in the broad field of atomic spectrometry.

This year's edition continues the tradition of providing a high-quality scientific program, featuring plenary and keynote lectures from renowned experts, oral, short, and poster presentations, and opportunities for networking in a warm and collaborative atmosphere. The diversity of topics covered, from fundamental studies to applied research in environmental, food, biological, and industrial analysis, reflects the dynamic and multidisciplinary nature of our community.

We are grateful for the enthusiastic participation of all attendees, the invaluable contributions from our invited speakers, and the support of sponsors and partners who made this event possible. We also hope you will enjoy not only the stimulating scientific discussions but also the cultural and social experiences that this meeting offers.

Welcome to the 17th Rio Symposium on Atomic Spectrometry – may this event inspire new ideas, strengthen collaborations, and create lasting memories.

Marco Aurélio Zezzi Arruda
Chair of 17th RSAS

RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY

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General Information

EVENT VENUE

Hotel Fonte Colina Verde

Address: Rua Veríssimo Prado, 1500, São Pedro – SP – Brasil

Phone: +55 (19) 3481 9999

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E-mail: reservas@hotelcolinaverde.com.br

Website: https://www.hotelcolinaverde.com.br/

POSTER INFORMATION

The 17th RSAS will have two poster sessions, on November 13th, from 14:00h to 15:00h, and on November 14th from 14:20h to 15:20h. Posters must be fixed on their allocated space in the day of they will be presented. After the session, posters must be removed by the authors.

MEDIA DESK

All speakrs with presentations must go to the Media Desk to test the presentation material. This is very important so that your lecture can be presented without problems.

CERTIFICATES

The certificates will be available to the participants in digital form, at the 17th RSAS webpage, in the participant area (https://eventos.galoa.com.br/8o-espeqbrazil-e-17o-rsas/page/5485-welcome?lang=en).

EMERGENCY NUMBERS

Ambulance / Medical service: 192

Military police: 190

Fire department: 193

Committees

Organizing Committee

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Helmar Wiltsche, Graz University of Technology, Austria

Jan Kratzer, Czech Academy Sciences, Czech Republic

Jiří Dědina, Czech Academy Sciences, Czech Republic

Joanna Szpunar, French National Research Center, France

Joaquim de Araújo Nóbrega, UFSCar, Brazil

Joerg Feldmann, Karl-Franzens-Universität Graz, Austria

Márcia Foster Mesko, UFPel, Brazil

Maria das Graças Andrade Korn, UFBA, Brazil

Maria Montes-Bayón, University of Oviedo, Spain

Maria Tereza Weitzel Dias Carneiro Lima, UFES, Brazil

Martín Resano, University of Zaragoza, Spain

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Ramon Murray Barnes, University of Massachusetts Amherst, USA

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Rodolfo Wuilloud, National University of Cuyo, Argentina

Ryszard Lobinski, French National Research Center, France

Tatiana Dillenburg Saint´Pierre, PUC-Rio, Brazil

Viktor Gábor Mihucz, Faculty of Science, Eötvös Loránd University, Budapest, Hungary

Waldo Emerzon Quiroz Venegas, Pontificia Universidad Católica de Valparaíso, Chile

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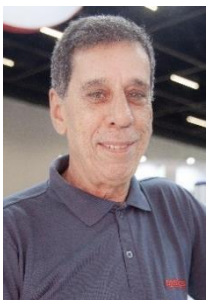
Tributes

"In recognition for the outstanding contribution to the field of Atomic Spectrometry"

Érico Marlon de Moraes Flores

Federal University of Santa Maria, Brazil



Luiz Carlos Bravo dos Santos

Nova Analítica, Brazil

María Montes-Bayón

Universidad de Oviedo, Spain

Ryszard Łobiński

French National Research Center (CNRS), France

RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY

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Opening ceremony

Ryszard Łobiński
CNRS, France

Closing ceremony

Daniel Lázaro Gallindo Borges
Federal University of Santa Catarina, Brazil

Ewa Bulska
University of Warsaw, Poland

Ralph Edward Sturgeon
National Research Council Canada, Canada

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Plenary Lectures

Érico M. M. Flores
Federal University of Santa Maria, Brazil

Ewa Bulska
University of Warsaw, Poland

Joanna Szpunar
French National Researcher Center, France

María Montes-Bayón
University of Oviedo, Spain

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Invited Speakers – Keynotes

Alicia Mollo

Carlos A. Perez

Claudia Blindauer

Dirk Schaumloeffel

Jan Kratzer

Joaquim Nóbrega

Jörg Bettmer

Marcia Mesko

Maria Tereza W.D.C.L.

Rodolfo Wuilloud

Tatiana Saint'Pierre

Viktor G. Mihucz

Waldo E. Q. Venegas

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RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY

Sao Pedro, Sao Paulo, Brazil

November,12th to 14th, 2025

SCIENTIFIC PROGRAM

RSAS 2025

17th Rio Symposium ON ATOMIC SPECTROMETRY

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November, 12th to 14th, 2025

12- Wednesday			13- Thursday			14- Friday		
Time	Activity	Speaker	Atomic & Fluorescence spectrometry			X-ray, Raman, Mössbauer, SIMS and Synchrotron		
			Activity	Speaker	Time	Activity	Speaker	Time
			Keynote 1	Jan Kratzer	8:30-09:00h	Keynote 8	Dirk Shöuloefell	8:30-09:00h
			Keynote 2	Alicia Molo	09:00-09:30h	Keynote 9	Viktor G. Mihucz	09:00-09:30h
			Keynote 3	Maria Tereza	09:30-10:00h	Keynote 10	Carlos Perez	09:30-10:00h
			Keynote 4	Rodolfo Wuilloud	10:00-10:30h	Oral talk 8	Vanessa Alves	10:00-10:15h
			Oral talk 1	Valentina Giacomino	10:30-10:45h	Oral talk 9	Ketolly N. S. Leal	10:15-10:30h
			Coffee-break	-	10:45-11:05h	Silver	Perkin-Elmer	10:30-10:50h
			Oral talk 2	Morgana L. da Rocha	11:05-11:20h	Coffee-break	-	10:50-11:15h
			Diamond	Analytik Jena	11:20-11:50h	Hyphanated/multimodal techniques		
Free day excursion			Chemometrics/Metrology in spectrometry			Keynote 11	Claudia Blindauer	11:15-11:45h
			Plenary 2	Ewa Bulska	11:50-12:25h	Keynote 12	Waldo Quiroz	11:45-12:15h
			Oral talk 3	Jorge Carlos Yánez Solorza	12:25-12:40h	Oral talk 10	Higor B. de Oliveira	12:15-12:30h
						Oral talk 11	Antonio Celso	12:30:12:45h
			Lunch	-	12:40-14:00h	Lunch	-	12:45-14:00h
			Poster session 1	PTB 01 to 33	14:00-15:00h	Silver	Agilent	14:00-14:20h
				AAS 01 to 12		Poster session 2	PTB 34 to 65	14:20-15:20h
				TNA 01 to 10			AAS 13 to 24	
				HYT 01 to 03			TNA 11 to 20	
			Plasma-based techniques				TXR 01 to 03	
14h	Accreditation	Organizing committee	Plenary 3	Maria Montes-Bayón	15:00-15:35h	Trends and new approaches		
14:15-17:00h	Short course 1	Clesia C. Nascentes and Marcia A. M. S. Veiga	Keynote 5	Marcia Mesko	15:35-16:05h	Plenary 4	Joanna Szpunar	15:20-15:55h
			Keynote 6	Tatiana Saint'Pierre	16:05- 16:35h	Keynote 13	Joaquim Nóbrega	15:55- 16:25h
			Coffee-break	-	16:35-16:55h	Oral talk 12	Gilberto Coelho	16:25-16:40h
	Short course 2	Thiago O. Araujo	Keynote 7	Jörg Bettmer	16:55- 17:25h	Gold	Anton Paar	16:40- 17:00h
	Workshop	Ciro E. M. Herrera and Edenir R. P. Filho	Gold	Thermo/Nova Analítica	17:25- 17:45h	Coffee-break	-	17:00-17:20h
			Oral talk 4	Magdalena Borowska	17:45- 18:00h	Plenary 5	Érico M. M. Flores	17:20- 17:55h
			Oral talk 5	Gisele Simone Lopes	18:00- 18:15h	Closing session - Devoted to Curtius/Welz	Ewa Bulska	17:55- 18:15h
18:30h - 20:00h	Opening ceremony RSAS	Organizing Committee	Oral talk 6	Flavio Venancio Nakadi	18:15- 18:30h		Daniel Gallindo	18:15- 18:35h
			Oral talk 7	Jörg Feldmann	18:30- 18:45h		Ralph Sturgeon	18:35- 18:55h
20:00h - 20:40h	Opening plenary	Ryszard Lobinski	Short dwell time session SBQ-Jovem	1. Nikol Vlčková	18:45-18:50h	Closing ceremony	Organizing Committee	18:55-19:30h
				2. Leticia M. Rodrigues	18:50-18:55h			
				3. Vitoria H. Cauduro	18:55-19:00h			
				4. Luiz G. S. Rocha	19:00-19:05h			
				5. Ana Flávia L. M. N.	19:05-19:10h			
				6. Vinicius P. Souza	19:10-19:15h			
20:45h	Cocktail	-	Atomic Dinner	-	20:30h	Bottle party	-	20:30h

Legend
Short course/Workshop
Opening/Closing ceremony
Plenary
Keynote
Oral talk
Sponsor/Support
Poster/ Short dwell time
Coffee-break/ Lunch
Cocktail/ Dinner

SCHEDULE – 17th Rio Symposium on Atomic Spectrometry

November, 12th – Wednesday

Short courses and Workshop:

- **14:15-17:00h** - Short course 1: **"Forensics Applied to Spectrometry"** - Clesia C. Nascentes and Marcia A. M. S. Veiga
- **14:15-17:00h** - Short course 2: **"Analytical Method Validation"** - Thiago O. Araujo
- **14:15-17:00h** - Workshop: **"Spectrometry devoted to solid sampling"** - Ciro E. M. Herrera and Edenir R. P. Filho

Conference opening:

- **18:30-20:00h** - Opening ceremony
- **20:00-20:40h** - Opening plenary: **"Supplanted or Evolving? Revisiting Atomic Spectrometry's Place in Trace Element Speciation Analysis"** - Ryszard Lobinski

20:45h - Cocktail

November, 13th – Wednesday

Session "Atomic & Fluorescence Spectrometry":

- 8:30 – 9:00 h - Keynote presentation 1: "**Volatile Species Atomization in Ambient Plasmas for Trace Determination of Metals by Atomic Spectrometry" -** Jan Kratzer
- 9:00 – 9:30 h - Keynote presentation 2: "**Advances in direct vapour generation atomic spectrometry in complex matrix" –** Alicia Molo
- 9:30 – 10:00 h - Keynote presentation 3: "**Challenges in Environmental Analysis by Atomic Spectrometry"** - Maria Tereza Weitzel Dias Carneiro
- 10:00 – 10:30 h - Keynote presentation 4: "**Advancing Greener Total and Speciation Elemental Analysis Through Alternative Solvents"** - Rodolfo G. Wuilloud
- 10:30 – 10:45 h - Oral talk 1: **"Determination of P and S in Argentina's meat samples by High Resolution Continuum Source Molecular Absorption Spectrometry"** - Valentina Giacomino

10:45 – 11:05 h – Coffee-break

- 11:05 – 11:20 h – Oral talk 2: **"Assessment of Pd Nanoparticles as Chemical Modifiers and Preconcentration Agents for Cd Determination in River Water by HR-CS GFAAS"** - Morgana L. da Rocha
- 11:20 – 11:50 h – Diamond sponsor presentation, Analytik Jena: **"Trace Analysis Made Simple: The Wonders of High-resolution Atomic/Molecular Absorption Spectrometry"** - Daniel L. G. Borges

Session "Chemometrics/Metrology in Spectrometry":

- 11:50 – 12:25 h – Plenary 2: **"Chemical Metrology in the Era of Omics Sciences"** – Ewa Bulska
- 12:25 – 12:40 h - Oral talk 3: **"Illuminating the copper industry: How LIBS and hyperspectral imaging are transforming mining analytics and processes"** – Jorge Carlos Yánez Solorza

12:40 – 14:00 h – Lunch

Poster session 1: 14:20 – 15:20 h

- Plasma-based Techniques: PTB 01 to PTB 33
- Atomic & Fluorescence Spectrometry: AAS 01 to AAS 12
- Trends and New Approaches: TNA 01 to TNA 10
- Hyphenated/multimodal Techniques: HYT 01 to HYT 03

Session "Plasma-based Techniques":

- 15:00 – 15:35 h – Plenary 3: **"Quantitative Elemental Analysis in Single Cells: From ICP-MS to Mass Cytometry"** - Maria Montes-Bayón
- 15:35 – 16:05 h – Keynote presentation 5: **"Sample Preparation Strategies for Determination of Non-Metals and Their Species by Mass Spectrometry Techniques"** – Marcia Mesko
- 16:05 – 16:35 h - Keynote presentation 6: **"Retrospective of the Work Developed at Labspectro (Laboratory of Atomic Spectrometry), at PUC-Rio"** - Tatiana Saint'Pierre

16:35 – 16:55 h – Coffee-break

- 16:55 – 17:25 h – Keynote presentation 7: **"The Role of ICP-MS and Other MS-Techniques in the Characterization of Biogenic Nanoparticles"** - Jörg Bettmer
- 17:25 – 17:45 h – Gold sponsor presentation, Thermo/Nova Analítica: "**Innovations in Microwave Sample Preparation for Elemental Analysis" -** Mariana Ortega
- 17:45 – 18:00 h – Oral talk 4: **"Development of a Spectrometric Analytical Platform for Studying Selenium Nanoparticles in Environmental Contexts"** - Magdalena Borowska
- 18:00 – 18:15 h – Oral talk 5: **"Development and Application of Sustainable Vapor Generation Methods for Trace Element Analysis by Spectrometric Techniques"** - Gisele Simone Lopes
- 18:15 – 18:30 h – Oral talk 6: **"Single-event Analysis of Discrete Entities Using Microwave-induced Nitrogen Plasma–mass Spectrometry"** - Flávio Venâncio Nakadi
- 18:30 – 18:45 h – Oral talk 7: **"Fluorine - The Dark Side of Atomic Spectrometry" -** Jörg Feldmann

Short-dwell time Session:

- 18:45 – 18:50 h – Short dwell time presentation 1: **"A Novel Atmospheric Pressure Glow Discharge Hydride Atomizer for Atomic Absorption Spectrometry: Performance Evaluation"-** Nikol Vlčková
- 18:50 – 18:55 h – Short dwell time presentation 2: **"Tracing Copper Fungicide Uptake and Distribution in Pea Plants and Soil Using 65Cu Isotope Labeling"**– Leticia M. Rodrigues
- 18:55 – 19:00 h – Short dwell time presentation 3: **"Seasonal Evaluation of Inorganic Contaminants in Sediments of River Affected by Mining Rejects"** - Vitoria H. Cauduro
- 19:00 – 19:05 h – Short dwell time presentation 4: **"Investigation of Predictor Parameters for P Determination in Soil by SD-LIBS"** - Luiz G. S. Rocha

- 19:05 – 19:10 h – Short dwell time presentation 5: "**Enhancing LIBS Performance With Silver Nanoparticles Synthesized on Paper by Ring-Oven"** – Ana Flávia L. M. Nascimento
- 19:10 – 19:15 h – Short dwell time presentation 6: **"Plasma-Mediated Vapor Generation: Application for Hg Determination in Fish Samples After Microwave-Induced Combustion"** – Vinicius Picoloto Souza
- 20:30 h – Atomic Dinner

November, 14th – Wednesday

Session "X-ray, Raman, Mössbauer, SIMS and Synchrotron Techniques":

- 08:30 – 09:00 h – Keynote presentation 8: **"Elemental Imaging – Current Challenges and Future Prospects" -** Dirk Schaumlöffel
- 09:00 – 09:30 h – Keynote presentation 9: "**Iron Bioaccessibility from Vegan Dietary Supplements" -** Viktor G. Mihucz
- 09:30 – 10:00 h – Keynote presentation 10: **"Nano-Analytical Techniques at the Carnaúba Beamline for Experiments in Several Research Areas of Science"** – Carlos A. Pérez
- 10:00 – 10:15 h – Oral talk 8: **"Integration of Solid Phase Extraction and EDXRF: Nickel Determination Using DMG-Modified Cotton Fabric" -** Vanessa Alves
- 10:15 – 10:30 h – Oral talk 9: **"Real-time FRET Analysis of Zinc, Albumin, and Fatty Acid-mediated Modulation of Insulin Oligomerization" -** Ketolly N. S. Leal
- 10:30 – 10:50 h – Silver sponsor presentation, Perkin-Elmer: **"From Colloids to Parasites: Revealing Selenium Nanoparticle Uptake in Leishmania by Single Event ICP-MS"**- Jefferson R. Souza

10:50 – 11:15 h – Coffee-break

Session "Hyphenated/multimodal Techniques":

- 11:15 – 11:45 h – Keynote presentation 11: "**The Impact of Non-Esterified Fatty Acids on Zinc Speciation and Dynamics in Blood Plasma"** - Claudia Blindauer
- 11:45 – 12:15 h – Keynote presentation 12: "**Direct Determination of Lithium in Brine Samples Using Handheld LIBS Without Sample Treatment: Sample Introduction by Venturi System"** - Waldo Quiroz
- 12:15 – 12:30 h – Oral talk 10: "**Influence of Particle Size in the Direct Sewage Sludge Analysis by Laser-Assisted Technique"** - Higor B. de Oliveira
- 12:30 – 12:45 h – Oral talk 11: "**An Innovative Laser Ablation Laser Ionization (LALI) Mass Spectrometry Technique for Solid Material Analysis"** - Antonio Celso

12:45 – 14:00 h – Lunch

- 14:00 – 14:20 h – Silver sponsor presentation, Agilent: **"Technological Innovations in Atomic Spectrometry: Advancing Automation and Applications with Agilent ICP-OES and ICP-MS/MS"** - Bruno M. Siqueira

Poster session 2: 14:20 – 15:20 h

- Plasma-based Techniques: PTB 34 to PTB 65
- Atomic & Fluorescence Spectrometry: AAS 13 to AAS 24
- Trends and New Approaches: TNA 11 to TNA 20
- Techniques Based on X-ray, Raman, and Mössbauer: TRX 01 to TRX 03

Session "Trends and New Approaches":

- 15:20 – 15:55 h – Plenary 4: "**Unravelling Selenium Metabolism Through the Lens of Mass Spectrometry" -** Joanna Szpunar
- 15:55 – 16:25 h – Keynote presentation 13: "**Microwave-Assisted Sample Preparation: Where Are We Heading To" -** Joaquim Nóbrega
- 16:25 – 16:40 h – Oral talk 12: "**Direct Solid Sampling by Plasma-Mediated Vapor Generation" -** Gilberto Coelho
- 16:40 – 17:00 h – Gold sponsor presentation, Anton Paar: **"Detection and Quantification of Titanium Dioxide (E171) in Food Using Raman Spectroscopy" -** Renata Nascimento Caetano
- 17:00 – 17:20 h – Coffee-break
- 17:20 – 17:55 h – Plenary 5: "**Challenges for the Determination of Rare Earth Elements at Low Concentrations" -** Érico M. M. Flores

Closing Session - Devoted to Curtius/Welz:

- 17:55 – 18:15 h – **The Role of Calibration in Atomic Spectrometry to Support the Research on Biologically Active Substances" -** Ewa Bulska
- 18:15 – 18:35 h – **Tackling Challenging Samples With Alternative Approaches: A Brief Overview of Adilson's and Bernhard's Heritage in Modern Elemental Analysis" -** Daniel L. Gallindo
- 18:35 – 18:55 h – **Evidence for Nanoparticle Formation During PVG… Easy…. but The Bumps Along the Way…!" -** Ralph Sturgeon

Closing ceremony: 18:55 – 19:30 h

20:30 h – Bottle party

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ABSTRACTS

OPENING CONFERENCE

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Supplanted or Evolving? Revisiting Atomic Spectrometry's Place in Trace Element Speciation Analysis

R. Lobinski[1,2*]

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The behavior of trace elements—whether essential or toxic—hinges on the chemical species in which they circulate through biological systems and the environment. Recognition of this fact has driven a decades-long quest for analytical strategies that discriminate not merely total-element concentrations but their discrete molecular or ionic forms [1].

Early speciation studies relied on isolating individual metallocompounds in milligram quantities for offline NMR characterisation. The advent of element-specific detectors coupled to chromatography (AAS, ICP-OES, ICP-MS) revolutionised the field, pushing detection limits into the sub-picogram range and shifting the analytical target from whole molecules to the atoms embedded within them [2].

High-resolution chromatographic or electrophoretic separations offered species-level selectivity that proved powerful for anthropogenic pollutants and metallodrug metabolites, yet remained insufficient for the complex, endogenous and environmental pools of metal species. With electrospray ionisation and high-resolution, high-accuracy (HRAM) mass spectrometry, the centre of gravity of analytical methodologies moved once again—from chromatographic peak capacity to the mass spectrum itself. Accurate mass profiling and isotope pattern recognition now allow direct targeting of intact metal-bearing molecules.State-of-the-art FT-ICR and Orbitrap instruments can resolve ions differing by the mass of a single electron (≈0.5 mDa) and measure their masses with sub-ppm precision, enabling near-comprehensive inventories of element species in omics-scale extracts. Such capability underpins emerging environmental metallomics, where dozens of metal species are mapped simultaneously across biotic compartments [3,4].

This lecture will examine how atomic-spectrometric foundations have been challenged yet enriched by the rise of molecular MS, charting the trajectory from atom-focused detection to holistic molecule-level speciation. We will ask whether atomic spectrometry has been supplanted—or has in fact evolved—into an indispensable partner in decoding the environmental and biological roles of trace metals.

[1] D.M. Templeton, F. Ariese, R. Cornelis, L.G. Danielsson, H. Muntau, H.P. van Leeuwen, R. Lobinski, Pure and Applied Chemistry, 2000, 72,1453-1470.

[2] J. Szpunar, R. Lobinski, Hyphenated Techniques in Speciation Analysis, RSC, Cambridge, 2003. [3] P. Flis, L. Ouerdane, L. Grillet, C. Curie, S. Mari, R. Lobinski (2016) New Phytologist, 2016, 211, 1129–1141.

[4] F. Calderón-Celis, I. González-Álvarez, M. Fabjanowicz, S. Godin, L. Ouerdane, B. Lauga, R. Lobinski, Environmental Science and Technology, 2023, 57, 17302–17311.

PLENARY LECTURES

RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY
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Chemical Metrology in the Era of Omics Sciences

Ewa Bulska[a*]
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The dynamic growth of omics sciences, including genomics, metabolomics, and particularly proteomics, has transformed modern analytical chemistry. Proteomics, which focuses on large-scale studies of proteins and their functions, relies on highly sensitive techniques such as mass spectrometry and chromatography. The reliability of results in such research depends directly on the accuracy, traceability, and reproducibility of chemical measurements. Chemical metrology provides the conceptual and practical foundation for ensuring these qualities, supporting the validity of results used in biomedical, pharmacological, and environmental studies.

Results of chemical measurements underpin many decisions related to human health, food safety, and environmental protection. Applying metrological principles is essential to ensure that analytical data are valid and trustworthy. The diversity of analytes, their concentrations, and the chemical matrices involved requires an individual approach to each analytical task. The quality of results therefore depends on proper validation of analytical procedures and on the responsible interpretation of data.

Chemical metrology plays a key role in maintaining quality, repeatability, and comparability of results across laboratories. Validation procedures in accordance with ISO/IEC 17025 and ISO 15189 include calibration of instruments, monitoring of chromatographic conditions, and development of consistent analytical protocols.

The strengths and weaknesses of chemical metrology are particularly visible in biomedical research, where complex sample preparation and highly sensitive measurements are required. Sample contamination, poor calibration, or overreliance on automated data processing may lead to incorrect conclusions about biomarkers, disease mechanisms, or therapeutic outcomes.

The presentation will highlight examples showing that responsibility for the validity of measurement results requires not only detailed knowledge of analytical methods but also awareness of their limitations. Only the combination of methodological rigor with critical scientific reflection allows chemical metrology to ensure reliable and meaningful results that can be responsibly used in research and decision-making. In addition, methodologies for building standardized protocols supporting quality assurance in proteomics measurements will be presented, illustrated by case studies on the safety assessment of fluorinated pharmaceuticals.

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QUANTITATIVE ELEMENTAL ANALYSIS IN SINGLE CELLS: FROM ICP-MS TO MASS CYTOMETRY

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Thus, the development of analytical/biotechnological strategies that enable the exploration of heterogeneity between cells and within populations, previously assumed to be homogeneous, is an active area of research. Particularly in the field of elemental analysis, the use of inductively coupled plasma mass spectrometry (ICP-MS) as detector for single cell studies has been growing enormously since the year 2005 when the first publication on its use for monitoring individual bacteria was out. Single-cell ICP-MS (SC-ICP-MS) has been now successfully applied to monitor elemental components in either monodispersed suspended cells (e.g. bacteria, yeast or microalgae) or to adherent human cells growing in monolayers. Indeed, a crucial choice for these single-cell experiments is the method for introducing individual cells into a format compatible with the downstream elemental analysis [1]. However, the real breakthrough of ICP-MS in the field of biomedicine for single cell analysis arose associated to the commercialization of the so called “mass cytometer”. Flow cytometry has been widely applied over the years for the analysis of biomarkers in individual cells by labelling the molecules of interest with specific antibodies carrying fluorescent probes. The main drawback associated to the spectral overlap of the fluorophores was overcome by using antibodies linked to rare earth metals through metal chelating polymers as reporters. This technique is known as mass cytometry (CyTOF), implies the use of an ICP-MS with a time-of-flight detector in combination with a specific low flow sample introduction system [2].

In this work, we will illustrate the capabilities of both instrumental configurations for addressing the use of new therapeutic strategies for cancer treatment, including the use of nanotransporters or immunotherapy. Immunotherapies represent a broad and rapidly growing group of therapies having a substantial impact on cancer outcomes. Their strength is in their potential to activate the immune system to specifically target cancer cells without the broadly damaging side effects of many conventional chemotherapeutics. Thus, in this presentation, the main objective is to optimize and compare two powerful analytical techniques: sequential single-cell ICP-MS (sc-ICPMS) using a quadrupole-based mass analyser and simultaneous mass cytometry using a time-offlight ICP-MS for multiparametric single cell analysis (CyTOF) for the two types of studies. These instrumental approaches will be studied for their ability to provide detailed insights into cellular uptake, distribution, and drug delivery efficacy.

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UNRAVELLING SELENIUM METABOLISM THROUGH THE LENS OF MASS SPECTROMETRY

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Selenium (Se) is a trace element with a paradoxical role in living organisms, acting as both a vital nutrient and a potential toxin depending on its concentration and chemical form. At appropriate levels, selenium is essential for cellular function, redox balance, and immune responses, largely due to its incorporation into selenoproteins. However, excess selenium or its presence in toxic inorganic forms (e.g., selenite, selenate) can disrupt metabolic processes and lead to oxidative damage. One of th Selenium (Se) is a trace element with a dual role in living organisms, functioning as a vital nutrient or a potential toxin depending on its concentration and chemical form. At physiological levels, Se supports cellular function, redox balance, and immune responses, primarily through its incorporation into selenoproteins. However, in excess or in inorganic forms (e.g., selenite, selenate), Se can disrupt metabolism and cause oxidative damage. A main challenge in selenium research is its complex speciation in biological systems. Several case studies will be presented to illustrate how mass spectrometry continues to uncover the intricacies of selenium biochemistry across diverse biological systems.

The complexity of selenium speciation is especially pronounced in microorganisms widely used for Se supplementation in humans and animals. These organisms can bioaccumulate and convert inorganic selenium into more bioavailable and less toxic organic species. Studies aim to enhance biotechnological processes and to produce selenospecies with potential health benefits. Yeast strains such as *Saccharomyces cerevisiae*, *Candida utilis*, *Yarrowia lipolytica*, and *Rhodotorula glutinis* show diverse Se metabolizing capacities, resulting in selenium metabolic profiles requiring detailed characterization[1]. Similar variability is observed in probiotics, *e.g., Lactobacillus reuteri* and *Bifidobacterium longum*[2,3]. Comprehensive selenium profiling is difficult due to the diverse physicochemical properties of its metabolites. The author's lab has developed synergistic protocols combining inorganic (ICP MS) and organic (ESI MS^n) MS. This integrated approaches demand, however, careful optimization to meet the requirements of both techniques. ICP MS ensures quantitative control of selenium species' stability, while high-resolution Orbitrap ESI MS offers mass accuracies below 1 ppm and multi-stage fragmentation capabilities for the structural elucidation and confirmation of already known and novel selenocompounds.

In mammals, selenium metabolism is further complicated by the presence of selenosugars, which may represent a detoxification pathway and account for a substantial portion of hepatic selenium. These sugar derivatives can conjugate with low molecular weight (LMW) thiols and proteins, potentially modulating their function[4,5]. To investigate the binding of selenosugars to proteins in mammalian liver, a combined PAGE-LA-ICP MS approach was employed. Protein extracts from animals exposed to different Se levels were analyzed under both denaturing and native conditions, with and without chemical reduction. This methodology revealed that selenosugars form conjugates with proteins via labile sulfur–selenium bonds. Upon reduction, these bonds were cleaved, resulting in the release of selenosugar moieties). The results may support the role of selenosugars as part of a detoxification mechanism involving covalent, yet reversible, protein modifications.

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CHALLENGES FOR THE DETERMINATION OF RARE EARTH ELEMENTS AT LOW CONCENTRATIONS

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Rare earth elements (REE) have been used in industrial, geological, medical, and agricultural applications. For this reason, the mineral reserves exploration has increased significantly in the last years, which can naturally lead to an increase of the concentration of these elements in soil, water, and consequently in living beings. Given possible exposures, REE has been listed as “New and Emerging Risks to Occupational Safety and Health” by the European Agency for Safety and Health at Work (EU-OSHA). Nowadays, there is a need for suitable methods for the determination of rare earth elements (REE) in many matrices and some of the analytical techniques used for this purpose are neutron activation analysis (NAA), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). Inductively coupled plasma mass spectrometry can be considered as the most suitable technique for the determination of REE, enabling good sensitivity and multielement capability. The determination of REE by ICP-MS has been generally performed using nebulization systems, making necessary the use of high efficiency sample preparation methods with low acidity in final digests to minimize interferences. Additionally, it is well known that the digestion of some matrices having a high content of carbon as, e.g., crude oil, graphite, blood, bcarbon nanotubes, is not a simple task, making necessary very frequently the use of time-consuming sample preparation methods. Some options include the direct analysis by ETV-ICP-MS or using a high efficiency digestion system. Nowadays, there is a trend for the development of methods requiring lower reagent consumption, less analytical steps and lower waste generation combined with high efficiency of digestion. In addition, it is important obtaining digests that are suitable for determination techniques avoiding excessive dilution or higher blank levels. Taking into account the difficulties involved in REE determination in high carbon content matrices, modern methods and trends in sample preparation will be discussed as well as the feasibility of using electrothermal vaporization system coupled to ICP-MS for REE determination.

[**CNPq, INCT-Bio, CAPES, FAPERGS**]

KEYNOTE LECTURES

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VOLATILE SPECIES ATOMIZATION IN AMBIENT PLASMAS FOR TRACE DETERMINATION OF METALS BY ATOMIC SPECTROMETRY

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Hydride generation (HG)[1] is a useful sample derivatization step in trace element analysis applicable to several analytically and toxicologically important elements, including As, Se, Te, Pb, Sn Sb, Bi and Ge. Quantitative and matrix-free analyte introduction into the atomic spectrometric detector can be reached using HG. Hydride atomizers based on flame, heated quartz tube (QTA) or ambient plasmas are employed in atomic absorption spectrometry (AAS). QTAs are the most common hydride atomizers[1] in AAS, offering high sensitivity universally for all hydride forming elements with the only exception of Ge, for which significantly impaired sensitivity is reached. Recently, ambient plasmas such as volume dielectric barrier discharges (DBDs)[2] have been reported as an alternative to QTAs. However, significant differences in sensitivity were found among individual hydride forming elements. Another type of (micro)plasma source usable as a hydride atomizer in AAS is an atmospheric plasma glow discharge (APGD). To achieve the maximum sensitivity of HG-AAS, both, the hydride generation as well as the subsequent hydride atomization step have to be efficient.

The mechanism of hydride atomization in DBD and APGD based atomizers and the fate of free analyte atoms was investigated using various advanced spectrometric techniques. Laser induced fluorescence (LIF) was employed as a useful diagnostic tool capable of determination of spatial distribution of free analyte atoms in the plasma atomizers as well as quantifying their absolute concentration, leading to assessment of atomization efficiency[3-5]. Hydrogen radicals, as important species responsible for hydride atomization in all types of atomizers, were detected by two-photon absorption LIF (TALIF)[6]. The variability in sensitivity for various hydride forming elements in the plasma atomizers can be explained by element dependent decay kinetics of free atoms by deposition. The results found by these techniques are in perfect agreement with the observations made by AAS.

Moreover, both types of plasma discharges have been described by their voltage-current characteristics and studied by time-resolved optical emission spectrometry. Significant differences between DBD and APGD in time development of the discharges will be discussed.

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Advances in direct vapour generation atomic spectrometry in complex matrix

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Chemical vapour generation is a commonly used sample introduction technique in analytical atomic spectrometry for trace element determination. Prior to vapour generation the sample is usually digested in acidic media with microwave assistance for organic matrix removal.

The aim of this work is to advance in the study of vapour generation for analytical purposes through its direct application to complex samples; within them, as an example, honey was therefore chosen due both for its analytical complexity and its relevance as an environmental biomonitor and as an extremely valuable food due to its nutritional and medicinal properties. Its composition is determined by the type of flower and environment where it originates as well as the processing and storage conditions. In that sense, contaminants, natural or anthropogenic, present in the hive surroundings or in the industrial process may reach the final product too.

Considering the advantage that honey is soluble in water and the mineral composition releases easily to the media, vapour generation can be directly accomplished with the minimum sample treatment: laborious and time consuming steps of sample digestion are avoided, analyte losses or contamination prevented and the dilution factors can be handled, at first instance, to make a reliable determination according to the amount of analyte expected. Nevertheless, due to the physical and chemical characteristics of the sample, a high content of carbohydrates remain in solution, enabling the corresponding interferences.

Some of the examples chosen for this talk are the challenges found in lead determination by hydride generation microwave induced atomic emission spectrometry[1] and cadmium determination by hydride generation atomic fluorescence spectrometry.

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CHALLENGES IN ENVIRONMENTAL ANALYSIS BY ATOMIC SPECTROMETRY

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Atomic spectrometry techniques like Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), are powerful tools for determining the elemental composition of environmental samples. Their high sensitivity, selectivity, and multi-element capability make them indispensable for monitoring pollutants in water, air, soil, and biota.[1] However, the application of these techniques in environmental samples has significant challenges. Matrix effects, arising from the complex and variable composition of environmental samples, are still a main concern. These effects can influence the atomization and ionization processes, leading to signal suppression or enhancement and ultimately affecting the accuracy of quantitative measurements. Sample preparation procedures, often involving digestion, extraction, and pre-concentration steps, introduce potential sources of contamination and analyte loss, demanding rigorous control.[2] Furthermore, the increasing demand for ultra-trace level determination of emerging contaminants necessitates continuous advancements in instrument sensitivity and the development of effective interference removal strategies. This lecture will further discuss these challenges and explore recent developments and future perspectives aimed at overcoming these limitations in the pursuit of reliable environmental analysis using atomic spectrometry. In this context, results about seawater and sediment samples obtained using different sample pretreatments and spectrometric techniques will be presented and discussed.

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[Capes, CNPq, Fapes, Fest, Ufes]

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ADVANCING GREENER TOTAL AND SPECIATION ELEMENTAL ANALYSIS THROUGH ALTERNATIVE SOLVENTS

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Atomic spectrometry-based techniques are widely employed for ultra-trace determination of elements. However, to attain precise, reliable, and sensitive results, it is imperative to complement sensitive elemental detectors with efficient sample preparation methods encompassing separation and preconcentration processes for analyte enrichment and matrix elimination.

Moreover, one of the pivotal milestones in sample preparation has been the incorporation of green chemistry principles, including waste minimization, the use of safer solvents, and the development of miniaturized procedures that directly align with emerging techniques dedicated to total and speciation elemental analysis. Among the various methods available, liquid-liquid extraction, cloud point extraction, and solid-phase extraction have been instrumental in achieving these objectives. When executed at the microscale level, these techniques have the potential to significantly reduce the environmental footprint associated with solvents, reagents, and waste generation.[1]

In recent years, the use of alternative solvents for sample preparation has drawn growing interest, as they offer a safer and more sustainable option compared to conventional organic solvents, which are often toxic, volatile, and flammable. These alternative solvents have enabled the development of simpler, more compact, cost-effective, and environmentally conscious analytical methods for the determination of trace elements. Among the most promising are ionic liquids (ILs), surfactants, and deep eutectic solvents (DES), which have seen expanding application in trace element analysis.[2] The integration of ILs and DES with miniaturized techniques not only reduces reagent consumption and waste generation but also aligns well with green chemistry principles. This presentation will explore effective approaches for using these solvents in combination with nanomaterials to develop separation and preconcentration methods for trace elements and chemical species determination. Emphasis will be placed on modern microextraction methods—such as dispersive liquid-liquid microextraction (DLLME) and dispersive micro-solid phase extraction (D-μ-SPE)—and their synergy with atomic spectrometric techniques to improve analytical performance and environmental sustainability.

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SAMPLE PREPARATION STRATEGIES FOR DETERMINATION OF NON- METALS AND THEIR SPECIES BY MASS SPECTROMETRY TECHNIQUES

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

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[**CAPES, CNPq, FAPERGS**]

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Retrospective of the work developed at Labspectro (Laboratory of Atomic Spectrometry), at PUC-Rio

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In this lecture, the work developed at Labspectro, the scientific group coordinated by me in the Department of Chemistry at PUC-Rio, in recent years, will be briefly presented. The results obtained in the Girls in Science projects, funded by CNPq and FAPERJ, which is the development agency of the state of Rio de Janeiro, which since 2013 have encouraged high school students from public schools in the state with a Young Talent scholarship and undergraduate students from PUCRio with scientific initiation scholarships, in a research that involves the chemical analysis of hair, will be presented. The study that compared the mineralogram of natural and dyed and/or straightened hair, between men and women, and between people with different skin colour resulted in the master's thesis of Gabrielly Peregrino. The research comparing the hair composition of smokers and non-smokers resulted in the master's degree of Natália S. Rego. Still related to the topic, the dissertation works of Verônica L. Estevão and Jessica Lira researched the composition of hair dyes, investigating a possible source of contamination by potentially toxic elements, which fortunately has not been proven. In another line of research, we had the master's degree of João Victor Meirelles, who investigated the elemental and molecular composition of cannabis oil samples, in partnership with Professor Mônica Padilha, from the Federal University of Rio de Janeiro (UFRJ), who co-supervised him.

If there is time, we will present the research developed during the internship as a Visiting Professor Abroad, at UniOvi, Oviedo, Spain, with a scholarship from the CAPES PrInt project, and the doctoral work of Rafael Rocha, in partnership with and with funding from Petrobras.

[**CNPq, CAPES, FAPERJ**]

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The Role of ICP-MS and Other MS-Techniques in the Characterization of Biogenic Nanoparticles

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Many (micro-)organisms are capable to produce biogenic nanomaterials once exposed to suitable precursors like metal ions. Their production follows a green chemistry strategy generally avoiding hazardous chemicals and harsh experimental conditions. Due to their antibiotic, anti-inflammatory and anti-cancerous activities numerous biogenic nanoparticles (NPs) have attracted great attention for their potential use in medical and pharmaceutical studies.
This presentation intends to give an overview on the characterisation of such biogenic nanoparticles by mass spectrometric techniques. The investigated objects originated from different organisms like bacteria (Cu NPs) and fungi (Se NPs) after incubation with the corresponding precursor ions [1, 2]. Their characterization required several steps: Extraction of the NPs was performed by mechanical lysis of the cells. The nanoparticulate fractions were analysed by single-particle inductively coupled plasma-mass spectrometry (sp-ICP-MS) and transmission electron microscopy (TEM) as complementary tool. This strategy allowed us to characterize the present NPs in terms of shape, size and size distribution.
In addition, the natural surface modification (in this case, the protein corona surrounding biogenic Se NPs) was explored by a dedicated combination of an extraction method [3] and liquid chromatography electrospray ionization-tandem mass spectrometry (LC-ESI-MS/MS) [4]. The results revealed the presence of multiple proteins giving hint to the formation of such nanomaterials.

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ELEMENTAL IMAGING – CURRENT CHALLENGES AND FUTURE PROSPECTS

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Imaging and imaging techniques represent a rapidly expanding domain of significant interest within the scientific community. This remarkable progress can be attributed to our ability to perceive information much better when presented visually. Indeed, images facilitate the rapid reception of large amounts of data. In science, visual observation has always been an important way for acquiring new knowledge and then communicating it with the help of images. Noteworthy advances, such as the development of microscopes, marked critical milestones in unraveling the complexities of the microworld [1]. In current research, there is a growing interest on integrating structural information with chemical data: specifically, how can we detect chemical elements in each pixel of an image and measure their concentrations? To address this question, a variety of atomic spectrometry techniques are currently employed to chemically map the surfaces of samples within the micro to nanometer scale. This lecture will highlight important analytical tools for elemental imaging, including secondary ion mass spectrometry (SIMS), especially NanoSIMS, laser ablation ICP-MS, and synchrotronbased X-ray absorption spectroscopy. The application of these techniques spans a multitude of fields, encompassing biology, medicine, geology, and materials science, as will be demonstrated through examples from our current research. Additionally, this presentation will address the limitations and emerging challenges associated with these techniques, along with prospective developments toward two- and three-dimensional multimodal imaging.

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IRON BIOACCESSIBILITY FROM VEGAN DIETARY SUPPLEMENTS

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In recent years, the vegan diet has been proposed as a therapeutic approach that can potentially reduce the risk of chronic, non-communicable diseases, while maintaining an adequate nutritional intake[1]. Nevertheless, animal welfare and ethics are the primary drivers behind this diet. However, vegan diets have also been associated with a greater risk of fractures, caused by low Ca intakes[2]. According to several scientific/professional associations and expert groups, a vegan diet should not be recommended for children because of lacking vitamin B_{12}, docosahexaenoic acid, Fe, vitamin D, and Ca[3]. Children following this diet should undergo careful monitoring of their growth and overall development from medical and dietetic professionals if their parents are against for their infants to follow at least an ovo-lacto-vegetarian diet[3]. Although there is strong scientific evidence that plantbased diets (e.g., vegetables, legumes, fruits, whole grains, nuts, and seeds) have benefits for health and environment especially for adults[2,4,5], yet only 8 percent of the global population follows a vegetarian or vegan diet[6]. At the same time, according to WHO, Fe deficiency anaemia affects roughly one billion of individuals globally[7], and it is one of the top ten worldwide health issues[8]. Iron dietary supplements are highly recommended to overcome and prevent Fe deficiency problems. The present lecture will be focusing on studying bioaccessibility of iron (Fe) from vegan dietary supplements containing either inorganic [Fe(II) sulphate or Fe(III) pyrophosphate] or organic Fe in form of salt [e.g., Fe(II) fumarate] and chelates with amino acids such as Fe(II) bisglycinate through incubation in synthetic gastric and duodenal juices. Total amounts of Fe were also determined by inductively coupled plasma optical spectrometry after microwave-assisted digestion performed with quartz glass inserts containing a mixture of nitric acid and hydrogen peroxide placed into Teflon vessels. Proper mass balance could be set up for Fe as all fractions resulted during the bioaccessibility studies after adequate sample processing. Generally, dissolution of the studied Fe compounds in the highly acidic simulated gastric juice (i.e., pH = 1.5) was much higher than in the simulated duodenal juice of pH = 6.8. Higher dissolution rate was observed at pH = 6.8 for the Fe compound applying amino acids for chelation. Moreover, when vitamin C was added to the tablets containing Fe(II) bisglycinate, the amount of Fe that can be absorbed in the stomach and small intestine of humans was about 50%. The ratio of ferrous and ferric ions in the solid samples was determined by Mössbauer spectroscopy. Estimation of the daily Fe intake based on the results obtained reinforced that the chelated Fe forms can supply the highest amount of Fe but not exclusively. Therefore, an equilibrated diet is of primordial importance for a sustainable life and health.

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NANO-ANALYTICAL TECHNIQUES AT THE CARNAÚBA BEAMLINE FOR EXPERIMENTS IN SEVERAL RESEARCH AREAS OF SCIENCE

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CARNAÚBA[1] is an acronym for Coherent X-ray Nanoprobe Beamline, which is a nanofocused, multianalytical, and coherent X-ray imaging beamline of Sirius, the 4th generation synchrotron source of the Brazilian Synchrotron Light Laboratory. Its design is all-achromatic mirror-based optics, with a 4-bounce Si(111) crystal monochromator (4CM) that provides resolving power of $\Delta E/E = 10^{-4}$ in monochromatic mode, and KB (Kirkpatrick-Baez) mirrors, which allows beam nano-focusing in two experimental stations: TARUMÃ (Tender-to-hard X-ray for sub-micro analysis)[2], which works with submicrometric beam and variable sample environment; and, SAPOTI (Scanning Analysis by Ptycho for Tomographic Imaging)[3], with nanometric beam (30 nm x 30 nm) working in cryogenic and ultra-high vacuum environment. CARNAÚBA covers the energy range from 2.05 to 15 keV and works in both pink (high flux) and monochromatic beams (high energy resolution) modes, with capabilities for 2D and 3D experiments based on X-ray absorption and X-ray scattering that include: X-ray diffraction (XRD), X-ray absorption (XAS), X-ray fluorescence (XRF), X-ray excited optical luminescence (XEOL), Bragg and ptychographic coherent diffraction imaging. The TARUMÃ endstation is the first in operation, with innovative instrumentation solutions for experiments *in-situ*, *in-operando*, *in-vivo*, and cryogenic, covering a large scientific program that ranges from agriculture, soils and plant science, cultural heritage, biology, geophysics, catalysis, to energy materials, and other areas In this talk, a general overview of the Carnauba beamline along with a description of several dedicated arrangements for the TARUMÃ endstation will be presented. This presentation will also show several examples of 2D/3D imaging capabilities of the CARNAÚBA beamline for samples of relevance in several research areas of science.

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THE IMPACT OF NON-ESTERIFIED FATTY ACIDS ON ZINC SPECIATION AND DYNAMICS IN BLOOD PLASMA

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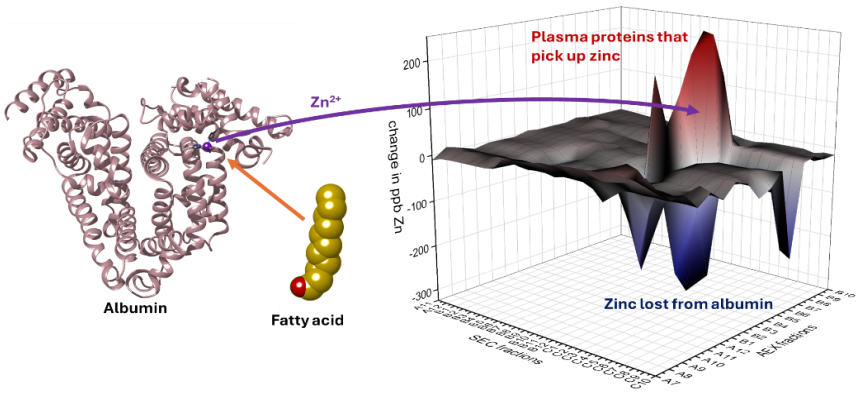
At concentrations around 600 µM and a binding constant of ca. 10^7 M^{-1}, serum albumin dominates the speciation of zinc in mammalian blood plasma. This protein is also the major carrier for nonesterified fatty acids (NEFAs). The binding affinities of Zn^{2+} and NEFAs to albumin are linked through an allosteric mechanism, with elevated levels of NEFAs greatly reducing the zinc-binding capacity of albumin.[1] Plasma NEFA levels are highly dynamic, with levels rising as a consequence of fasting and stress. Chronically elevated plasma NEFAs are encountered in several disease states, including obesity, metabolic syndrome and type 2 diabetes.[1] The changes in plasma zinc speciation due to elevated NEFAs affect processes within plasma[2] as well as potentially zinc export rates from plasma into cells.[3]

To understand the consequences of the NEFA-induced displacement of zinc from human serum albumin (HSA), it is critical to identify proteins that "pick up" this displaced zinc. To this end, we have developed a metalloproteomic workflow for the separation of human plasma, based on anionexchange chromatography followed by size-exclusion chromatography. Protein-containing fractions were analyzed for zinc, iron and copper by Inductively-Coupled Plasma Mass Spectrometry. Blood plasma with and without added NEFA (myristate) was analyzed in this manner, and fractions with altered zinc contents were analyzed by semi-quantitative proteomics (using emPAI; exponentially modified protein abundance index to estimate relative protein levels). Subsequently, metal concentrations and protein abundances were correlated across fractions. This approach yielded several candidate proteins receiving zinc displaced from albumin. Future work will validate these candidates, with a view to linking these to physiological processes. The talk will discuss the analytical approach and potential downstream effects on health and disease.



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Direct determination of lithium in brine samples using handheld LIBS without sample treatment: sample introduction by venturi system

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Chile is the second-largest lithium producer in the world, behind Australia and SQM (Sociedad Química y Minera de Chile) is the world's largest lithium producer, competing for the top position with the company Albemarle. Its position is due to the high efficiency of its operations in the Salar de Atacama, which has natural brines with one of the highest lithium concentrations in the world and benefits from low production costs.

The process of obtaining Li_2CO_3 battery grade from brines begins with the extraction of lithium-rich brine, which is then pumped into solar evaporation ponds to concentrate the lithium. Subsequently, chemical precipitation treatments are applied to remove Mg and Ca ions, and lithium carbonate is precipitated by adding Na_2CO_3 yielding high-purity Li_2CO_3 which is used in battery manufacturing for energy storage mainly in the field of electromobility.

Fast and accurate quantification of Li in brines is critical for decision-making during the production process, as it directly affects process efficiency and the purity of the final product. Traditional methods such as ICP or FAAS often fall short in this regard due to the time required to collect, transport, and treat the samples to make them compatible with these technologies. In situ methods for metal determination with minimal sample preparation have traditionally relied on portable X-ray fluorescence (XRF) analyzers[1]; however, these are not suitable for Li determination due to its low atomic number. Recently, portable devices based on laser-induced breakdown spectroscopy (LIBS) have entered the market, although they are primarily optimized for solid samples[2].

The main challenge in directly analyzing aqueous samples using LIBS lies in the limited energy efficiency of the process and the splashing effect caused by the laser impact on water. Due to water's high surface tension, the laser-induced impact generates droplets that can contaminate the instrument, leading to reduced precision and decreased sensitivity of the analytical signal.

Our study showed the direct determination of Li content in brines for the control of industrial mining processes using a portable LIBS device based on the direct laser impact on the sample, without any sample treatment, through the design of a sample injection system based on the Venturi effect. Our results demonstrated that the utilization of the 653.3 nm hydrogen line as an internal standard reduces the model calibration fitting error from 0.440 root mean square error in a standard calibration curve to 0.123 on the internal standard curve. Conversely, the development of a Venturi effect-based injection device using compressed air converts the brine into a fine mist which decreases splashing, resulting in an up to 10-fold error reduction, all without the necessity of employing an internal standard. Our results, evaluated by comparing them to the ASTM D3561-11 standard method using flame atomic absorption spectrometry, indicate that it is feasible to determine the lithium content in brine samples with an error of under 20%[3].

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Microwave-Assisted Sample Preparation: Where are we heading to?

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Frequently, sample preparation is the most critical step in analytical procedures devoted to elemental inorganic analysis. The conversion of solid samples in representative solutions generally requires the use of concentrated acids at high temperatures. The advent of microwave-assisted sample preparation has been providing major developments in this area and the use of closed vessels rapidly heated by microwave radiation is broadly accepted as a powerful strategy compatible with trace analysis requirements. We have seen several developments either based on new technologies and devices, such as single reaction chamber systems and microwave-induced combustion in disposable vessels, or on new ideas, such as digestions using diluted solutions of reagents and even digestions without using any acids. These developments led to the proposal of attractive analytical procedures and sample preparation evolved from an old art to a modern science. Nowadays, we need to evaluate the greenness of these microwave- assisted procedures and evolution will rely on procedures with sound analytical performance, but also which follow all requirements of green analytical chemistry. These aspects will be discussed and examples will be presented considering where we are and where we are heading to.

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CLOSING CONFERENCE Devoted to Curtius/Welz

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THE ROLE OF CALIBRATION IN ATOMIC SPECTROMETRY TO SUPPORT THE RESEARCH ON BIOLOGICALLY ACTIVE SUBSTANCES

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The role of atomic and molecular spectrometry in chemical analysis cannot be overemphasized. Atomic absorption spectrometry and mass spectrometry techniques are used to determine elemental signatures, as well as to determine isotopic composition used to study isotopic fractionation or for the isotope dilution protocols. Molecular spectroscopy is used to evaluate the molecular composition of the given object towards assure the complementary information of the analytical goals, when biologically active compounds are of primary interest.

In each case, one of the most important steps ensuring the validity of measurement results is the proper calibration of the measuring device, i.e. selecting the appropriate strategy for obtaining the relevant relationship between the analyte content and the analytical signal. This means that in each case it is not a routine procedure, but tailored to the needs and purpose of using the analytical results.

In this lecture, examples of different applications of atomic and mass spectrometry will be discussed in the context of instrumentation development as well as measurement methodology. Examples will include interesting applications of studies from elemental to isotopic composition, including isotopic fractionation. Always with consideration of a properly selected calibration strategy.

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Tackling challenging samples with alternative approaches: a brief overview of Adilson's and Bernhard's heritage in modern elemental analysis

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Adilson Curtius and Bernhard Welz were remarkable individuals, who dedicated their lives to science. They were the organizers of the first Rio Symposium on Atomic Spectrometry, which is now a consolidated international event, currently celebrating its 17th anniversary. Adilson was an early enthusiast of atomic absorption spectrometry (AAS) and was ultimately dedicated intensely to investigations using inductively coupled plasma mass spectrometry (ICP-MS). Bernhard Welz is one of the fathers of AAS: he will forever be remembered as the scientist, following the steps of the late Alan Walsh, who spoke around the world about the wonders of the referred technique. They both shared a passion to elucidate processes and create methods dedicated to elemental analysis using AAS and ICP-MS. Hence, the main goal of this presentation is to provide a brief overview of the contribution of these remarkable scientists to the development of the most popular techniques for elemental analysis. Challenging applications, such as the analysis of biological fluids, crude oil, rocks, coal, etc. will be briefly discussed, with techniques that include chemical vapor generation, direct solid analysis, slurry sampling and extraction and pre-concentration, to mention a few. The heritage of these two pioneers in elemental analysis is immense and they have paved the way to many other talented scientists, who keep carrying on investigations in this important field of the analytical sciences.

[CNPq]

EVIDENCE FOR NANOPARTICLE FORMATION DURING PVG… EASY…. BUT THE BUMPS ALONG THE WAY…!

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Although photochemical vapor generation (PVG) of metals/semi-metals and halogens provides an alternative and sometimes unique route for their enhanced sample introduction efficiency into spectrochemical and mass spectrometric sources, much remains to be explored[1]. Fundamental mechanisms of analyte synthesis may be accounted for based on photolytic radical mediated processes[2]. However, less comprehensive information is available with which to explain the significant impact of the presence of mg/L concentrations of added transition metal "mediators", which appear to catalytically influence the yields of a number of volatile analytes, notably the carbonyls of W, Mo, Os, Ru, Rh, Ir and Re. The function of these mediators has been suggested to arise as a result of formation of nanoparticles (NPs), yielding surface sites onto which the reactants selectively engage in photocatalytic reactions[2,3]. Although this model appears credible, direct experimental evidence has not been forthcoming. This presentation briefly summarizes progress in this direction and highlights several obstacles and limitations hampering NP detection and characterization which would serve to validate their impact as a function of experimental PVG parameters.

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SHORT COURSE 1

Forensics Applied to Spectrometry

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X-Ray Fluorescence: theory and applications in forensic science

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X-ray fluorescence (XRF) is a widely used analytical technique in materials science and forensic investigations due to its ability to determine elemental composition in a non-destructive manner[1]. XRF operates based on the interaction between high-energy X-rays and matter. When an atom is exposed to incident X-rays, inner-shell electrons may be ejected, creating an unstable electron configuration. This vacancy is subsequently filled by an electron from a higher energy shell, resulting in the emission of secondary (fluorescent) X-rays. These emitted X-rays have energies characteristic of specific elements, allowing for qualitative and quantitative analysis of the material[2]. XRF is a powerful and versatile tool that has been applied in various areas of forensic science. Key applications include: i) Gunshot Residue (GSR) Analysis - XRF can detect and identify elements like lead (Pb), barium (Ba), antimony (Sb) and sulfur (S) in GSR particles, helping to determine whether a suspect has recently discharged a firearm; ii) Glass Fragment – the elemental composition can help differentiate between glass from different sources of glass, linking fragments found on a suspect's clothing to a specific broken object at the crime scene; iii) Soil and Trace Evidence Analysis - by comparing the elemental composition of soil or dust samples, investigators can establish links between a suspect, a victim, and a crime scene; iv) Paint and Coating Analysis - in hit-and-run or vandalism cases, XRF can assist in comparing paint fragments from a crime scene to suspected objects or vehicles, by generating elemental "fingerprints" unique to specific paint formulations; v) Toxicology and Poisoning Cases - XRF is used to detect toxic metals such as arsenic, mercury, or lead in tissues, hair, or other biological samples in suspected poisoning cases; and vi) Documents examination - inks and paper may contain trace elements that vary by manufacturer, and XRF can be used to differentiate inks, detect alterations, or identify forged documents without damaging the evidence. The main advantages of XRF in forensic science include its non-destructive nature, rapid analysis, minimal sample preparation, and portability—especially with the advent of handheld XRF devices[2]. However, the technique also presents certain limitations. It has reduced sensitivity to light elements (e.g., carbon, nitrogen, and oxygen) and limited penetration depth, which makes it most effective for surface analysis[3]. Consequently, XRF is often used in conjunction with other analytical techniques—such as scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) or inductively coupled plasma mass spectrometry (ICP-MS)—to obtain more comprehensive forensic data.

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Spectrochemical analysis in forensic science: techniques, applications and perspectives

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Spectrochemical techniques play a central role in forensic chemistry by enabling the qualitative and quantitative determination of elements in a wide variety of evidentiary materials. Classical atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission spectrometry (ICPOES) remain valuable for the determination of trace metals in various matrices, while inductively coupled plasma mass spectrometry (ICP-MS) has emerged as the technique of choice due to its high sensitivity, multielement capability, and capability for isotopic analysis. Applications include: (i) glass fragments: LA-ICP-MS is currently standardized (ASTM E2927-23) for forensic comparison of soda–lime glass, enabling micro-destructive analysis and likelihood ratio approaches; (ii) gunshot residue (GSR): ICP-MS and LIBS provide complementary information to SEM-EDS, especially in the context of lead-free ammunition, with potential for estimating shooting distance and persistence studies; (iii) isotopic profiling: multi-collector ICP-MS allows the use of strontium and lead isotope ratios for geolocation and human provenance, contributing to forensic anthropology and missing persons investigations; (iv) speciation analysis: hyphenated techniques (HPLC-ICP-MS) provide species-specific toxicological information, particularly for arsenic and mercury; and (v) rapid field analysis: laser-induced breakdown spectroscopy (LIBS) enables on-site elemental screening of soils, documents and coatings, combining portability with chemometric classification. The main advantages of spectrochemical methods are their versatility, sensitivity, and broad applicability across inorganic forensic scenarios. Limitations include the need for destructive sampling in some cases, interlaboratory harmonization, and the development of validated databases for statistical interpretation. Current trends indicate integration with portable techniques, expansion of isoscapes (isotopic landscapes), and the adoption of likelihood ratios for evidence interpretation. Together, spectrochemical and complementary non-destructive methods, such as XRF, provide a robust analytical framework for characterizing and interpreting forensic evidence.

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[**CAPES, CNPq, FAPESP**]

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SHORT COURSE 2

Analytical Method Validation

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Analytical Method Validation

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The development of biomaterials, nanotechnology, and other fields of science as well as decisions about commerce, health and environment are heavily based on analytical results, thus, inadequate results lead to waste of time and resources, and jeopardize the wellbeing of society. Analytical method validation is key for the guarantee of quality of data produced in laboratories. The analytical chemistry community is used to the main concepts of validation and many analytical organizations and regulatory agencies throughout the world issue method validation guides[1]. The central goal of analytical methods validation is to assure that the data produced is adequate for the intended use. Validation is a systematic approach to demonstrate objectively, with experimental evidence, that the method is fit for purpose. Many strategies to validate a methodology are available, and the most suitable for each application should be selected. The evaluation of parameters that can influence the results is the most used approach in the chemical area and common parameters evaluated to assess method performance are: selectivity, limits of detection/quantification, linearity, trueness, precision and measurement uncertainty. The experimental set-up and data treatment must be designed to evidence the compliance of the method with the intended application and the criteria used to evaluate these parameters are key for the guarantee of fitness for purpose. There is a myriad of strategies for method validation presented in the literature, with different statistical approaches and criteria to evaluate the parameters vary largely depending on application. This variability and lack of fixed criteria commonly causes great concern on analysts less familiar with the validation systematic.
The objective of this course is to contextualize method validation within quality assurance systematic, quality system standards (such as 17025), and the metrological concepts involved, such as traceability and comparability. The dynamic of the course is based on discussions with participants about the concepts of the main parameters evaluated during method validation, present different examples and strategies for some analytical problems and indicate how can they evaluate their working analytical methods, develop a validation strategy, and stablish appropriate criteria to assess fitness for purpose. The short course focus on clarifying the principles behind every validation parameter, so participants can transfer the strategies seen in class or in the literature to their own daily problems.

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Acknowledgments: Inmetro

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WORKSHOP

Spectrometry Devoted to Solid Sampling

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LA-ICP-OES and LA-ICP-MS: Basic Fundamentals and Some Applications

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Laser Ablation–Inductively Coupled Plasma Optical Emission Spectrometry (LA-ICP-OES) and Laser Ablation–Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) are advanced solid sampling techniques that combine laser-based material removal with high-temperature plasma excitation or ionisation for elemental analysis. In both methods, a pulsed, high-energy laser beam is focused on the sample surface, causing localized heating, melting, and vaporisation of material. The resulting aerosol is transported by a carrier gas—typically argon or helium—into an inductively coupled plasma (ICP). The ICP, sustained by a radio-frequency electromagnetic field, provides temperatures in the range of 6,000–10,000 K, ensuring complete atomisation of the sample particles. In LA-ICP-OES, the excited atoms and ions in the plasma emit photons at characteristic wavelengths. These emission lines are dispersed and detected by an optical spectrometer, allowing multi-element detection with good sensitivity, wide dynamic range, and robust performance in complex matrices. The technique is well-suited for rapid screening, high-throughput analysis, and situations where simultaneous multi-element capability is a priority.

In LA-ICP-MS, the ionised atoms produced in the plasma are extracted into a mass spectrometer—such as a quadrupole, sector field, or time-of-flight analyser—where they are separated based on their mass-to-charge ratios (m/z) and quantified. LA-ICP-MS achieves extremely low detection limits (down to parts per trillion), high sensitivity for trace and ultra-trace elements, and the ability to determine isotopic ratios with high precision, making it particularly valuable for geochemical, forensic, and isotopic studies. While LA-ICP-OES provides faster multi-elemental emission data and robust matrix tolerance, LA-ICP-MS offers unparalleled sensitivity and isotopic measurement capability. The selection between the two depends on analytical goals, sensitivity requirements, and the complexity of the sample matrix. In some research and industrial contexts, both techniques are employed in parallel to exploit their complementary strengths. Some of the novel applications include elemental and isotope mapping of tissue samples [1]; analysis without the use of internal standards[2]; direct analysis of catalysts[3]; and isotopic ratios[4], among many others.

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Laser-Based Techniques for Direct Solid Sample Analysis

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Analytical chemistry has made significant strides in developing methods for the analysis of food, environmental samples, and technological materials, particularly in elemental characterization. Among instrumental techniques, inductively coupled plasma optical emission spectrometry (ICP OES) and ICP mass spectrometry (ICP-MS) have become prominent. However, these methods typically require acid digestion for sample preparation, converting solid samples into homogeneous aqueous solutions. This process often involves oxidizing acids, which can increase preparation time and analytical costs. To address these challenges, direct solid sample analysis techniques have gained attention, with laser-induced breakdown spectroscopy (LIBS) and laser ablation (LA) coupled with ICP OES or ICP-MS emerging as versatile alternatives. This course explores the principles and advantages of LIBS and LA, with a focus on calibration and quantitative analysis.

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Technological Innovations in Atomic Spectrometry: Advancing Automation and Applications with Agilent ICP-OES and ICP-MS/MS

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Atomic spectrometry continues to evolve rapidly, driven by increasing demands for productivity, analytical precision, and flexibility in complex applications. We will showcase the latest technological innovations from Agilent Technologies in ICP-OES, ICP-MS and ICP-MS/MS platforms, with a focus on intelligent automation, workflow integration, and expanded analytical capabilities.

We will highlight the role of the ADS 2 (Advanced Dilution System) in transforming routine ICP-OES operations. This automated dilution and reanalysis system enables efficient handling of samples outside the calibration range, significantly reducing manual intervention and enhancing data reliability. When integrated with the ICP Expert software, ADS 2 supports decision-making through analytical intelligence and ensures full traceability of the process[1].

In the ICP-MS domain, we will explore the advanced capabilities of the Agilent 8900 ICP-MS/MS, which combines the robustness of collision/reaction cell technology with the selectivity of tandem quadrupole operation. Emerging applications in complex matrices — such as food, environmental, and geological samples — will be discussed, where spectral interference suppression and ultra-trace quantification are critical. Use cases involving elemental speciation, nanoparticle analysis, and isotopic studies will also be presented, demonstrating the 8900's potential for both research and quality control.

This talk aims to illustrate how Agilent is redefining the boundaries of atomic spectrometry by delivering solutions that integrate automation, intelligence, and analytical performance to meet the current and future challenges of modern laboratories.

1 https://www.agilent.com/cs/library/applications/an-low-to-high-matrix-7850-icp-ms-5994-7114en-agilent.pdf

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Trace analysis made simple: the wonders of high-resolution atomic/molecular absorption spectrometry

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High-resolution continuum source atomic absorption spectrometry (HR-CS AAS) has established itself as a breakthrough in spectrometric analysis in the past decades. The technique has unique features, including the visualization of the entire spectral interval under investigation with pm-range resolution and unsurpassed background correction capabilities. These characteristics are particularly interesting to provide data on the most complex analytical situations, which include direct analysis of solids and slurries, investigations focused on spectral regions that are densely populated by molecular bands and simultaneous determinations. The spectral "visibility" at high resolution also allowed to expand the application of AAS to non-metals, which tend to form diatomic molecules that generate fine rotational spectra in the gas phase, originating the so-called *high-resolution molecular absorption spectrometry* technique (HR-MAS). Hence, the analytical possibilities associated to HR-CS AAS and HR-MAS are numerous and increasing. In this context, a brief overview will be presented focusing on the employment of the ContrAA instrument to carry out applications such as the direct analysis of polymers, geological samples, nanomaterials, biological samples, fuels, etc., including direct analysis of solids, slurries and the application of *dilute-and-shoot* processes to trace analysis. Applications will also encompass fractionation and quantification studies based on interaction with nanoparticles and the monitoring and quantitative analysis of non-metals *via* rotational bands of diatomic molecules for a series of samples. Overall, the remarkable potential of HR-CS(M)AAS to solve the most complex analytical situations and to reduce the demands of sample preparation will be demonstrated by several examples of successful applications of the technique.

[**CNPq, Analytik Jena AG**]

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FROM COLLOIDS TO PARASITES: REVEALING SELENIUM NANOPARTICLE UPTAKE IN LEISHMANIA BY SINGLE EVENT ICP-MS

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The single particle-ICP-MS represents one of the most promising innovations in mass spectrometry allowing not only the determination of total chemical element but also the characterization of individual nanoparticles in colloidal suspensions. This approach provides information about size distribution, particles concentration, to discriminate between nanoparticles and dissolved elements, parameters which cannot be accessed by traditional analytical methods. Additionally, the interface between analytical chemistry and biology, the sp-ICP-MS becomes more relevant by allowing the quantification of nanoparticles internalized by cells or microorganisms, bringing light to the hidden aspects related to the endocytosis mechanisms and, consequently, to the populational heterogeneity. This interesting information can be used to elucidate mechanisms of toxicity, biodistribution and therapeutic effects in cellular level. Thus, sp-ICP-MS emerges as an important tool in bioanalytical chemistry, expanding the frontier of the knowledge in nanoscience and its applications. In this scenario, the interest in silver, gold and selenium nanoparticles has shown increasing interest in recent years due to their physical-chemical properties and potential to be applied, for example, in antimicrobial and antibacterial research. Among them, SeNPs are particularly attractive because selenium is an essential trace element which has antioxidants and therapeutic properties. Here, we present preliminary work encompassing synthesis, physicochemical characterization, and initial biological evaluation with focus on single-particle ICP-MS and single-cell ICP-MS as complementary, high-information analytical tools. Four nanoparticle systems were prepared i) SeNPs coated with chitosan ii) SeNPs coated with bovine serum albumin (BSA), iii) AgNPs stabilized with polyvinyl alcohol (PVA) and AuNPs. All nanoparticles were characterized by dynamic light scattering (DLS), transmission electron microscopy (TEM), UV-Vis and sp-ICP-MS to obtain size distributions, particle number concentrations, zeta potential and hydrodynamic diameter. The optimized operational conditions of sp-ICP-MS were used, and the acquisition of the analytical signal was done by using dwell time of 50 μs and acquisition time of 100 seconds. Gold nanoparticles were used to obtain transport efficiency which were approximately 4,0 % by using a cyclonic spray chamber coupled to a concentric micronebulizer operating at 0,2 mL/min of sample flow rate. The size distribution obtained by sp-ICP-MS were in good agreement with TEM and the average size of nanoparticles were 29 nm (AgNP), 80 nm (chitosan-SeNP), 42 nm (BSA-SeNP) and 92 nm (AuNP). For biological application, Leishmania promastigotes were incubated with BSA- and chitosan-coated SeNPs under dose- and time-controlled conditions. Growth curves were recorded, and the single cell-ICP-MS was used to determine the content of selenium intracellular. For this purpose, a total-consumption spray chamber coupled with a micronebulizer operating at 10 μL/min of sample flow rate was used as sample introduction system. The single cell-ICP-MS enabled to evaluate the selenium content endocytosed by Leishmania promastigotes making possible to observe not only the average absorption but also the distribution of selenium into the cell which were not symmetric highlighting the heterogenous processes involved possibly due to subcellular populations.

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INNOVATIONS IN MICROWAVE SAMPLE PREPARATION FOR ELEMENTAL ANALYSIS

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Microwave-assisted digestion has evolved into the predominant sample preparation method for elemental analysis, providing superior speed, reproducibility, and safety compared to conventional wet-chemical approaches. The introduction of closed-vessel systems marked a significant milestone, allowing precise control of temperature and pressure, and enabling the complete digestion of a wide variety of organic and inorganic matrices. This technology has become indispensable in modern analytical laboratories, where the quality of digestion directly influences both accuracy and precision in subsequent spectroscopic analyses such as ICP-OES and ICP-MS.

In recent years, continuous innovation has refined the design and functionality of microwave digestion systems, addressing key analytical challenges including sample diversity, matrix complexity, and throughput demands. These systems integrate advanced sensors and control algorithms that ensure uniform heating and reproducible conditions across vessels, optimizing digestion efficiency. In addition, their modular architecture enables versatility beyond traditional digestion, supporting applications such as solvent extraction, evaporation, and concentration within the same microwave platform.

Complementing these developments, the emergence of Single Reaction Chamber (SRC) technology has introduced a new paradigm in sample preparation. Unlike conventional rotor-based systems, SRC digestion occurs in a single high-pressure chamber where multiple samples, in different matrices and acid compositions, can be processed simultaneously under identical conditions. This configuration eliminates variability between vessels, minimizes acid consumption, and enhances both operational simplicity and environmental sustainability.

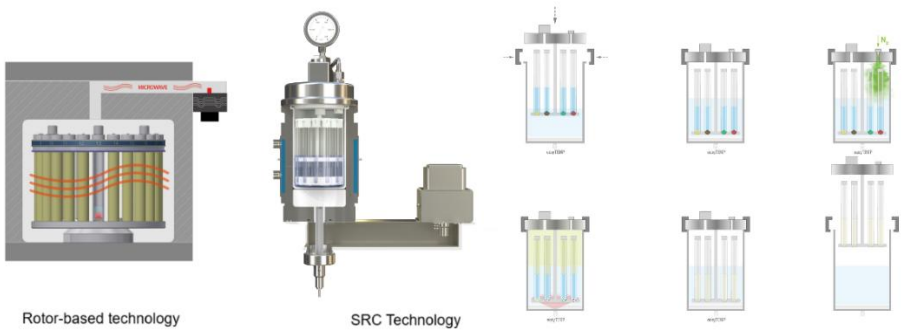

Figure 01: Microwave labstation technologies

The Total Sample Prep Workflow approach complements these technological advancements by minimizing contamination, improving recoveries, and reducing analyst time. By optimizing pre-analysis steps, it enhances data quality, consistency, and safety, contributing to a more efficient, sustainable, and cost-effective laboratory workflow.

Figure 02: Total sample preparation workflow for elemental analysis

The author gratefully acknowledges MILESTONE for providing the microwave technology and Nova Analítica for supporting this presentation at the 17th Rio Symposium on Atomic Spectrometry.

Detection and Quantification of Titanium Dioxide (E171) in Food Using Raman Spectroscopy

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Titanium dioxide (TiO_2) is extensively used as a white pigment in paints, plastics, pharmaceuticals, cosmetics, toothpaste, and as a food additive (E171) due to its opacity and high chemical stability [1–4]. The anatase form, which dominates food-grade TiO_2, is resistant to heat, light, and pH changes, remaining unaffected by most food processing steps[3]. It is commonly found in candy, bakery products, chewing gum, ice cream, and cheese[2]. However, growing toxicological evidence has raised concerns regarding the safety of TiO_2 ingestion. Studies have shown that TiO_2 nanoparticles can be absorbed through the gastrointestinal tract [4,5] and may induce carcinogenic effects in animal models[1,4,5]. As a result, the French health authority concluded in 2019 that the safety of TiO_2 could not be guaranteed, leading to a national ban on its use in food from January 2020[2,6]. Therefore, rapid, reliable, and non-destructive analytical methods are needed for regulatory compliance and quality control. This application report presents Raman spectroscopy using the Anton Paar Cora 5001 as an effective technique for both the detection and quantification of TiO_2 in food matrices. Raman spectroscopy is particularly suitable because anatase TiO_2 exhibits strong and characteristic Raman bands, most prominently at 143 cm^{-1}, which do not overlap with sugar signals, enabling clear identification even at concentrations below 1 % without sample preparation[3,7]. Commercial candy samples listing TiO_2 in their ingredients were analyzed, and all spectra showed the pronounced anatase peak, confirming the presence of the additive. For quantification, icing sugar samples containing 0-1 % TiO_2 were prepared. The peak area ratio of the anatase band at 640 cm^{-1} to the sugar reference peak at 850 cm^{-1} showed a linear correlation with TiO_2 content[8]. Using the built-in “Simple Quantification Tool” of the Cora 5001, the method achieved a limit of detection of 0.014 % and a limit of quantification of 0.046 % TiO_2[9]. This model allows direct calculation and reporting of TiO_2 content on the instrument, minimizing user intervention and improving reproducibility. Overall, Raman spectroscopy with Cora 5001 is a fast, user-friendly, and non-destructive method for the identification and quantification of titanium dioxide in food. Its high sensitivity, minimal sample preparation, and suitability for routine analysis make it an excellent tool for food industry laboratories and regulatory authorities in light of increasing restrictions on E171.

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SECTIONS

Atomic and Fluorescence Spectrometry

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Comparative evaluation of blood decomposition methods for multielement analysis by plasma spectrometry

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The socioeconomic model, centered on industrial and agricultural production, sustains technological and economic development; however, it imposes significant environmental and human costs. Consequently, people have been extensively exposed to toxic substances, such as Persistent Organic Pollutants (POP) and Potentially Toxic Elements (PTE)[1], some of which are associated with neurological disorders, cancer, and other adverse health outcomes. Accurate diagnosis relies on obtaining as much quantitative information as possible from the patient's body. In this context, the development of reliable, rapid, and reproducible methods for elemental determination in biological matrices is essential. This study presents a comparative evaluation of decomposition methodologies for blood samples, a matrix selected for its worldwide representativeness as a real-time biomarker. The technological improvement of the atomic spectrometry (mainly plasma techniques, i.e., ICP-MS and ICP OES) for multielement determination and the necessity of green methods employment is a constant issue. The most common protocol for blood samples preparation, based on treatment with bidistilled nitric acid, heating, and dilution, shows limitations such as poor recovery for some elements, long preparation time, and residual acid effects on the sample introduction system, accelerating its degradation. To address these issues, alternative protocols were evaluated, including hydrogen peroxide addition[2], Triton X-100 incorporation, and an acetic acid–based procedure[3]. The details of all treatments are summarized in Table 1.

Table 1. Summary of blood decomposition treatments (T).

T	Reagents	Heating	Blood Volume	Diluent	Final Volume	Dilution
1	HNO_3 (1 mL)	Yes	0.5 mL	—	10 mL	1:20
2	HNO_3 (1 mL) + H_2O_2 (0.1 mL)	Yes	0.5 mL	—	10 mL	1:20
3	—	No	0.2 mL	0.5% HNO_3 + 0.1% Triton X-100	10 mL	1:50
4	—	No	0.2 mL	0.5% HNO_3 + 0.5% Triton X-100	10 mL	1:50
5	—	No	0.2 mL	10% acetic acid + 0.1% Triton X-100	10 mL	1:50

The effects of different sample preparation procedures (reagents, quantities, heating and dilution) for the blood decomposition were evaluated. To avoid the use of strong acids, the nonionic surfactant Triton X-100 will be evaluated considering its interaction with hydrophobic matrix components, which can improve the elemental recovery and the feasibility of decomposition without heating. Recoveries were assessed against certified values of Seronorm Level 2 and 3, by using a PerkinElmer Optima 7300 DV ICP OES equipment for the determination of the major elements and a PerkinElmer NexION 1000 ICP-MS equipment for the determination of the minor and trace elements. The five proposed sample preparation methods will be comparatively evaluated concerning accuracy, feasibility and greenness.

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INVESTIGATION ON MICROPLASTIC AND TRACE ELEMENTS POLLUTION IN AQUATIC ENVIRONMENTS AT THE REGION OF THE ABC PAULISTA

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Plastic pollution remains one of the most serious environmental, social, and economic challenges today. Once plastics enter the environment, they undergo biological and physicochemical processes that change how they behave and move within ecosystems[1]. Larger plastic debris can break into smaller pieces, known as microplastics (MPs), ranging from 1 µm to 5 mm. The ingestion of these MPs poses a significant threat to living organisms, potentially causing physical harm. Additionally, MPs act as carriers for contaminants: when combined with pollutants, they can transfer these substances to organisms that ingest them[2]. The accumulation of potentially toxic elements (PTEs) is especially concerning, as high levels can lead to toxicity and health issues[2,3].

This study aimed to measure PTEs concentrations and identify microplastics in rivers from the ABC Paulista region and to explore the relationship between water quality parameters and these contaminants. Eight sampling sites were chosen along downstream sections of the Tamanduateí River and nearby areas surrounding residential, industrial, and tourist zones. The concentration of chemical elements were measured by inductively coupled plasma mass spectrometry (ICP-MS), while microplastics were identified and counted following standardized NOAA (National Oceanic and Atmospheric Administration) protocols. The analysis included one-way ANOVA and correlation tests. Results showed that sediment contained 2 to 1,000 plastic particles per kilogram, mostly made of polyethylene, polypropylene, and fibers. Meanwhile, analysis of leaves, water, and sediments revealed elevated average concentrations of potentially toxic metals, especially Cd, Pb, Sb, and Hg, with maximum levels between 0.7 and 20 mg kg^{-1}. These findings highlight the widespread presence of highly toxic contaminants across various environmental matrices, underscoring the potential risks they pose to both aquatic ecosystems and human health.

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SONOCHEMICAL VAPOR GENERATION (SVG) FOR MERCURY DETERMINATION IN FISH SAMPLE

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Mercury is a toxic element often found in the form of the metal ion, Hg^{2+}. Once available in the environment, Hg can undergo bioaccumulation and biomagnification throughout the food chain, contaminating populations and causing serious health and environmental problems. In addition, Hg and its compounds are generated in various industrial processes, and their determination is often performed by CVG (chemical vapor generation) coupled with a spectrometric detection technique.[1] The CVG approach requires the use of reducing agents (usually sodium borohydride) in the presence of an inorganic acid (HCl). One can note that these reagents, especially sodium borohydride, are considered toxic with associated environmental impact, expensive, unstable, and potentially give rise to high analytical blanks.[2,3] Alternatively, a ultrasound (US)-assisted reaction in batch system was evaluated for the generation of Hg^0 from Hg^{2+} (sonochemical vapor generation, SVG), allowing the use of diluted green reagents (organic acids).[3] The SVG system used in this work employed a sonoreactor directly coupled to a US probe (20 kHz) immersed in a glass reactor in which Hg^{2+} was reduced to Hg^0 and transported to a quartz cell placed in the optical beam of an FAAS instrument. The parameters evaluated for the determination of Hg were: reducing agent type (organic acid: formic, acetic and propanoic acid; alcohol: ethanol, methanol and isopropyl alcohol) and concentration (0.1; 0.2; 0.5 and 1.0 mol L^{-1}), carrier gas (N_2; 0.5; 1.0 and 1.5 L min^{-1}), sonication time (0.5, 1, 2, 2.5, 5, 7.5, and 10 min), acoustic amplitude (20, 30, 40, 50, 60, and 70%), and the linear range (0.1 µg L^{-1} to 800 µg L^{-1}). Optimal SVG conditions were 0.5 mol L^{-1} formic acid, 0.3 mL min^{-1} carrier gas (N_2), 5 min of sonication (50% acoustic amplitude, 1316 W L^{-1}), and the quartz cell operating at room temperature (flame off), which presented a linear range from 0.5 µg L^{-1} to 800 µg L^{-1}. Once optimized, the system was evaluated for Hg determination in fish sample (dogfish and shark) and in the CRM (certified material reference) DOLT 4 (dogfish liver). Before the SVG, the samples and CRM were microwave digested (250 mg with 6 mL of 14 mol L^{-1} HNO_3). After the samples were determined by SVG-AAS (proposed method; calibration curve from 0.5 – 60 µg L^{-1}) and CVG-MP-AES (reference method, microwave-induced plasma atomic spectrometry; calibration curve from 1 - 100 µg L^{-1}). The result found in the CRM by SVG-AAS (2.45 ± 0.17 µg g^{-1}) agreed with the certified value (2.58 ± 0.22 µg g^{-1}), and the values found for the fish sample were compared with those by CVG-MP-AES, which agreed. The limit of detection (LOD) and the limit of quantification (LOQ) of the proposed SVG system were determined as 0.015 and 0.05 ug g^{-1}, respectively. The proposed SVG-AAS method was efficient for the determination of Hg at relatively low concentrations, using dilute reagents, relatively short reaction times, and a simple operational system (easy to assemble).

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[CAPES, CNPq, FAPERGS, and UFSM]

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Development of an analytical methodology for the determination of mercury in WEEE by CV-AFS

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Mercury is among the most hazardous environmental pollutants and has been classified by the World Health Organization as one of the top ten chemicals of major public health concern. Its significance arises from its severe health risks, long-range atmospheric transport, environmental persistence, and bioaccumulation in food chains[1-3]. Urban mining refers to the recovery of valuable materials—such as precious metals and rare earth elements—from anthropogenic sources, particularly Waste Electrical and Electronic Equipment (WEEE). This process reduces dependence on primary mining and supports the circular economy by reintegrating recovered resources into production cycles, thereby enhancing resource efficiency[4]. However, despite these benefits, the urban mining of WEEE can also serve as a significant source of mercury emissions. Consequently, accurate detection and control of mercury are essential to safeguard both environmental integrity and human health. In this context, the present study proposes the development and validation of a reliable analytical procedure for mercury quantification in WEEE using cold vapor atomic fluorescence spectrometry (AFS). This technique offers a low detection limit (<1 μg L^{-1}) and a wide linear calibration range extending to the mg L^{-1} level. Reliable quantification depends on two critical steps: efficient generation of mercury vapor and its effective transfer to the AFS system. To address these requirements, parameters associated with the chemical reduction of Hg were optimized univariately using a fixed standard concentration of 0.1 μg L^{-1} to ensure result comparability. $SnCl_2$ was employed as the reducing agent, and both its concentration (0–15%) and the concentration of HCl used for dissolution (0–15%) were systematically investigated. Additionally, the effect of HCl as the carrier solution (0–15%) and the concentration of potassium permanganate (0–0.10%) as a stabilizing agent in Hg standards were evaluated. The working range was 0.05–0.5 μg L^{-1} of Hg, with a coefficient of determination (R^2 > 0.999). Limits of detection (LOD) and quantification (LOQ) were calculated as three and ten times the standard deviation of the blank signal divided by the slope of the calibration curve, respectively. Instrumental LOD and LOQ were determined as 0.02 μg L^{-1} and 0.005 μg L^{-1}, respectively. Optimization studies revealed that the best analytical response was obtained using 2% $SnCl_2$ in 5% HCl as the reductant, with 1% HCl as the carrier solution. For the stabilizing agent, the optimal condition was 0.04% $KMnO_4$ in the mercury standards. Method validation was performed using a certified reference material (CRM), Clayt Soil 1 (LGCQC3004). The certified value was 670 mg kg^{-1}, while the experimental result was 672 ± 129 mg kg^{-1} (mean, n = 3; confidence interval at α = 0.05). No significant difference was observed between the certified and experimental values, confirming the accuracy of the method. Following optimization, the proposed procedure will be applied to WEEE samples to quantify mercury across different matrices. These analyses will provide essential data for assessing potential environmental and health risks associated with the improper disposal or recycling of electronic waste.

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Single-Standard Calibration in High-Resolution Continuum Source Flame Atomic Absorption Spectrometry

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Quantitative determinations in high-resolution continuum source flame atomic absorption spectrometry (HR-CS F AAS) are usually performed by using conventional calibrations (External Calibration, Matrix-Matched Calibration, Standard Addition, Internal Standardization) and recently by non-conventional methods (Standard Dilution Analysis, Internal Standard Addition, Multi-Energy Calibration). Simpler, faster, accurate calibration methods using a single standard have been investigated to minimize waste, reduce solution handling and costs.

In this work, the Single Standard Multi-Point Calibration (SS-MPC), previously applied to Raman spectroscopy[1], is now evaluated for HR-CS F AAS. The generation of multi-signals was obtained by wavelength-integrated absorbance (WIA) at different detector pixels or measuring at regions adjacent to the central wavelength of a spectral line (Wing). The SS-MPC calibration was preliminary tested in the determination of Cu, Mg, Mn, K, and Fe in the following certified reference materials: CRM-IPT10A Bronze; CRM-Agro C1005a Sugarcane Leaves; CRM-Agro FO-01/2012 *Brachiaria brizantha*; CRM-Agro C1003a Tomato Leaves.

Regarding WIA, calibration curves with correlation coefficients ≥ 0.9710 were obtained. Found results for all analytes were in agreement with those obtained by comparative external calibration at a 99% confident level (t-test). Limits of quantification (mg/L) for Cu, Mg, Mn, K, and Fe were 0.10, 0.18, 0.05, 0.22 and 0.15 respectively. Relative standard deviations (RSDs) were 15% (Cu), 2% (Mg), 4% (Mn), 7% (K) and 15% (Fe).

With regards to Wing, different lines at the left (SS-MPC$_l$) or at the right (SS-MPC$_r$) of the central line of analytes were in cases of symmetry, without causing a significant impact on the results. Calibration curves with correlation coefficients ≥ 0.9925 and 0.9850 were obtained for SS-MPC$_l$ and SS-MPC$_r$, respectively. Results for analytes obtained by SS-MPC (Wing) were in agreement with those found by external calibration at a 99% confident level (t-test). Limits of quantification (mg/L) for Cu, Mg, Mn, K, and Fe were calculated as 0.20, 0.25, 0.02, 0.20 and 0.14 (SS-MPC$_l$), and 0.24, 0.31, 0.05, 0.30 and 0.11 (SS-MPC$_r$), respectively. SS-MPC$_l$ and SS-MPC$_r$ furnished similar RSDs: 19% (Cu), 1% (Mg), 3% (Mn), 2% (K) and 13% (Fe).

These findings reveals that single-standard calibration is a promising strategy for HR-CS F AAS. Therefore, the results contribute to the advancement of calibration methodologies in atomic spectrometry, offering more economical, faster, and greener calibration without significant loss of accuracy. Ongoing studies aim to consolidate the applicability of SS-MPC calibrations, broaden their scope, and improve method robustness, thereby reinforcing the potential of HR-CS FAAS for the reliable determination of metallic elements in diverse matrices.

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Study of Acidic and Acid-Free Microwave Digestion Protocols for Manganese Measurement in Human Plasma via Factorial Design

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Manganese (Mn) is a trace element essential for bone development, energy metabolism, antioxidant defense, protection against free radicals, and regulation of the nervous system.[1] Mn also serves as a cofactor for numerous enzymes involved in nitrogen, oxygen radical, carbohydrate and cholesterol metabolism.[1] Moreover, Mn is associated with the activity of superoxide dismutase. Proper regulation of manganese is crucial for normal biological function, as even slight deviations from optimal Mn levels can cause significant damage to physiological systems.[1,2] Dysregulation of Mn adversely affects the central nervous system. Chronic exposure to elevated Mn concentrations can lead to tremors, gait disturbances, and difficulty concentrating, potentially progressing to Parkinsonian syndromes or other neurodegenerative disorders.[1] On the other hand, manganese deficiency has been linked to osteoporosis, diabetes mellitus, carcinogenesis, increased susceptibility to infections, and epilepsy.[2] Consequently monitoring to maintain healthy manganese levels is essential. Although direct injection of a diluted suspension is commonly used in analytical sample preparation procedures, microwave-assisted digestion is more commonly used because it minimizes matrix interference and reduces instrument maintenance. In this study, acidic and acid-free microwave-assisted digestion conditions for manganese determination in human plasma was evaluated. A factorial experimental design was employed to maximize the analytical signal while minimizing reagent use, cost, and processing time. The manganese signal was monitored by graphite furnace atomic absorption spectrometry (GF AAS). Blood samples were collected from healthy individuals (n=10), and plasma was isolated by centrifugating at 20,000 rpm for 10 minutes. An experimental design was generated using the free version of Minitab© software, with the following parameters acid (hydrochloric or nitric), acid concentration (0, 7.5 and 15%), digestion time (5 or 30 minutes) and digestion temperature (50 or 185 °C). A total of four factors with two replicates per condition were investigated, resulting in 48 experimental runs. Following microwave digestion, all samples were analysed by GF AAS under instrumental conditions recommended by the manufacturer. The optimal conditions from the factorial design for Mn determination in blood plasma were 15% (v/v) hydrochloric acid at 185°C for 30 minutes. Reliable model fit was obtained with S value of 0.002, and coefficient of determination (R^2) 78.3%. Acid and concentration were the most influential variables, with p-value, respectively of 0.00 and 0.001. Interaction among acid, concentration, and time was also statistically significant (p-value= 0.011). The next step is to do a spike and recovery test to evaluate whether H_2O and HCl, used as a diluent, provide the same Mn recovery. And to apply these conditions to samples from patients with epilepsy to further investigate manganese metabolism under pathological and treatment conditions.

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Spectrochemical analysis of e-cigarette aerosols: development of a lab-built acid-trapping collector

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Electronic cigarettes have become increasingly popular among younger people in recent years, mainly because of their high customization options, wide variety of flavors, and attractive visuals. However, the use of these devices has raised health concerns among users. These devices work by releasing an aerosol from a liquid solution, called e-liquid, through an electronic component powered by a rechargeable battery. In Brazil, vapes are illegal, meaning these products are obtained through illegal means. To evaluate the inorganic composition of the aerosol and e-liquid, this study proposed developing a lab-built extraction system that simulates the puffs, followed by the analysis of the extract via Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and Graphite Furnace Atomic Absorption Spectrometry (GF AAS). After an initial screening using X-ray fluorescence (XRF), the following analytes were selected: Zinc (Zn), Cadmium (Cd), Nickel (Ni), Lead (Pb), and Arsenic (As). The e-liquid was collected and subjected to acid digestion before analysis by ICP OES and GF AAS to determine its inorganic composition. The aerosol extraction system was constructed with an acid trap solution connected to a mechanical pump. After verifying the sealing and optimizing the conditions (pH, volume of trapping solution, and the number of puffs), the extracts were analyzed by GF AAS and FIA-HG AAS. Table 1 shows the mean concentrations obtained for 30 puffs (equivalent to one cigarette) across three vapes.

Table 1. Techniques and elements identified in the quantification of e-liquid and vape aerosol. (n=3)

Element	E-liquid concentration	Technique	Mass in aerosol/30 puffs	Technique
Zinc	0.29 ± 0.11 mg/kg	ICP OES	129 ± 24 µg	GF AAS
Cadmium	3.37 ± 0.01 µg/kg	GF AAS	0.26 ± 0.22 ng	GF AAS
Nickel	17 ± 3 µg/kg	GF AAS	4,250 ± 69 ng	GF AAS
Lead	36 ± 10 µg/kg	GF AAS	287 ± 23 ng	GF AAS
Arsenic	-	-	182 ± 34 ng	FIA-HG AAS

The comparison between e-liquid and aerosol revealed distinct behaviors for the elements measured. Cadmium was found at lower concentrations in the aerosol compared to the liquid, indicating partial retention within the cartridge foam. Zinc showed similar concentrations in both phases, which, considering the different measurement units, suggests a high transfer efficiency into the vapor. Nickel was more concentrated in the aerosol, pointing to an additional source from metallic parts of the device, such as heating coils and resistors. Lead, absent in the e-liquid but detected only in the aerosol, clearly originates from metallic materials within the cartridge, likely from alloys or solder. Arsenic was present in significant amounts, raising health concerns. Its exclusive presence in the aerosol supports the idea that impurities in the device's metal components are released during vaporization. These findings demonstrate that the vaporization process not only transfers contaminants from the liquid but also releases toxic elements from the internal structure of the e-cigarette, increasing health risks for users. The proposed, cost-effective collection system allows routine monitoring of toxic elements in e-cigarette emissions and provides evidence that metal mobilization from the device is an additional source of exposure.

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[PUB/USP, CAPES, CNPq, FAPESP]

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Fluorine - the dark side of atomic spectrometry

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In this lecture we will point out what the difficulties are in fluorine detection using atomic spectrometry. In most cases fluorine is detected as a metal monofluorine in HR GF MAS, ICPMS, LIBS, MIP-AES. Here we will discuss how fluorine can be detected in atomic form and what it takes to detect flourine directly with ICPMS.

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SAMPLE PREPARATION METHOD FOR THE DETERMINATION OF BROMINE AND IODINE IN FACIAL MAKEUP BY ICP-MS

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Cosmetic products are formulations composed of natural or synthetic ingredients designed for application to the human body for purposes such as perfuming, cleansing, or enhancing appearance, as in the case of makeup[1]. According to the U.S. Food and Drug Administration (FDA), individuals typically use between 6 and 12 cosmetic products per day, potentially exposing themselves to approximately 160 ingredients. In addition to the declared components, these formulations may also contain trace amounts of contaminants, including toxic elements, which can pose health risks depending on the frequency, route, and duration of exposure[2]. Therefore, rigorous quality control of these products is essential. One of the main challenges in this context is the sample preparation of complex matrices such as makeup, since many methods described in the literature rely on acidic reagents, which hinder the determination of volatile elements. Mesko et al. (2019) demonstrated an efficient method using microwave-initiated combustion (MIC) for eyeliner pencils, enabling the determination of Cl and F[3]. In 2025, this approach was successfully applied to mascara and eyeliner for the determination of Cl, F, Br, I, and S, with ion chromatography employed in both studies. However, the application of this approach to various types of makeup remains largely unexplored. Consequently, the present study aimed to optimize a unified sample preparation method for the determination of bromine and iodine in different makeup matrices using ICP-MS. For the solid samples, 200 mg of sample and 400 mg of microcrystalline cellulose (used as a combustion aid) were employed, except for the eye pencil, which was decomposed using 300 mg of sample and only 50 mg of combustion aid. For the semi-solid samples, no combustion aid was required, and 500 mg of sample was decomposed. Sample preparation for MIC was carried out in a microwave oven (Multiwave 5001, Anton Paar, Austria) using closed containers pressurized with 20 bar of O_2. An absorbent solution of 100 mmol L^{-1} NH_4OH was employed to retain the analytes. Combustion was initiated by an NH_4NO_3 ignition solution, previously absorbed onto filter paper and placed on a quartz support. The samples, wrapped in polyethylene film, were positioned above this assembly[3]. The resulting solutions were compatible with a variety of analytical techniques, for the determination of bromine and iodine, inductively coupled plasma Mass Spectrometry (ICP-MS) was employed using a (iCAP MTX, Thermo Fisher Scientific, Germany). Sample introduction was performed with a MicroMist nebulizer connected to a two-stage Peltier-cooled spray chamber, using a carrier gas flow rate of approximately 1 L min^{-1}. The plasma power was set to 1550 W. Limits of quantification (LOQ) and detection (LOD) were calculated based on the analysis of ten analytical blanks. For Br, the LOQ was 0.22 mg kg^{-1} and the LOD was 0.14 mg kg^{-1}; for I, the LOQ was 0.05 mg kg^{-1} and the LOD was 0.03 mg kg^{-1}, addition and recovery tests demonstrated recoveries ranging from 92 to 101%. In the determination of Br quantifiable levels found only in samples of orange (1.39 ± 0.17 mg kg^{-1}), green (2.90 ± 0.13 mg kg^{-1}) and blue (26.34 ± 2.13 mg kg^{-1}) children's eyeshadow, and in a sample of adult eyeliner (103.4 ± 1.82). For iodine, quantification was possible in all eyeshadow samples, with concentrations ranging from 0.11 ± 0.01 mg kg^{-1} (black adult eyeshadow) to 5.70 ± 0.20 mg kg^{-1} (brown adult eyeshadow). The method proved effective for the determination of Br and I in all samples, with the highest concentration found in children's products. These findings underscore the relevance of this investigation and highlight the importance of monitoring potentially hazardous elements in cosmetics intended for this vulnerable population.

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Recycled PET-Based Composites with Iron Nanoparticles for Mercury Removal from Water

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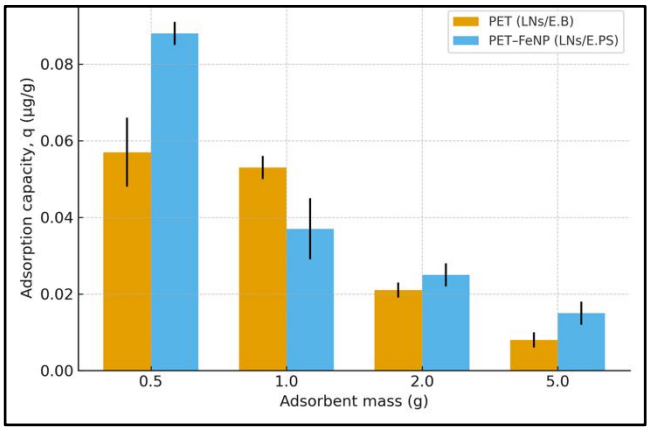
Illegal mining has caused severe environmental degradation in protected areas, releasing mercury into rivers through alluvial gold exploitation. Part of this mercury is emitted into the atmosphere, while the remainder accumulates in soils and surface waters. Considering this scenario, the present study investigated the development of a recycled PET–FeNP composite as a potential material for mercury remediation in contaminated water. To this end, PET fragments were chemically modified by alkaline treatment (2 % g/L NaOH, detergent, and deionized water) and subsequently exposed to a nanoparticle dispersion. Adsorption tests were carried out using a 50 µg/L Hg(II) solution (pH 5, 5.0 mL) in vials containing 0.5–5.0 g of either modified PET (LNs/E.B) or the PET–FeNP composite (LNs/E.PS), under agitation (155 rpm, 60 min). After exposure, the supernatant was analysed by Cold Vapor Atomic Absorption Spectroscopy (CV AAS) at 253.7 nm, using 0.2 % g/L $NaBH_4$ (alkaline medium) as the reducing agent and 3 % mL/L HCl as the carrier. The calibration curve (5–100 µg/L) showed $R^2 > 0.997$, with LoD and LoQ of 0.9 and 3.1 µg/L, respectively.



Previous studies have shown that PET itself is capable of interacting with metal ions. Lanzl et al. (2012) reported that aromatic groups in terephthalate moieties contain delocalized electrons that may interact with cationic species, while Sizmur et al. (2025) demonstrated that under acidic conditions, PET may adsorb mercury predominantly through physisorption or electrostatic interactions, since hydroxyl groups remain protonated. These mechanisms help explain why modified PET (LNs/E.B) alone was able to reduce Hg(II) concentrations in solution. However, when adsorption performance is normalized by sorbent mass (q, µg/g), a more evident trend emerges: the PET–FeNP composite consistently shows higher specific adsorption capacity than PET, particularly at low sorbent doses (0.5 g). This indicates that, although PET contributes to mercury binding, the incorporation of iron nanoparticles improves the efficiency of the material on a mass basis. The observed decrease in q with increasing sorbent mass does not reflect material saturation, but rather the limited amount of mercury available in the system: as the solid-to-liquid ratio rises, the same total amount of Hg is distributed across more grams of sorbent, reducing the calculated adsorption capacity per gram. These findings underscore the importance of assessing both residual concentration (Cr) and adsorption capacity (q) to evaluate new sorbent materials properly. Both modified PET and the PET–FeNP composite were effective in removing mercury from solution. Literature evidence supports that PET alone can adsorb Hg(II) through electrostatic or physisorption mechanisms. However, the present results clearly indicate that the addition of iron nanoparticles enhances adsorption efficiency, particularly at low sorbent doses. Therefore, the PET–FeNP composite appears to be a more promising material for mercury remediation than PET alone. Further work should aim to optimize FeNP loading, improve experimental reproducibility, and test under environmentally relevant conditions to validate the composite's applicability in real water treatment scenarios.

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Determination of Trace Elements in Blood by ICP-MS: Evaluation of the Collision and Reaction Cell in Mitigating Spectral Interferences

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The health of a living organism is intrinsically linked to the presence of essential chemical elements within concentration ranges that fulfill the requirements of the biological system. Increasingly, research has revealed significant associations between either excessive exposure to or insufficient levels of specific elements and the development of chronic diseases[1], highlighting the critical need for analytical techniques capable of accurately monitoring elemental concentrations in biological matrices. Inductively coupled plasma mass spectrometry (ICP-MS) stands out as a powerful technique for trace element analysis due to its sensitivity, wide linear range, and multielemental determination capability. However, spectral interference remains a challenge, particularly in complex matrices such as blood[2]. This study aimed to assess the limitations of the standard (STD) mode for multielemental determination in blood and to evaluate the performance of reaction and collision cells as interference mitigation strategies. For analysis, samples were first subjected to acid digestion and then measured using an ICP-MS equipment, model NexION 1000, PerkinElmer. Method validation was conducted with certified reference materials Seronorm Level 1 and 2 (human whole blood), ensuring the accuracy, precision, and overall reliability of the analytical protocol. Initially, analyses were conducted in standard mode, yielding recoveries between 93% and 120% for Ca, Cd, Co, Cu, Fe, Hg, Mg, Mn, Pb, Sr and Zn. However, As, Cr, Ni, Se and V could not be accurately measured in STD mode. For these elements, analyses were performed using the kinetic energy discrimination (KED) mode with helium as collision gas and the dynamic reaction cell (DRC) mode with methane as reaction gas. The effectiveness of interference correction by each cell mode, KED or DRC, was strongly dependent on the analyte concentration. In general, the concentrations of these elements in Seronorm L1 are close to the limits of quantification and could not be accurately determined in any cell mode. For concentrations over 10 µg L^{-1}, KED proved effective only for V, whereas the DRC mode successfully enabled the quantification of Se. Further evaluation of the dynamic reaction cell (DRC) mode using methane as reaction gas will be conducted under varying conditions to more effectively mitigate spectral interferences, aiming to identify the best approach for analyzing these elements in biological matrices.

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Method development for identification and quantification of TiO_2 nanoparticles by HR-CS GFAAS

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Titanium dioxide (TiO_2) nanoparticles can be found in a variety of products, such as sunscreens, cosmetics, and packaging materials, and in recent years, numerous studies have investigated the environmental impact of these nanoparticles, particularly in aquatic ecosystems and marine organisms. Atomic spectrometry techniques are the main methods used for Ti determination in its elemental form, especially plasma-based techniques such as ICP-OES and ICP-MS, which offer the advantage of high sensitivity. Ti determination by high-resolution continuous-source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) shows to be an alternative, demonstrating high sensitivity and selectivity, being useful for analyzing different types of samples. This technique is also suitable for future applications, where the method is intended to be applied for the detection and quantification of TiO_2 nanoparticles in live coral samples collected from reefs along the Brazilian coast. The possibility of direct solid sampling (SS) with this technique is particularly attractive for this application. This study aims to develop a method for Ti quantification by HR-CS GFAAS and apply it as a complementary method for characterizing TiO_2 nanoparticles. For this method, the wavelength of 364.2675 nm was selected for Ti, and a graphite furnace without a platform was used. After investigation, platinum was selected as the chemical modifier, and 10 µL of a 100 µg L^{-1} Pt solution (1 µg Pt) was used. For the heating program, the following temperatures were used: 110 °C for the drying stage, 1400 °C for pyrolysis (ramp of 300 °C/s), and 2650 °C for atomization (ramp of 1500 °C/s). A calibration curve was constructed with standard solutions in the range of 20–100 µg L^{-1} of Ti, resulting in $R^2 = 0.9999$, a limit of detection (LOD) of 4.5 µg L^{-1}, and a limit of quantification (LOQ) of 14.9 µg L^{-1}. Recent studies, reported in the review by Resano et al.[1], discussed the possibility of applying HR-CS GFAAS to nanoparticle identification, highlighting differences in the appearance times of nanoparticles and free ions in time-resolved absorbance spectra, with delay in the appearance time for nanoparticles. In this work, a suspension of TiO_2 nanoparticles (100 µg L^{-1} Ti) was analyzed and compared with a 100 µg L^{-1} Ti standard solution (ionic form) to evaluate absorbance and peak appearance time. The results showed that the absorbance for TiO_2 nanoparticles was considerably lower (about 35%) compared to the ionic Ti solution, although no significant differences in peak appearance time were detected. These studies suggest that complete atomization and quantification of the nanoparticles would require even higher temperatures, which is not feasible, since the maximum temperatures allowed by the equipment for atomization are already being used. Further studies are being carried out to investigate the differences in sensitivity related to the Ti species (free ions vs. nanoparticles) and to develop identification methods for these species.

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Rapid assessment of essential and potentially toxic elements in certified and non-certified omega-3 supplements by ICP-based techniques

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The consumption of dietary supplements, such as omega-3 fish oil, has increased significantly in recent decades because of their beneficial effects in reducing inflammatory processes and the risk of atherosclerosis and other chronic diseases. However, quality standards established by the *International Fish Oil Standard* (IFOS)[1], related to both organic and inorganic composition, directly influence the price and efficacy of these supplements, classifying them as certified or non-certified. Although non-certified supplements are generally sold at lower prices, concerns remain regarding their equivalence in terms of composition and quality. Additionally, differences in the presence of essential and potentially toxic elements may affect both nutritional efficacy and long-term safety. In this study, we evaluated the inorganic composition of 12 certified and 26 non-certified omega-3 fish oil supplements sold in Brazil, using ICP OES and ICP-MS with minimal sample preparation. Ca, Mg, Na, and P were measured by ICP-OES (5100 VDV, Agilent Technologies), while Ag, Al, As, Ba, Cd, Cr, Cu, Fe, Hg, K, Mn, Mo, Ni, Pb, Sn, Ti, V, and Zn were quantified by ICP-MS (iCap, Thermo Scientific). Analyses were performed by dissolving fish oil samples in ICP-grade solvent (P/N 54362, Sigma-Aldrich, St. Louis, USA), avoiding time-consuming microwave-assisted digestion steps. The methods were validated in terms of linearity, limits of detection and quantification, precision, and accuracy, ensuring the reliability of the results. Certified samples showed concentration ranges and medians of: Na: 0.06–254 mg/kg (median 28.2 mg/kg); K: <0.001–511 mg/kg (median 3.1 mg/kg); Ca: <0.01–311 mg/kg (median 7.0 mg/kg); Pb: <1–44 ug/kg (median 7 ug/kg); Ti: <1–343 ug/kg (median 5 ug/kg); Zn: <0,01–5,997 mg/kg (median 1,180 mg/kg); Fe: <10–525 ug/kg (median 53,5 ug/kg); Hg: <1 ug/kg;. Non-certified samples exhibited ranges and medians of: Na: <0.001–3.6 mg/kg (median 0.22 mg/kg); K: <0.001–0.30 mg/kg (median 0.015 mg/kg); Ca: <0.01–2.8 mg/kg (median 0 mg/kg) ; Pb: <1 ug/kg; Ti: <1 ug/kg; Zn: <10–241 ug/kg (median 14 ug/kg); Fe: <10–412 ug/kg (median 0 ug/kg); Hg: <1 ug/kg;. Higher concentrations of essential elements (Zn and Fe) were observed in certified samples, while Hg remained below the detection limit in both groups, indicating safety with respect to toxicity. The observed differences between certified and non-certified supplements reflect relevant variations in nutritional composition and inorganic quality, potentially impacting both biological efficacy and long-term safety. The combined use of ICP OES and ICP-MS proved essential for identifying these discrepancies in the inorganic components of omega-3 supplements sold in Brazil, highlighting their potential as an important tool for monitoring dietary supplement quality in the national market.

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Development of novel atmospheric-pressure discharge atomizers for hydride forming elements

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Coupling hydride generation with atomic absorption or fluorescence spectrometry is a well-established technique for trace element and speciation analysis, enabling efficient, and matrix-free introduction of analytes into the detector. While heated quartz tube atomizers and diffusion flames remain the most widely used hydride atomizers, alternative plasma-based atomizers - particularly dielectric barrier discharges (DBD) and atmospheric-pressure discharges (APD) - have gained attention. The DBD can efficiently atomize As, Se, Sb, and Bi hydrides while reaching poor sensitivity for Pb, Sn, and Ge. In particular, Ge is detected with low sensitivity even in the most common hydride atomizers.

Consequently, APD-based atomizers were developed and investigated in this work to overcome the low sensitivity observed in DBD for the elements mentioned above (Pb, Sn, Ge). Four APD designs were developed and tested. The first APD construction resembled the design of the diffusion flame, using a quartz capillary nested within a stainless steel anode and an opposing tungsten rod cathode. The zone of atomization was shielded with argon flow to prevent the entrance of oxygen from the ambient atmosphere. However, the discharge was unstable with this construction. The second design, based on two opposite rod electrodes, demonstrated stable discharge and obtained signal was comparable to that of diffusion flames. Thus, this design could be a robust alternative, and it is ready for optimization using an atomic fluorescence spectrometer. The other two APD designs tested were derived from the quartz tube atomizer. In the first arrangement, analyte hydride was introduced through a quartz and stainless steel capillary in a parallel direction with the plasma. In the second arrangement, analyte hydride was introduced through an inlet arm perpendicularly to the plasma and the opposite tungsten rod electrodes. The atomization area was protected from the ambient atmosphere by the optical tube eliminating the need for additional argon. The last design was selected as the most promising, and its performance was compared to the DBD and heated quartz tube atomizer. Current-voltage characteristics were evaluated, as they are crucial parameters for discharge performance. Due to the limited atomization efficiency achieved with commercially available high-voltage and direct current power sources, custom pulsed direct current power sources were developed. Various configuration will be presented.

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

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Variations in nickel and vanadium concentrations in marine oil spill events

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Evaporative weathering is one of the main processes that alters the composition of petroleum after its release into the environment. This phenomenon can eliminate up to 75% of the volume of light crude oil in just a few days, while medium crude oils evaporate up to 40% and heavy crude oils around 5%.[1] As light constituents are volatilized, a relative enrichment of fractions with higher molecular weight and lower volatility, such as asphaltenes and sulphur compounds, occurs. As a result, trace metals such as nickel (Ni) and vanadium (V), which are associated with the heavier fractions, become useful markers of advanced stages of weathering.[2] Studying this interaction in crude oils classified by the American Petroleum Institute (API) as light (43.1°API), medium (29.8°API), and heavy (17.1°API), according to the American Society for Testing and Materials (ASTM), this parameter contributes to understanding the dynamics of chemical transformation. The samples were distilled at top temperatures of 150°C+, 200°C+, and 250°C+, corresponding to the exposure time of the oil slick at sea.[3] The sulphur and asphaltene contents were determined by ASTM D4294 and D6560 methods, respectively. The samples were subjected to microwave-assisted acid digestion. For the *overnight period,* approximately 100 mg of the sample was weighed into a quartz vessel, and 7 mL of concentrated nitric acid was added. The following day, 1 mL of hydrogen peroxide and 2 mL of deionized water were added. The operating conditions and heating program used were adapted[4] as follows: 110°C for 5 min, held for 15 min, 200°C for 6 min, also held for 15 min, and cooling to 40°C. After cooling, the solution was filtered and diluted to 50 mL in a propylene flask. For analysis, the solutions were diluted fivefold. The analytical curve was constructed from a concentrated aqueous nitric acid solution with a 14 points preparation: 0-50 µL. $L^{-1.}$ The monitoring of the ^{60}Ni and ^{51}V isotopes in the Agilent Technologies equipment, model 7850 ICP-MS followed the configuration: RF 1550 W; plasma gas flow rate 15 $L.min^{-1,}$ auxiliary 0.90 L. min^{-1}, and nebulizer 1.03 $L.min^{-1}$. The concentrations increased along with the increment of weathering promoted by evaporation. After evaporation at 250°C+, the nickel (Ni) content in the fresh oil increased from 2035.63 $\mu g.kg^{-1}$ to 2377.17 $\mu g.kg^{-1}$, representing a variation of +17%, while vanadium (V) increased from 115.36 $\mu g.kg^{-1}$ to 292.80 $\mu g.kg^{-1}$, representing a significant increase of +153.78%. In the average oil, Ni increased from 11115.42 $\mu g.kg^{-1}$ to 13540.53 $\mu g.kg^{-1}$ (+22%) and V from 10317.28 $\mu g.kg^{-1}$ to 12291.44 $\mu g.kg^{-1}$ (+19%). In heavy oil, Ni varied from 11,505.15 $\mu g.kg^{-1}$ to 12,923.93 $\mu g.kg^{-1}$ (+12%) and V from 22,019.34 $\mu g.kg^{-1}$ to 24,729.79 $\mu g.kg^{-1}$ (+12%). The increase in asphaltenes, consisting of porphyrins, highlights the structural association between the monitored metals and the organic fractions, reinforcing the impact on the marine ecosystem due to the persistence of these components after spill situations at sea[2].

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Assessment of Pd Nanoparticles as Chemical Modifiers and Preconcentration Agents for Cd Determination in River Water by HR-CS GFAAS

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Cadmium is a heavy metal that can be hazardous to environmental and human health, even in trace levels.[1] In this way, the extraction and/or preconcentration of this element from environmental samples, such as river water, is important to obtain information about the composition and monitoring of potential contamination.[2] High-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) is widely used for Cd determination. However, the determination of this element at trace-level can be challenging, especially in complex matrices. Thus, nanoparticles (NPs) can be used as an alternative for the extraction and preconcentration of Cd in environmental samples, minimizing the potential interferences and improving the method´s limit of detection (LOD). Considering that Pd is also widely used as a "universal" chemical modifier, this project aims to develop PdNPs capped with 3-mercaptopropionic acid (MPA) to assess its potential as a chemical modifier and preconcentration agent for Cd determination by HR-CS GF AAS in river water. In this way, the synthesis of PdNPs was performed in an aqueous medium by using ascorbic acid as a reducing agent. The characterization of PdNPs was performed by checking the size via dynamic light scattering (DLS), transmission electron microscopy (TEM), and inductively coupled plasma mass spectrometer in single particle mode (spICP-MS), where the median size was 56 ± 14 nm. The temperature program of HR-CS GFAAS was optimized for river water under three conditions: using $Pd(NO_3)_2/Mg^{2+}$ (0.01%/0.5% m/v) as a chemical modifier (condition A), using Pd NPs as a chemical modifier (condition B), and without chemical modifiers (condition C). The pyrolysis and atomization temperatures for condition A were 900 and 1900 ºC, for condition B were 700 ºC and 1900 ºC, and for condition C were 500 and 1900 ºC, respectively. Besides the temperature of pyrolysis for the universal chemical modifier being higher than that of PdNPs, using the PdNPs, the absorbance is significantly greater, according to the t-test for pairs, at a 95% confidence level. In addition, the evaluation of the preconcentration property of the PdNP was performed by adding 1 µg L^{-1} of Cd^{2+} in buffer pH 4 in two systems: one with and the other without PdNPs. After 1 h of stirring, both systems were centrifuged at 3600 rpm for 10 min, and the absorbance in HR-CS GFAAS for Cd in both supernatants was evaluated. According to ANOVA from the t-test, at a 95% confidence level, there was a significant difference in the absorbance, indicating that Cd is interacting with the PdNPs. A multifactorial planning 2^k, where k is the number of parameters of the extraction, which was time of extraction (10; 35; 60 min), Volume of Pd NPs (100; 300; 500 µL), pH (3; 5; 7), was used to evaluate the parameters with significant influence in the preconcentration of Cd^{2+}. According to ANOVA, with 95% confidence, there is no lack of fit, and the parameters volume of PdNP and pH significantly influenced the response. In this way, the Doehlert methodology surface will be applied to both significant parameters. The goal is to achieve optimal conditions that increase the extraction efficiency of Cd^{2+} from environmental samples. The results indicate that the developed material is promising to use as a chemical modifier and for the preconcentration of Cd^{2+} in environmental samples.

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A novel atmospheric pressure glow discharge hydride atomizer for atomic absorption spectrometry: performance evaluation

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Several analytically important elements such as As, Se, Sn, Sb, Pb, Te, Bi and Ge can be quantitatively converted to their corresponding volatile hydrides and introduced into the atomic spectrometric detectors to achieve their ultratrace determination. Derivatization by hydride generation (HG) also results in reduced risks of interferences and sensitivity improvement, by an order of magnitude, when compared to liquid sample nebulization. HG can be coupled to any atomic spectrometric detector, including atomic absorption spectrometry (AAS), atomic fluorescence (AFS) or optical emission spectrometry (OES) and inductively coupled plasma mass spectrometry (ICP-MS). AAS is still the most common detector for routine use in trace element analysis. The most frequently used hydride atomizers in AAS are externally heated quartz tubes (QTA)[1,2]. However, plasma-based atomizers such as dielectric barrier discharge (DBD) or atmospheric pressure glow discharge have been proven as promising alternatives to QTA recently.

APGD is a non-equilibrium discharge formed between two electrodes powered by high DC or pulsed voltage (1-10 kV). The discharge gap varies between 1-5 mm with 10-100 mA discharge current[3]. Plasma gas temperature reaches from 1500-3500 K with electron density of 10^{14}-10^{15} cm^{-3}. The APGD hydride atomizer design was derived from a quartz body of a QTA. Instead of the resistive heating of its optical arm, two electrodes were inserted into its central part to sustain the discharge (0.5 kV, 30 mA) in the optical axis of the spectrometer.

Atomization conditions have been optimized individually for As, Se, Sb, Sn, Te, Bi and Pb. The effect of following parameters on analyte response was investigated: input voltage of the power source, the discharge gas nature (Ar vs He) and its flow rate, as well as the role of the water vapour and aerosol co-generated. Subsequently, analytical figures of merit, including limits of detection (LOD) and sensitivity were determined under the optimum conditions. LODs ranged between 0.1 and1.5 ng ml^{-1}, while sensitivities from 0.03 to 0.3 s ng^{-1} were found. These values were compared to other hydride atomizers, namely QTA and DBD. Moreover, a detailed interference study was conducted involving other hydride forming elements and mercury as model interferents. The resistance towards interferences is, apart from sensitivity and LOD, an important feature to assess the robustness of the newly developed method and its applicability to routine use. Response of model solutions in presence of equal, 10-fold and even 100-fold excess of the interferent over the analyte was studied. The most significant interferents for each analyte will be discussed. The competitiveness of APGD hydride atomizers with respect to QTA and DBD will be outlined.

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Speciation of Iron Released from Nanoparticles in Artificial Sweat

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Iron oxide nanoparticles (IONPs) are present in the environment as a result of both natural processes and anthropogenic activities. A notable example is their formation in aquatic environments as a consequence of mining operations and the disposal of mining waste.[1] These particles can lead to dermal exposure, particularly through contact with contaminated water, which may pose potential health risks. The toxicity of metal-based nanoparticles is closely related to their ability to be absorbed and reach specific tissues. In this context, the fraction of a substance that is available for absorption, denominated as bioaccessibility, plays a key role[2,3]. For nanomaterials, this bioaccessible fraction includes both ionic and nanoparticulate forms.

In this study, we investigated the bioaccessible fraction of IONPs after contact with two different artificial sweat formulations, as well as the speciation of the ionic iron released. Initially, goethite, hematite, and magnetite nanoparticles were synthesized and characterized without the use of functionalization or stabilization agents to mimic an environmental condition. The artificial sweats were prepared according to the UNE EN 1811:2023 standard of the European Committee (pH 6.5) and the NIHS 96-10 specification of the Swiss watch industry (pH 4.7). Then, the IONPs were submitted to both in a water bath at 36,5 ºC and agitation of 100 rpm, taking aliquots at 0, 3, 6, 12, and 24 hours. The ferrous/ferric ions were speciated using the reaction with 1.10-ortophenantroline, which is selective to Fe^{2+}, and hydroxylamine to reduce Fe^{3+} to total ionic iron determination using a UV-Vis spectrophotometer at 510 nm. The nanoparticulate iron in dispersion was determined by Graphite Furnace Atomic Absorption Spectrometer (GFAAS) using $Mg(NO_3)$ as matrix modifier.

In the NIHS sweat, a slight release of Fe^{2+} from all nanoparticles was observed over time, with higher release in magnetite, which contains both ionic forms in its structure. Meanwhile, Fe^{3+} showed a greater release than Fe^{2+}, and hematite proved to be more stable against degradation compared to the other nanoparticles. In EN sweat, no release of Fe^{2+} and only a small amount of Fe^{3+} were observed for all nanoparticles, with no significant increase up to 24 hours.

When comparing the dispersion of nanoparticulated iron in sweat, NIHS was more effective at stabilizing the nanoparticles than EN. However, in both cases, goethite showed the highest stability, followed by hematite and magnetite, respectively.

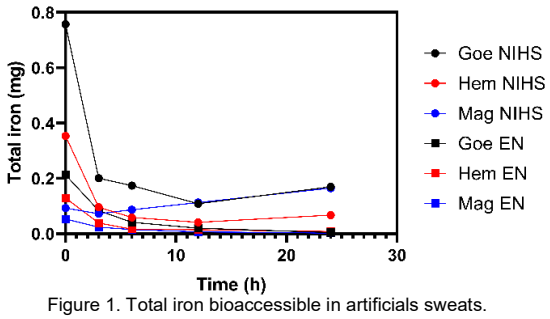

Figure 1. Total iron bioaccessible in artificials sweats.

In summary, the bioaccessibility of iron nanoparticles is heavily affected by both the nanoparticle composition and the physicochemical properties of sweat. NIHS sweat, with its lower pH and the proximity of the nanoparticles' isoelectric point to neutral values, promotes a higher release of iron species compared to EN sweat (Figure 1). Among the materials tested, goethite showed the greatest stability, followed by hematite and magnetite. These findings emphasize that the interaction between nanoparticles and biological fluids influences their stability and dissolution, factors essential for evaluating their potential for dermal permeation and related health risks.

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Evaluation of Acid and Acidless Microwave Digestion Methods for Iron Determination in Human Plasma: A Factorial Design Approach

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Iron (Fe) plays a vital role in key physiological processes, including oxygen transport, DNA synthesis, energy metabolism, and immune regulation[1]. The majority of iron in the human body is bound to hemoglobin, with smaller fractions involved in enzymatic activity or stored as ferritin[2]. Maintaining iron homeostasis is critical, as both deficiency and overload are associated with adverse outcomes such as anemia, oxidative stress, and metabolic dysfunction. Moreover, plasma iron levels may be influenced by pharmacological agents, including statins and antiplatelet drugs, potentially exacerbating anemia in susceptible individuals[3]. Consequently, accurate monitoring of plasma iron concentrations in these populations is essential.

Reliable quantification of iron requires appropriate sample preparation. Microwave-assisted acid digestion using nitric acid (HNO_3) is the standard method however, its high cost and difficulty of acquisition present a limiting factor for its use. Hydrochloric acid (HCl) offers a more economical alternative without compromising analytical performance[4]. This study aimed to evaluate the efficiency of acid-based and acid-free microwave digestion procedures for iron determination in human plasma using a factorial design approach.

Microwave digestion optimization was performed using pooled plasma samples from 10 healthy volunteers, processed in a microwave oven (Anton Paar). A full factorial design was implemented using Minitab© software, incorporating four factors at two levels with a central point: acid type (HNO_3 or HCl), acid concentration (0%, 7.5%, and 15% v/v), digestion time (5 or 30 minutes), and temperature (50–185 °C), resulting in 48 experimental runs. The 0% acid condition used only deionized water. Iron concentrations were measured via graphite furnace atomic absorption spectrometry (GFAAS), yielding a limit of detection (LOD) of 0.254 µg/L and a limit of quantification (LOQ) of 0.846 µg/L. The method demonstrated a robust linear range (5–100 ppb) with $R^2 = 0.9919$ and high statistical significance ($p = 1.20 \times 10^{-26}$). Precision was confirmed with a relative standard deviation (RSD) of 8.71% across ten replicates at 20 ppb Fe. Instrumental parameters were applied in accordance with the manufacturer's recommendations.

Statistical analysis revealed that acid type, concentration, and temperature significantly influenced the analytical response ($p = 0.000$), with $R^2 = 94.30\%$ and regression standard error $S = 0.0089$. All two-way interactions were statistically significant ($p < 0.005$), except those involving digestion time; the other interactions, including the four-way interaction, were not significant.

A full factorial design identified 7.5% (v/v) HCl at 185 °C for 5 minutes as the optimal condition for microwave-assisted digestion of human plasma for iron (Fe) determination. Interestingly, digestion using water alone also yielded iron concentrations consistent with expected levels in plasma, suggesting a practical and simplified alternative for sample preparation. To further assess the efficacy of both approaches, spike-and-recovery experiments will be performed to evaluate whether HCl digestion ensures superior recovery or if water-based digestion provides comparable or enhanced performance.

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Evaluation of a 3D-printed polymeric platform for the determination of Pd, Pt and Ru complexes in cancer cells by HR-CS GF AAS

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The research for new anti-tumor compounds aims to overcome the limitations of conventional, platinum-based treatments, such as toxicity and cellular resistance. Metal complexes of palladium and ruthenium have been noted for their cytotoxic activity *in vitro*[1,2]. One challenge in applying new compounds is identifying if the metal complex remains in the intracellular environment and acts directly on the cell death process[2]. The High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry (HR-CS GF AAS) is an attractive technique for evaluating metal complexes anticancer activities in intracellular medium because it allows direct sampling, fast and effectiveness elemental determination in small sample size. But the high temperatures needed to atomize Pt-group elements may accelerate the degradation of graphite sample holders (and tubes). The aim of this study is the construction and evaluation of a 3D-printed polymeric platforms[3] for the determination of Pd, Pt and Ru complexes in intracellular medium of breast and ovarian cancer cells by solid sampling HR-CS GF AAS. A filament with a diameter of 1.75 mm was produced from natural PLA using an extruder Filmaq 3D CV. Thus, PLA platforms were made 3D printing using the Creality K1 printer. Breast cancer cell samples (MDA-MB-231) were treated with solutions containing palladium and platinum metal complexes at 7 µmol L^{-1} and 19 µmol L^{-1} concentrations, respectively. Ovarian cancer cells (A2780) were treated with ruthenium complex solutions (1 µmol L^{-1}). Standard solutions containing 800 µg L^{-1} Pd, 300 µg L^{-1} Pt, and 900 µg L^{-1} Ru were used to optimize the heating programs of atomizer, on order to ensure complete decomposition of both the matrix and PLA platform. Commercial pyrolytic graphite platforms were also used in determinations for comparative purposes. The external calibration curves for Pd (2.5–12.5 ng), Pt (0.5–11.0 ng) and Ru (0.3–1.5 ng) showed linear correlations ≥ 0.9997 (Pd), 0.9992 (Pt) and 0.9993 (Ru) when using PLA platform.; the corresponding curves using pyrolytic graphite platforms were 0.9946 (Pd), 0.9993 (Pt) and 0.9997 (Ru). Results for analytes determination obtained with PLA platform were statistically similar to those obtained with commercial pyrolytic graphite platforms at the 95% confidence level. Recovery tests were performed on cancer cell samples spiked with 1.0 and 6.0 ng Pd, 1.0 and 10 ng Pt, and 0.5 and 1.0 ng Ru. Recoveries using PLA platforms were within 81-107% (Pd), 89-109% (Pt) and 80-108% (Ru); recoveries using graphite platforms were 81-107% (Pd) 100-109% (Pt), and 81-106% (Ru). The relative standard deviations (RSD) ranged from 1 to 14% (Pd), 2 to 6% (Pt) and 1 to 2% (Ru) for PLA; the corresponding RSD for graphite platforms were 3–13%, 2.6–3% and 2–15%.The limits of quantification (LOQ) using PLA platforms (1.0 ng Pd, 0.3 ng Pt, and 0.1 ng Ru) were close to those for graphite platforms (0.8 ng Pd, 0.2 ng Pt and 0.1 ng Ru), demonstrating the analytical feasibility of PLA platforms. Polymeric platforms may be considered a promising, low-cost alternative with good analytical performance for determining Pd, Pt and Ru complexes in intracellular environment of cancer cells.

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Evaluation of Major Element Composition in Mineralized Solid Samples Using Basalt from the Pitanga Formation

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Mineral carbonation is a promising long-term strategy for carbon capture and storage (CCS), which aims to mitigate climate change by permanently immobilizing CO_2 in stable mineral phases.[1] Mafic and ultramafic rocks, particularly basalts, are natural candidates for this process due to their abundance and high reactivity with CO_2, leading to the formation of solid carbonates and the carbon immobilization in environmentally safe forms.[2] Understanding the geochemical behavior of major elements during basalt–CO_2 interactions is essential for evaluating the efficiency of mineral carbonation, but reliable quantification requires advanced analytical methodologies capable of handling complex matrices. This study investigates the distribution and retention of major elements, Al, Na, Mg, K, and Ca. A high-Ti basalt sample from the Pitanga Formation was submitted to hydrothermal reactions in a batch reactor at 150 °C and 80 bar CO_2 partial pressure. Experiments were conducted using high-ionic-strength water and a water-to-rock mass ratio of 5:1, with reaction durations of 5, 10, 20, and 30 days. After reaction, the solid products were digested using a Multiwave PRO microwave digestion system (Anton Paar) for subsequent analysis of major elements by HR-CS FAAS. For digestion, approximately 0.05 g of each sample was weighed into vessels and treated with 4.0 mL HNO_3, 1.5 mL HF, and 1.0 mL HCl in two digestion steps. In a third step, 5.0 mL of a 4.5% (m/v) H_3BO_3 solution was added to each flask. The digests were transferred to 50 mL polypropylene tubes, and then diluted to a final volume of 50 mL. Elemental quantification was performed using a ContrAA 700 (Analytik Jena), equipped with a xenon lamp emitting a continuous spectrum (190–890 nm), a high-resolution double monochromator, and a CCD detector. Al was determined using a nitrous oxide–acetylene flame.For Al determinations, the concentration of KCl used as an ionization suppressor was optimized by testing the following concentrations: 0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, and 7% (m/v). The results showed that 5% (m/v) KCl provided the best performance, in agreement with the findings of Filho and Neto (2009)[3]. Optimal instrumental conditions for Al were: wavelength 396.152 nm; C_2H_2–N_2O flow 240 L h^{-1}; burner height 9 mm; aspiration rate 6 mL min^{-1}; integration time 8 s; and KCl concentration 5% (m/v). For Na, Mg, K, and Ca, the best conditions were: wavelengths of 589.5924, 285.2125, 766.4908, and 422.6728 nm for Na, Mg, K, and Ca, respectively; C_2H_2–air flow of 60 L h^{-1}; burner height of 8 mm; aspiration rate of 4.5 mL min^{-1}; integration time of 10 s; La_2O_3 concentration of 0.60% (m/v); and KCl concentration of 0.25% (m/v), based on the method reported by Schwartzhaupt et al. (2025)[4]. CP ±1 was used for signal evaluation of all elements. Method accuracy was evaluated using two certified reference materials (CRMs), showing good agreement with certified values for Al, Na, and K (95 to 105%) with no significant difference (t-test, 95% confidence level). The method also demonstrated acceptable precision (RSD < 5%) and limits of detection of 2, 0.04, 0.03, 0.2, and 0.04 mg L^{-1} for Al, Na, Mg, Ca, and K, respectively. However, the accuracy for Mg and Ca was not satisfactory (agreement of 58 to 72%), and other method optimizations are being carried out. Thus, the proposed methodology is suitable for the determination of Al, Na, and K, but requires refinement for the quantification of Ca and Mg. This study shows that advances in HR-CS FAAS can improve the geochemical understanding of mineral carbonation, connecting analytical innovation to climate change mitigation via CCS.

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Cadmium extraction from human serum using restricted-access magnetic nanoparticles followed by FAAS analysis

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The determination of substances in complex matrices poses considerable challenges, often demanding multiple preparation stages to selectively isolate the analyte from diverse interferences[1]. Conventional solid-phase extraction sorbents generally exhibit low selectivity, limiting their efficiency in impurity removal[2]. In this scenario, functionalized magnetic nanoparticles emerge as a promising alternative, reducing preparation time while minimizing adsorption-related interferences[3]. In this work, restricted-access magnetic nanoparticles were synthesized and characterized for the extraction and preconcentration of cadmium in human serum, with subsequent quantification by Flame Atomic Absorption Spectrometry (FAAS). Characterization was performed through Fourier-transform infrared spectroscopy, thermogravimetric analysis, zeta potential determination, and protein exclusion assays, confirming the successful synthesis and coating with bovine serum albumin (BSA). Optimization of cadmium adsorption was carried out using a full factorial design, establishing the following optimal conditions: sorbent mass, 15.00 mg; pH, 5.0; eluent, 5.0 mol L^{-1} HNO_3; and sample volume, 2.00 mL. Adsorption equilibrium was reached within 15 min, following pseudo-first-order kinetics, and the adsorption isotherm fitted the Langmuir model. The analytical method exhibited linearity between 0.1–1.0 mg L^{-1}, with detection and quantification limits of 0.025 mg L^{-1} and 0.085 mg L^{-1}, respectively. Precision values ranged from 1.26% to 5.11% (interday), while accuracy was between 91.26% and 98.87% recovery at different levels. These results demonstrate that the synthesized nanoparticles present strong potential for cadmium extraction and determination in complex biological matrices. As a future step, the optimized protocol will be applied to real human serum samples.

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Assessing elemental fractionation in food waste processing

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In recent years, growing attention to the environmental and socioeconomic impacts of food waste has driven the research for sustainable strategies for its reuse. According to the Food Waste Index Report, published in 2024 by the United Nations Environment Programme (UNEP), approximately 1.05 billion tons of food were wasted in 2022.[1] Food waste has a significant environmental impact, accounting for 8 to 10% of global greenhouse gas emissions. Therefore, it is essential to develop appropriate protocols for the treatment and recovery of by-products through alternatives such as composting, conversion into energy, and/or valorization (extracting target elements and/or compounds), contributing to the reduction of environmental impacts and the strengthening of the circular economy.[2] In addition, food waste is a rich source of essential and non-essential elements, that are present in leftovers parts. In this context, some strategies can be used to investigate the elements recovery and propose their potential reuse (as supplements, fertilizers or other applications). Microwave hydro-diffusion and gravity (MHG) is a technology increasingly investigated for valorization purposes. However, only few data regarding fractionation of elements are known. Based on that, the aim of this study was to evaluate the fractionation of essential (Ca, Cu, Fe, K, Mg, Mn, Na, and Zn) and non-essential (Al, Ba, Cr, and Sr) elements in food waste treated with MHG. In this study, five different types of food waste were obtained from the University Restaurant of the Federal University of Santa Maria, being scraps of: green cabbage, beetroot, carrot, Napa cabbage, onion, tomato, orange, zucchini. Samples were chopped, frozen, and stored in properly identified plastic packaging. Initially, the samples were characterized according to the content of moisture (ranging from 77 to 95%), ash (ranging from 4 to 9%), protein (ranging from 0.03 to 4%), lipids (ranging from 0.2 to 0.4%) and carbohydrates (ranging from 0.8 to 2%), following standard protocols provided by the Official Methods of Analysis (AOAC) 968.11, AOAC 920.153, AOAC 920.152, AOAC 996.06, and from the Brazilian Health Regulatory Agency (ANVISA) RDC nº 360 (2003), respectively. After that, the samples were submitted to a free-solvent extraction using an MHG system (model NEOS-GR MA126, Milestone, Italy). The extraction was carried out using 200 g of frozen sample for 15 min, at 500 W. The raw food waste, the co-produced powder and the co-product (liquid) resulting from the MHG extraction were digested by wet acid digestion prior to the elemental determination by microwave-induced plasma optical emission spectrometry (MIP-OES). Sample preparation was performed using 250 mg of sample, with 4.5 mL HNO_3 plus 0.5 mL HCl and 1 mL H_2O_2 (35% v v^{-1}) with microwave heating (Ethos Easy, Milestone, Italy). A heating program of 75 min (total heating time), with maximum temperature and pressure of 220 °C and 35 bar was used. After digestion, the elemental determination was carried out by MIP-OES (model 4210 MP-AES, Agilent, USA), under standard conditions, with conventional nebulization. Higher concentration of essential elements such as Ca, K, Mg, and Na was determined in all samples, with K being the highest essential element present (0.9 to 5.6 mg g^{-1}). After MHG, the highest concentrations of all elements was found in the co-produced (solid) for all food waste samples. Results ranging from 78% (Fe) to 103% (Na) were observed for green cabbage, 79% (Cr and Mn) to 102% (Fe) for beet, 77% (K) to 96% (Na and Al) for carrot, 80% (Zn) to 98% (K) for Napa cabbage, 83% (Al) to 99% (Na) for onion, 65% (Cr) to 98% (Al) for tomato, 84% (Cu) to 98% (Al) for orange, and 81% (Cu) to 98% (K and Mg) for zucchini. The fractionation of elements to the co-product (liquid) was at maximum 30% (Cu) for green cabbage, 19% (K) for beet, 23% (K) for carrot, 24% (Zn) for Napa cabbage, 16% (Sr) for onion, 35% (Cr) for tomato, 14% (Cu) for orange, and 20% (Cu) for zucchini. The results from elemental determination using MIP-OES provided a better understanding about the distribution of elements in MHG processing of food waste.

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Determination of P and S in Argentina's meat samples by High Resolution Continuum Source Molecular Absorption Spectrometry

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Meat has played a crucial role in human evolution and is an important component of health and well-being due to its nutrient-rich profile[1]. Specifically, non-metals such as phosphorus (P) and sulphur (S), influence a wide range of biological and metabolic processes, whose concentration in organisms is directly related to their dietary intake. In Argentina's Pampas Region, a significant deficiency of P and S in agricultural soils has been documented, highlighting the importance of evaluating their content in animal-derived foods, particularly in products intended for human consumption, such as pork and lamb meat. Non-metals are challenging elements to determine using atomic spectrometry (AS) because the primary emission lines of these analytes are in the vacuum-UV region. Therefore, it is difficult to determine them with conventional optical instruments because oxygen and water vapor produce strong absorptions[2]. With the introduction of High-Resolution Continuum Source Molecular Absorption Spectrometry (HR-CS MAS), the aforementioned problems for the determination of non-metals were overcome, using the generation of various diatomic molecules as an alternative for the quantification of these elements. The objective of this work was to develop an alternative and sustainable method for the determination of P and S in meat from the Argentina's Pampas Region, pork and lamb/sheep, using HR-CS MAS, with PO and CS as target molecules. The sample pretreatment was performed using ultrasound-assisted extraction (USAE). A Box Behnken design was used to optimize the experimental conditions, considering three factors (sample mass, time and volume of tetramethylammonium hydroxide (TMAH). The response surface methodology was implemented to find the best combination of factors that would allow the highest absorbance (desirability) of the analytes to be determined. The optimized experimental conditions were: 100 mg of sample, 300 µL of TMAH (25% $v.v^{-1}$) and 50 min of extraction time. Accuracy was validated by analysing Certified Reference Materials (NIST 8414 Bovine Muscle Powder, NBS 1577a Bovine Liver). For PO the optimum working temperatures were 1000°C and 2400°C for pyrolysis and atomization respectively, using $Ca(NO_3)_2$ as a chemical modifier. Additionally, the platform was covered with a solution of tungsten as a permanent modifier for the analysis. A simultaneous determination of atomic and molecular lines was performed in order to monitor whether all atomic P was converted into PO. In the case of CS, the optimal temperatures were 800°C for pyrolysis and 2600°C for atomization, using a Pd/Mg mixture as a chemical modifier. In addition, the environmental impact of the developed methodology was evaluated using green indices, such as AGREE, AGREEprep, and BAGI. The proposed procedure showed significant advantages in sustainability, particularly due to the reduction in the consumption of reagents and mass sample used. The combination of USAE and HR-CS MAS detection represents an accurate, efficient, and environmentally responsible alternative for the analysis of P and S in freeze-dried meat, contributing to the development of methodologies aligned with the principles of Green Analytical Chemistry. In addition to offering analytical and operational advantages, it provides a valuable tool for the nutritional study of regional meat products.

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Plasma-Mediated Vapor Generation: Application for Hg Determination in Fish Samples after Microwave-Induced Combustion

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Mercury determination is a crucial parameter for ensuring the safety of the consumers of fish.[1] The most common approach for Hg determination regards its conversion into volatile species, usually Hg^0, for subsequent spectrometric detection, promoting enhanced sample delivery and low limits of detection (LOD).[2] Plasma-mediated vapor generation (PMVG) is an approach that generates Hg vapor with no requirement for reagent.[2] Exploiting the collision of reactive species from the plasma with an aqueous interface, which leads to the formation of $H^{\bullet}$, a strong reductant agent.[2] However, the presence of NO_3^- remarkably impacts the PMVG efficiency.[2] In this sense, microwave-induced combustion (MIC) comes as an alternative for sample preparation that promotes the decomposition of samples via combustion reactions, allowing the absorption of the analyte in diluted solutions thus reducing the concentration of NO_3^- in the final solution.[3] Furthermore, the present study evaluated the suitability of MIC for further Hg determination by PMVG with high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) detection. The PMVG system was composed of a high-voltage power supply connected to a quartz tubular dielectric barrier discharge reactor by two copper foil electrodes. The gas flow was dried by passing it through a vessel containing NaOH pellets before the introduction into the HR-CS AAS optical path (170 mm long and 14 mm i.d.). The sample introduction into the reactor was performed using an orifice at its top; a quartz rod (10 mm long and 1 mm o.d.) at the bottom of the reactor prevented the flow of the liquid sample out of the plasma region. An Arduino UNO board was used to monitor the temperature inside the reactor, as well as to perform the automated opening and closure of the reactor and turn on and off the power supply during injection. For the MIC procedure, 500 mg of frozen Panga fish tissue (*Pangasius hypophthalmus*) samples were dried, ground, and pressed into pellets (4 ton for 2 min). The sample pellets were put in a quartz holder on a paper disk moistened with 50 µL of a 6 mol L^{-1} NH_4NO_3 solution and then placed into the quartz vessel pressurized at 20 bar with O_2. The microwave heating program was set to 800 W for 5 min and 20 min of cooling. The following power source parameters were evaluated according to the maximum output voltage: input voltage (30 to 60 V), duty cycle (1 to 100%), and frequency (1 to 150 kHz). The volume of injection (10 to 50 µL), the gas type (Ar and He), and the gas flow rate (50 to 170 mL min^{-1}) were evaluated by the maximum signal response to the injection of a 100 µg L^{-1} Hg^{2+} standard solution in ultrapure water. The optimum PMVG parameters were 60 V of input voltage, 50% of duty cycle, 32 kHz of frequency, 50 µL of injection, and 70 mL min^{-1} of Ar flow. Furthermore, the NO_3^- influence on PMVG performance was investigated by the comparison of the signal obtained for the injection of a 100 µg L^{-1} Hg^{2+} standard solution in water and in increasing concentrations of HNO_3 (0.01, 0.1, 1, 2, and 5 mol L^{-1}). No statistical differences were observed while comparing the signal for water-diluted solutions and solutions with up to 0.1 mol L^{-1} HNO_3. Allowing the use of 6 mL of 0.5 mol L^{-1} HNO_3 as absorbing solution, with dilution to 25 mL with ultrapure water after the MIC procedure. The LOD of the proposed method was 0.16 µg g^{-1} lower than the Hg limit established in Brazil and Europe (0.5 µg g^{-1}) for fish samples. The accuracy of the method was assessed by the analysis of a dogfish liver certified reference material (DOLT-4); no statistical differences were observed between the values obtained by the proposed method and the certified value. The obtained value for Hg determination by the proposed method in Panga fish samples was 0.40 ± 0.02 µg g^{-1}. In this sense, the present work proved the suitability of MIC to the determination of Hg by PMVG-HR-CS AAS, with low reagent consumption when compared to conventional Hg determination methods for fish samples.

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Plasma-Based Techniques

PRELIMINARY STUDY ON SAMPLE PREPARATION OF STINGLESS BEE HONEY USING DILUTED ACID FOR ELEMENTAL DETERMINATION

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Honey is a widely consumed and valued bee product due to its nutritional and medicinal properties, attracting interest from the food sector, researchers, and industry[1]. The National Health Surveillance Agency (Anvisa) of Brazil sets maximum limits for elemental contaminants in honeys produced from the genus Apis, but few rules attest to the quality of honey from stingless bees[2,3]. Validated sample preparation procedures for elemental determination in honey are still unavailable, highlighting the need for simple approaches. This study evaluated a straightforward acid dilution procedure: approximately 0.25 g of honey samples were weighed and diluted to 10 mL with 2% (v/v) HNO_3 for subsequent analysis. Honey samples from the species *Melipona capixaba* and *Melipona quadrifasciata* were collected at different locations in Espírito Santo, Brazil. For the analysis, 1 mL of the sample solution was diluted to 3 mL with 2% (v/v) HNO_3. As^{75}, Cu^{65}, Cd^{112}, Pb^{208}, and Fe^{56} were determined with mass spectrometer with inductively coupled plasma (ICP-MS). Interferences were corrected with the use of an internal standard (Rh, In, or Ga) and a collision gas (He). Accuracy was assessed by a standard addition test performed during sample preparation. Yielded recoveries of 117, 101, 93, 89, and 98% for As, Cu, Cd, Pb, and Fe were found, respectively. As, Cd, Pb, and Fe were below the limit of quantification (LOQ) in all samples. Cu was determined in all honey samples of the species *Melipona capixaba* between 59.5 and 123.4 μg kg^{-1}, which is below the limit determined for Cu in honey (300 μg kg^{-1}) by Anvisa. Honeys of the species *Melipona quadrifasciata* showed Cu concentrations below the LOQ (37.8 μg kg^{-1}). Among sample preparation strategies such as ultrasound-assisted procedures and microwave-assisted acid digestion, simple dilution of honey with dilute HNO_3 showed promising performance for multielement determination by ICP-MS. This approach reduces reliance on costly digestion equipment and makes honey analysis faster and more practical, while aligning with Green Analytical Chemistry (GAC) principles.

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RARE EARTH ELEMENTS AS KEY TRACERS OF THE GEOGRAPHICAL ORIGIN OF AMAZONIAN TIMBER

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The traceability of geographical origin has become a strategic tool for sustainable forest management and for combating illegal logging[1]. Despite its recognized ecological and biological importance, the Amazon rainforest has been undergoing an accelerated process of environmental degradation, driven by the intensification of agricultural, mining, and logging activities. With approximately 64% of the Amazon rainforest located within its territory, Brazil plays a central role in global strategies to mitigate deforestation. International regulations, such as the European Union Deforestation Regulation (EUDR)[2], increase the demand for effective systems of wood traceability and legality verification. From this perspective, chemical and isotopic patterns of Amazonian wood are being investigated to identify intrinsic characteristics that can support forensic analyses[3]. Thirty wood samples from ten different species were collected in the states of Acre (n = 10), Pará (n = 10) and Rondônia (n = 10) for elemental characterization. Analytical portions of 250 mg were weighed into PTFE vessels and subjected to microwave-assisted acid digestion using 4.5 mol L^{-1} HNO_3 and 9.8 mol L^{-1} H_2O_2 at 200 °C and 1800 W. The resulting solutions were analyzed using a triple quadrupole inductively coupled plasma mass spectrometer. The elements B, Ba, Ca, Ce, Co, Cr, Cs, Cu, Er, Eu, Fe, Gd, Ho, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sm, Sr, Tb, V, W, and Zn were quantified in the wood samples. PERMANOVA analysis revealed that statistically significant differences ($p < 0.05$) for Ba, Ce, Er, Eu, Gd, Ho, Sr and Tb were observed exclusively among states, with no effect of species. In contrast, for the other elements, both species and state contributed to the observed variability. Since the aim of this study was to discriminate samples by geographical origin, only the elements that varied exclusively among states were selected for further analysis. A machine learning approach was employed to classify samples by region and to estimate the relative importance of the chemical elements, using the Random Forest algorithm. Ba, Tb, Eu, Sr, and Er were the most important variables, emerging as key chemical markers for the geographical differentiation of the samples. To further demonstrate the discriminatory potential of elemental profile, decision tree models were also fitted. The trees were limited to a maximum depth of three levels to construct simplified and easily interpretable models. Even with this limitation, high classification accuracy was achieved, ranging from 96% to 100%, depending on the set of elements used in each model. The results demonstrate that rare earth elements, particularly Tb, Eu and Er, act as key tracers of the geographical origin of Amazonian timber. Their discriminatory potential, confirmed by Random Forest and decision tree models with accuracies up to 100%, highlights the value of REE-based elemental signatures as a robust forensic tool to strengthen traceability systems and support the enforcement of regulations in the forestry and wood industries.

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ARSENIC CONTENT IN BREAST MILK OF NURSING MOTHERS FROM CEARÁ-BRAZIL: A PRELIMINARY STUDY

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Human milk is the best food for newborns, containing all the necessary nutrients for the development of infants [1]. However, its composition can be influenced by maternal exposure to environmental contaminants, including toxic elements. Arsenic (As) is one of the most persistent toxic substances, to which humans are exposed primarily through water and food[2]. In the case of newborns, exposure to this element can occur through breast milk, which is concerning due to the adverse effects on infant development. Despite the relevance of the topic, data on the presence of As in human milk are still scarce in both the international and Brazilian literature. However, some few studies have revealed the presence of As species in breast milk samples. Additionally, there are data that showed the absorption and transfer of arsenic species from food to breast milk[3]. In this context, the objective of this study is to present preliminary data on the determination of As in breast milk samples from a human milk bank in the state from Ceará-Brazil. This study was approved by the Ethics Committee of State University of Ceara (Nº88400725.9.0000.5534). This is an observational, cross-sectional study conducted with a subsample of six human milk donations provided by a referral hospital in the state. To determine total As, 1.0 mL of the sample was decomposed in a microwave oven (Multiwave 3000) using 3.0 mL of nitric acid (HNO_3), 3 mL of H_2O, 2 mL of hydrogen peroxide (H_2O_2), and subsequently, the total As content was analysed by inductively coupled plasma mass spectrometry (ICP-MS). The As levels found in the samples ranged from 4.60 to 6.14 μg kg^{-1}.

Table 1. Concentration of arsenic in breast milk samples.

Sample	Concentration (μg kg-1) (Mean ±SD, n=3)	RSD%	Sample	Concentration (μg kg-1) (Mean ±SD, n=3)	RSD%
S1	4.73 ± 0.04	0.77	S4	4.60 ± 0.49	10.71
S2	4.67 ± 0.40	8.52	S5	5.04 ± 0.43	8.45
S3	6.14 ± 0.32	5.22	S6	4.74 ± 0.18	3.83

The levels found in this study were higher than those previously described in the literature (0.30 – 4.46 μg kg^{-1})[3]. These values may be associated with a higher consumption of seafood, which are the main sources of As in diets, along with rice. As a perspective, this project aims to analyze not only As in more breast milk samples, but also to investigate the As species present focusing on the toxic ones, such as inorganic As and arsenolipids. This study presents new and unexplored data for public health, being the first national study focused on the quantification of As in human milk.

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Quantification of Nb, Fe, Si and Ti in columbite enriched ore samples by LIBS

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Columbite ore is a raw material that has been gaining prominence in Brazilian mineral production. It is source of niobium, tantalum, iron, manganese, silicium, titanium, aluminum and other rare earth elements. Northern Brazil is rich on Fe-columbite ($(Fe,Mn)(Nb)_2O_6$) [1,2] in which niobium and iron are extracted in the form of the ferroniobium alloy, which is widely employed in automotive engineering and civil construction[3]. Due to the economic importance of this raw material, quality control is essential. The determination of elemental contents is usually performed by conventional analytical methods, such as inductively coupled plasma optical emission spectrometry (ICP OES), which requires tedious and time-consuming sample preparation. In this context, Laser-Induced Breakdown Spectroscopy (LIBS) emerges as an attractive tool that enables rapid, direct, and multi-elemental analysis [4]. However, matrix effects remain a major challenge for this technique. Fusing the samples into glass beads is a widely used strategy to overcome such effects, since this process reorganizes the matrix and makes the analytes more accessible to the laser [5,6].

This study aimed to develop a method for determining the contents of Nb, Fe, Si, and Ti in glass fused beads samples of columbite-enriched ore by LIBS, using external calibration obtained by using fused glass beads with proportions varying from 1:2 to 1:7 of standard: flux mixture of lithium tetraborate and lithium metaborate (66–34%). For this approach, 4 samples were prepared in the ratio of 1:3 (sample:flux). The measurements were done at the following LIBS instrumental parameters were used: spot size = 65 µm, delay time = 0.5 µs, laser energy = 20 mJ, Ar flow rate = 1 L min^{-1}, and number of pulses = 500. Calibration curves were obtained with R^2 values of 0.97848, 0.99318, 0.99932, and 0.98835 for Nb, Fe, Si, and Ti, respectively. For Nb and Si, it was possible to successfully quantify all samples, whereas for Fe and Ti, 3 and 2 samples could be quantified, respectively. The accuracy ranged from 84–94% for Nb, 86–99% for Fe, 86–96% for Si, and 93–97% for Ti. Limits of detection (LOD) and limits of quantification (LOQ) were determined according to IUPAC guidelines by doing ten measurements in a flux fused glass bead. LOD: 0.04, 0.01, 0.05 and 0.003% for Nb, Fe, Si and Ti. LOQ:0.1, 0.05, 0.2 and 0.01% for Nb, Fe, Si and Ti. Internal standards of Li and B were evaluated but represented in a critical reduction of accuracy.

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Long-term stability study by ICP-MS of tomato leaves reference material

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Metrological traceability plays a fundamental role in analytical chemistry, ensuring reliability and comparability of measurement results, essential aspects in areas such as food safety, environmental control and public health. In this context, certified reference materials (CRMs) occupy a central position in quality systems of analytical laboratories, being used from instrument calibration to method validation, contributing significantly to the precision and accuracy of analyses[1]. The CRM characteristics such as homogeneity and stability become particularly relevant, as they directly impact reliability over time and viability of continued use in laboratory routines. CRMs are mostly produced by renowned institutes located primarily in Europe and North America, making their acquisition relatively expensive. There is a significant shortage of reference materials for the agricultural sector in Brazil, which often requires importing these materials, at high costs hindering access for national laboratories. The Collaborative Center for Agricultural Defense funded by National Council for Scientific and Technological Development and Ministry of Agriculture, Livestock and Food Supply (CNPq – MAPA) was created in 2009 to produce national reference materials and organize interlaboratory comparisons. In 2012, the CRM-Agro – Reference Materials for Agriculture, Livestock, and Toxicology (CRM-Agro) produced the CRM-Agro C1003a – Tomato Leaves with plants of the sweet grape variety, grown in greenhouse at the Luiz de Queiroz College of Agriculture (ESALQ-USP). From the batch of 196 bottles containing 35 g, 10 bottles were randomly selected and kept since production under the following conditions: 7 bottles protected from light at temperature and humidity of 20-23°C and 40-60%, respectively, and 3 bottles in a freezer at -22°C (control bottles). In 2025, as part of the process of evaluating the long-term stability, 200 mg aliquots were taken from each of the 10 bottles, in triplicate. The samples were subjected to a microwave-assisted acidic digestion procedure using HNO_3 and H_2O_2 in a closed system at 200°C and 1800 W power. For analytical quality control, the certified reference materials NIST-SRM 1515 Apple Leaves, NIST-SRM 1573a Tomato Leaves and CRM-Agro C1004a Tomato Pulp were used. The chemical elements As, Br, Ca, Cd, Ce, Co, Cu, Eu, Fe, K, La, Mg, Mn, Na, Ni, P, Pb, Rb, and Sr were determined by triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS). The mass fraction of the chemical elements in the bottles stored at 20-23°C were consistent with those obtained in the control bottles kept at -22°C, with recoveries ranging from 80-114% for all chemical elements. Nonparametric ANOVA (Kruskal-Wallis) was used to analyze the data. According to the results obtained thirteen years after its production, the CRM-Agro C1003a – Tomato Leaves remains suitable for use in analytical quality control.

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Multi-element analysis of bovine liver using ICP-MS and MP AES

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Sample preparation is a crucial step in chemical analysis, particularly for complex biological matrices. In conventional acid digestion methods, the excessive use of reagents increases costs, occupational hazards, environmental impacts, and analytical blank values[1]. Therefore, the development of more efficient and sustainable protocols is essential to ensure accurate and reliable results, in line with the principles of green chemistry. In this study, different microwave assisted acid digestion methods were compared for bovine liver, simultaneously evaluating their analytical performance and sustainability. Analytical portions of 250 mg of the certified reference material CRM-Agro E3001a Bovine Liver were weighed into PTFE vials and digested in a microwave system at 180 °C and 1600 W for 25 min, using three different protocols: (A) 6 mL HNO_3 (12 mol L^{-1}) + 2 mL H_2O_2 (30% w/w); (B) 7 mL HNO_3 (9 mol L^{-1}) + 1 mL H_2O_2 (30% w/w); (C) 7 mL HNO_3 (4.5 mol L^{-1}) + 1 mL H_2O_2 (30% w/w). For analytical quality control, the certified reference materials SRM 1577c Bovine Liver and RM 8414 Bovine Muscle Powder were analyzed. The determination of Ca, Cd, Co, Cs, Cu, Fe, Mn, Mo, Rb, Se, Sr and Zn was performed using triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS), while K, Mg, Na and P were determined by microwave plasma atomic emission spectroscopy (MP AES). Relative standard deviations (RSDs) were below 5% for all elements, demonstrating high precision. Accuracy was confirmed by recoveries ranging from 89–119% for SRM 1577c and 79–115% for RM 8414. All three digestion methods proved effective for elemental quantification; however, the method with the lowest acid consumption stood out for its environmental benefits. Sustainability was assessed using the Analytical Eco-Scale[2], considering reagent use, energy consumption, waste generation, and occupational hazards. Method C, which employs fewer aggressive reagents, achieved the highest score (84) and is recommended from a sustainable analytical chemistry perspective. Overall, microwave-assisted acid digestion protocols provided high precision and accuracy in bovine liver analysis, with Method C offering equivalent performance while being more environmentally friendly, thus representing the best option from a green analytical chemistry standpoint.

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HYDROGEN PEROXIDE AS A GREENER ALTERNATIVE FOR MICROWAVE-ASSISTED DIGESTION OF HIGH-ORGANIC-MATTER SAMPLES

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Since the 1990s, green chemistry has become increasingly important in the planning and execution of experiments in laboratories worldwide.[1] In multielemental analysis using Inductively Coupled Plasma (ICP), where sample digestion is often required, a common trend has been the use of diluted acids (1–5 mol L^{-1}) combined with auxiliary reagents such as oxygen (O_2) or hydrogen peroxide (H_2O_2).[2] Acid-free sample digestion with H_2O_2, which is a greener alternative to acid-based digestion, remains relatively unexplored in the literature, even though it can provide results comparable to those obtained with diluted acid digestion.[3]

In this context, the present work aimed to investigate this promising approach. For that purpose, 100 mg of various complex-matrix samples containing different amounts of organic matter (OM), including lettuce and pine needles, the latter with as much as 98.1% OM[4], were digested with 3 mL of 30% (m/m) H_2O_2 in a microwave oven for 30 minutes (15 minutes heating, followed by 15 minutes at a constant maximum temperature of 220 ºC). After digestion, the solutions appeared clear (Fig. 1).

To evaluate digestion efficiency, the Residual Carbon Content (RCC), a widely used parameter in this context[2], was determined by ICP OES. For pine needles, the mean RCC was 0.268 ± 0.004%, while for lettuce, the residual dissolved organic carbon concentration was 4.24 ± 0.06 g L^{-1}, which is below the 8 g L^{-1} threshold known to prevent spectral interferences in ICP techniques.[5] Further optimizations will be carried out for each sample type, and the results will be discussed.

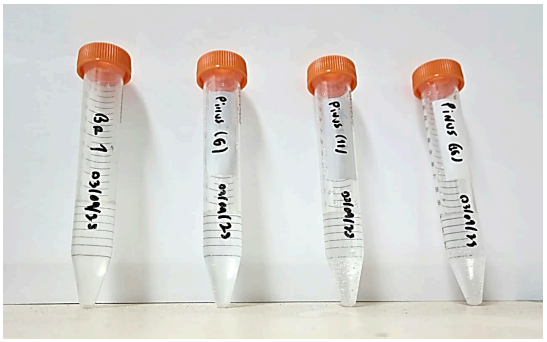

Figure 1. Photo of the solutions after sample decomposition through microwave assisted using 100 mg pine needle replicates and 3 mL of 30% (m/m) H_2O_2.

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Selenium nanoparticles synthesis and characterization by sp-ICP-MS

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Selenium is an essential trace element for humans, involved in various biochemical processes. Dietary intake, the primary source of this nutrient for humans, is variable, with its concentration in food changing according to the region of cultivation [1]. This may lead to selenium deficiency, which is associated with myocardial infarction, impaired nervous system function, and Alzheimer's disease [2]. Consequently, biofortification emerges as an alternative for nutritional supplementation. Selenium nanoparticles (SeNPs) represent an alternative selenium source compared to selenium salts, due to their properties and biocompatibility [3]. In this study, selenium nanoparticles were synthesized via two distinct methods and characterized using single particle-ICP-MS (sp-ICP-MS), dynamic light scattering (DLS), and transmission electron microscopy (TEM). In the first method, sodium selenite was mixed with 0.01 % chitosan in 4 % acetic acid (1:1), followed by a dropwise addition of ascorbic acid for the formation of ChSeNPs. Using this same method, SeNPs were also synthesized without the addition of chitosan, resulting in uncoated SeNPs. In the second method, sodium selenite was mixed with bovine serum albumin (BSA) and L-Glutathione reduced, followed by the dropwise addition of NaOH 1 mol L^{-1} until a color change was observed, resulting in the formation of BSASeNPs. These nanoparticles were washed three times with ultrapure water and analyzed by UV-Vis spectrophotometry to confirm SeNP formation, by DLS for zeta potential (ζ) determination, TEM for particle size, and sp-ICP-MS to determine particle size and concentration. The NPs synthesized via both methods exhibited a characteristic peak between 240 and 270 nm in the UV-Vis spectrum, confirming SeNPs formation. The uncoated SeNPs aggregated and precipitated, demonstrating no stability in solution, with a ζ of 11.0 ± 1.5 mV and aggregation and non-spherical morphologies, as observed by TEM. In contrast, both ChSeNPs and BSASeNPs exhibited stability in aqueous solution, with ζ of -15.2 ± 2.7 mV and -17.1 ± 1.0 mV, respectively. For the sp-ICP-MS analysis of ChSeNPs, a sample flow rate of 0.247 mL min^{-1}, a transport efficiency (TE) of 1.49 %, a dwell time of 50 µs, and an AFT of 475 V were employed. Helium was also used as a collision gas at a flow rate of 2 mL/min. An analytical curve of dissolved selenium was prepared, achieving a coefficient of determination of 0.998. The ChSeNPs exhibited a hydrodynamic diameter (*Dh*) of 393 nm by DLS, whereas the TEM diameter was 129 nm, a value which is proximate to the average size 110 nm obtained by sp-ICP-MS. These samples presented a concentration of 1.8 x 10^8 particles mL^{-1}. The BSASeNPs showed a *Dh* of 43.9 nm immediately after synthesis, which increased to 73.2 nm after 40 days (DLS), indicating particle aggregation. This finding was corroborated by sp-ICP-MS analysis after 63 days, which revealed a particle size of 89 nm and a concentration of 8.9 x 10^8 parts mL^{-1}, with a size detection limit (LOD) of 30 nm. On the other hand, sp-ICP-MS analysis of the uncoated samples demonstrated a broadly defined size distribution for the SeNPs, consistent with nanoparticle aggregation. Therefore, the application of surface coating is essential for stabilizing the material and achieving size uniformity. Post-synthesis aggregation is a process that hinders the material's application, requiring further studies to evaluate its long-term stability. It is critically important to control and adjust experimental conditions, in addition to meticulous nanoparticle characterization, to prevent the misidentification of double events in sp-ICP-MS analysis. Further investigations are required to better understand the synthesized selenium nanoparticles, which are intended for future application in plant biofortification.

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EXPLORING PO MOLECULAR SIGNATURES VIA SD-LIBS: A NEW FRONTIER FOR PHOSPHORUS SPECIATION ANALYSIS

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Laser-Induced Breakdown Spectroscopy (LIBS) has emerged as a versatile and powerful analytical technique for direct, rapid, and multielemental determinations without the generation of chemical waste. In addition to atomic emissions, LIBS also enables the detection of diatomic molecular emissions, which significantly broadens its analytical capabilities. In this context, molecules such as C_2, CN, CH, NH, and OH[1] have been extensively investigated in a wide range of applications, including forensic science, clinical diagnostics, environmental monitoring, food quality control, among others. When these molecular emissions arise from the incomplete fragmentation of organic compounds within the sample, the resulting spectrum may serve as a molecular fingerprint, enhancing the potential of LIBS for the characterization of complex matrices. Considering this capability, the detection of new molecular species further expands the applicability of the technique. Among such species, the PO diatomic molecule stands out, as it is traditionally monitored by high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS)[2] but remains unexplored using LIBS. Detecting PO via LIBS represents a strategic advancement, particularly for phosphorus speciation studies. This study presents a pioneering investigation exploring the potential of LIBS for the detection of PO molecular bands. For the proof-of-concept experiments, sodium, potassium, and calcium phosphates were analyzed. Three pellets were prepared for each salt, and 20 single-shot spectra were acquired per pellet to generate an average spectrum. The measurements were performed using an SD-LIBS system (LIBS coupled with an electric discharge device) to enhance sensitivity. To ensure controlled conditions, analyses were initially carried out under a continuous argon flow. Average spectra were analyzed qualitatively using HR-CS-AAS literature as a reference. To optimize PO detection, the effects of three instrumental parameters were evaluated: (i) argon flow rate, (ii) discharge voltage, and (iii) Q-switch delay. For the first time, our findings reveal the feasibility of SD-LIBS for detecting the PO diatomic molecule, opening new perspectives for molecular spectroscopy using LIBS and contributing to the development of advanced strategies for phosphorus speciation.

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PORTABLE LIBS: AN APPROACH FOR THE DETERMINATION OF LABILE PHOSPHORUS IN SOILS

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Phosphorus in soils occurs in different fractions, with labile representing the fraction readily available for plant uptake (P_{labile}), whereas most P remains strongly bound to soil minerals such as Fe, Ca, and Al ($P_{non\text{-}labile}$)[1]. Proper P management is crucial to avoid yield losses due to nutrient deficiency, while excessive fertilization is economically unfeasible and may lead to significant environmental impacts[2]. Therefore, accurate monitoring of P_{labile} is essential to support precision fertilization strategies and sustainable agricultural management. Conventional methods for P_{labile} determination, although widely used, rely on labor-intensive chemical extractions, require hazardous reagents, and generate analytical residues, making them time-consuming and costly. Laser-Induced Breakdown Spectroscopy (LIBS) emerges as a promising alternative, enabling rapid, direct, and multielement analysis without chemical waste. Recent technological advances have introduced portable LIBS systems (hLIBS), extending the applicability of the technique to in-field measurements and precision agriculture. In this study, the performance of a hLIBS system was evaluated for quantitative determination of P_{labile} in 60 soil samples with contrasting textures and P contents. Samples were homogenized, pressed into pellets, and analyzed using a SciAps Z-903 hLIBS. Spectra were normalized using the Ar II line at 349.05 nm and divided into calibration (42 samples) and validation (18 samples) sets. Selected input variables included P atomic lines (213.60, 253.69, 255.34 nm), a PO molecular band (247.46 nm), and Fe lines (315.87, 317.91, 393.28, 393.42, 396.76, 396.90 nm). A partial least squares (PLS) calibration model with centered preprocessing and eight latent variables achieved robust predictive performance (Rcal = 0.71), with validation results showing Rcal = 0.70 and a mean absolute error (MAE) of 20 mg/dm³ P. Considering the accuracy required for decision-making in agricultural management, these results highlight the potential of hLIBS as a simple, fast, clean, and portable tool for P_{labile} monitoring, enabling immediate and reliable on-site assessments.

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Interaction of biogenic CuNPs with soybean calli: multielement quantification based on Plasma Techniques

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Nanotechnology applied to agriculture has explored metallic nanoparticles as inputs for controlled release with lower environmental impact compared to conventional salts.[1] Among these, biogenic copper nanoparticles (CuNPs), obtained via green synthesis and stabilized by biomolecules from soybean (Glycine max) callus tissues, stand out for their potential to modulate plant nutrition, reducing phytotoxicity and leaching losses.[2] Callus cultures provide a reproducible model to study the uptake, translocation, and effects of nutrients on nutrient homeostasis under controlled conditions.[3] This study investigates the introduction of CuNPs (~10 nm) into soybean callus and their effects on macro- and micronutrient balance. The calli were exposed to a suspension of 1000 µg L^{-1} for 21 days in sterile medium; subsequently, the samples were subjected to microwave-assisted digestion in a closed container (H_2O_2). Macroelements (P, K, Ca, Mg, and S) were quantified by ICPOES, while trace elements (Fe, Mn, Zn, Cu, and Mo) were determined by ICP-MS. A marked increase in the concentrations of the nutrients Ca, K, P, S, Zn, and Mo, which play important roles in cell growth, membrane stabilization, osmotic regulation, and antioxidant defense, was observed. This pattern of nutrient accumulation suggests the activation of adaptation and defense mechanisms in response to stress induced by nanoparticle exposure. In contrast to the previously observed increases, a significant reduction in the levels of Mg, Mn, Fe, and Cu was detected (see Table 1). This decrease can be attributed to competitive interactions in ion transport, as Cu, Fe, and Mn utilize similar uptake pathways. Furthermore, mechanisms such as intracellular sequestration and active exclusion may have been activated to mitigate the accumulation of potentially toxic metals. These results demonstrate that treatment with CuNPs induces a disruption in the ionic homeostasis of calluses, triggering metabolic adjustments that prioritize the uptake of essential nutrients for maintaining cellular integrity and mounting an effective stress response.

Table 1. Comparative nutrient levels in soybean callus (Control vs CuNPs treatment)

Element	*Control (µg g^{-1})*	*CuNPs (µg g^{-1})*
Ca	210	270
K	720	860
S	780	930
Mn	390	310
Mg	330	220
P	240	330
Zn	560	620
Mo	13	18
Fe	3700	1000

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Analysis of the macro and micronutrient content in different mushroom species farmed in Ceara State

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Mushrooms are fungi that have quantities significantly of minerals and a great dietary impact therefore, this study sought to quantify the content of Al, As, B, Ca, Cu, Fe, K, Mg, Mn, P in samples of four different species of mushrooms usually used in diets by spectrophotometry methods to measure their dietary impacts and possible contamination. The species of mushroom: Shimeji (*Hypsizygus marmoreus*), Shitake *(Lentinula edodes),* Paris (*Agaricus bisporus) and Portobello (Agaricus bisporus)* has cultivated in municipality of Guaramiranga (4° 15′ 46″ S, 38° 55′ 58″ O) and purchased in a supermarket in Fortaleza City. Part of the samples were freeze-dried and another part was dried, before being milled and decomposed in a microwave-cavity oven using around 0.250 mg of sample, 2 mL of 60% m m^{-1} HNO_3, and 2 mL of 30% m m^{-1} H_2O_2. After this, the mixture was diluted and analyzed by ICP-OES. The results obtained were compared with the RDI (recommended daily intake) values determined by RDC No. 269/2005[1] and UL (Tolerable Upper Intake Level) values defined by the Institute of Medicine (2001, 2011), and ANVISA (BRAZIL, 2005)[1]. In addition, mushroom species were classified as sources or rich in minerals according to RDC No. 54/2012[2], whereby shimeji was considered a source of Mn and rich in Cu, Fe, Mg, and Zn, in addition to supplying the RDI of P, Se, and Zn. Shitake mushrooms were even more impressive, being classified as rich in Cu, Fe, Mg, Mn, P, Se, and Zn, with P, Se, and Zn reaching or exceeding the RDI. The Paris mushroom was classified as a source of Mn and rich in Cu, Fe, Mg, P, Se, and Zn, exceeding the RDI for P, Se, and Zn; however, it was observed that the Se content exceeded the tolerable upper limit (UL). Portobello mushrooms were classified as rich in Mn, Mg, Se, and Zn, with P and Se also exceeding the RDI, the latter exceeding the UL.

Table 1. Amounts (mg kg^{-1}) of minerals in mushroom samples analyzed by ICP-OES (Mean ± SD, n = 3)

Element	Shimeji	Shitake	Paris	Portobelo
Al	15.4 ± 0.17	9.46 ± 0.55	39.7 ± 1.8	20.2 ± 2.4
As	0.28 ± 0.02	0.147 ± 0.01	0.098 ± 0.01	0.237 ± 0.001
B	2.98 ± 0.13	14.9 ± 1.0	55.7 ± 0.3	14.4 ± 0.2
Ca	56.1 ± 2.4	126 ± 5	420 ± 4	198 ± 18
Cu	11.3 ± 0.1	7.08 ± 0.01	30.8 ± 0.9	0.467 ± 0.05
Fe	118 ± 10	97.5 ± 10.2	51.8 ± 1.7	42.2 ± 2.64
K	1074 ± 15	1033 ± 8	2101 ± 8	1796 ± 3
Mg	1293 ± 7	1284 ± 5	1300 ± 13	1185 ± 11
Mn	6.83 ± 0.50	21.4 ± 0.26	6.75 ± 0.04	7.22 ± 0.41
P	7711± 40	9142 ± 18	12475 ± 32	12823 ± 25
Se	0.712 ± 0.02	0.615 ± 0.09	4.03 ± 0.16	3.02 ± 0.18
Zn	63.2 ± 5.4	106 ± 1	57.0 ± 1.5	57.2 ± 0.3

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Alginate spheres applied in metal extraction via DPX for subsequent determination by ICP-MS

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In recent decades, population growth and industrial development have intensified aquatic pollution, including metals such as Pb, Cd, and Cr which, even at low concentrations, can present high toxicity, demanding sensitive analytical methods.[1] In this context, inductively coupled plasma mass spectrometry (ICP-MS) stands out due to its high sensitivity and multielemental analysis capability, being an excellent technique for environmental analysis and applications in competitive adsorption processes.[2] Among natural adsorbents, alginate is noticeable for its abundance, low cost, and presence of active functional groups.[3] In this work, the adsorption of Al, Ba, Cd, Co, Cr, Cu, Ni, Pb, and Zn onto alginate spheres for subsequent application in disposable pipette extraction (DPX) and determination of analytes by ICP-MS was evaluated. Alginate spheres were prepared by dripping a 2% (m v^{-1}) sodium alginate solution into a 2% (m v^{-1}) $CaCl_2$ solution. The adsorption pH (2-7) was also evaluated, and kinetic (10–1440 min, at 300 rpm) and equilibrium studies (25-300 mg of adsorbent) were carried out and fitted to pseudo-first-order and pseudo-second-order models (kinetics), as well as Langmuir and Freundlich models (equilibrium). For DPX extraction, a 3D-printed filter was developed for direct coupling to disposable tips. Optimization of the extraction and desorption process was performed in aqueous solution and in a multivariate way using a Doehlert design, monitoring analyte concentrations by ICP-MS. The alginate spheres (4 mm) were characterized by FTIR, confirming the presence of carboxylic and hydroxyl groups and, after extraction, their interaction with the analytes. The suitable pH for the experiments was pH 3.0. Kinetic studies indicated that adsorption follows a pseudo-second-order model, which provided excellent fitting for all metals (R^2 0.959–0.999), with higher adsorption capacities for Pb, Cu, and Cd, whereas Co^{2+} and Ni^{2+} showed the lowest adsorption capacities. Freundlich isotherms fitted the data better, confirming strong competitive adsorption, and highlighted that Cu, Co, and Ni presented high K_f values (>180 mg g^{-1}). The Doehlert design indicated that 50 mg of alginate and eight extraction cycles with 3 mL of sample provide good extraction efficiency. The developed filters for DPX proved to be suitable, low-cost and efficient for applications using alginate spheres as adsorbents. Experimental data fitted satisfactorily to the proposed model (adjusted R^2 = 0.6802). Desorption of the analytes was carried out with 0.2 mL of 5% v v^{-1}nitric acid solution and four desorption cycles. Calibration curves obtained with multielement solution and DPX extraction under optimized experimental conditions were constructed in the concentration range of 0.05–30 µg L^{-1} and presented R^2 ranging from 0.9921 to 0.9999. The obtained figures of merit indicated RSD < 10%, LODs in the ng L^{-1} range, suitable for applications of the proposed procedure in environmental samples. The results demonstrate the potential of alginate spheres for the extraction of metals from aqueous solutions. The 3D-printed filters developed for DPX are simple and low-cost compared to commercial DPX devices. The proposed method for metal determination combines the simplicity and efficiency of analyte extraction in alginate spheres with the low cost of a DPX procedure and the multielemental capability and low detection limits of ICP-MS.

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BIOACCESSIBILITY OF ESSENTIAL AND NON-ESSENTIAL ELEMENTS IN MEAT AND PLANT-BASED MEAT ANALOGUES

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Meat production is associated with significant environmental and public health challenges. Agriculture and farming are two of the main sources of greenhouse gas emissions, including methane and nitrous oxide. They also contribute to deforestation, biodiversity loss, and excessive water usage.[1] Due to changes in consumption habits, population growth, and growing environmental and public health concerns, plant-based meat analogues (PBMA) have attracted international attention. These products are considered more ethical and sustainable alternatives to animal-based foods.[2,3] A complete nutritional assessment requires determining the total concentration of essential and non-essential elements, as well as their bioaccessibility. It is essential to understand the amount of nutrients available for absorption by the body after digestion, which is determined by bioaccessibility. Bioaccessibility, along with bioavailability, provides more accurate information about the true nutritional impact of food components. It also shows how the presence of anti-nutritional compounds, such as fibers and phytates, and the chemical form of elements can affect absorption directly.[4] This study aimed to evaluate the bioaccessibility of essential and nonessential elements in tuna, ground beef, and chicken, as well as in their corresponding PBMA. The INFOGEST 2.0 in vitro digestion method was used for this purpose. This internationally recognized protocol simulates the oral, gastric, and intestinal phases of the human digestive system.[5] Inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) were used to quantify elements in soluble (bioaccessible) and insoluble (non-bioaccessible) fractions. The significant presence of certain elements, such as C, Ca, K, Mg, Na, P, and S, as well as the complex solution obtained after the in vitro digestion method (which is rich in salts and enzymes), can cause significant interferences in the determination step. Therefore, a study of interferences in the ICP-MS technique was carried out. This study makes possible to determine the optimal parameters for elements quantification and to identify the minimum dilution factor for INFOGEST 2.0 solutions to minimize interferences. While animal-based meats tend to have higher overall levels of Fe and Zn, the bioaccessibility of these minerals, as well as Ca, Mg, K, and P, was generally higher in PBMA samples. This fact can be attributed to the use of soluble mineral salts to fortify plant-based products, which facilitate the release of elements during simulated digestion. The presence of antinutritional compounds, which typically limit mineral bioavailability in plant-based products, appears as mitigated by industrial processing and fortification. Plant-based samples also contain nonessential elements, including Al, B, Ba, Cd, Ni, Sr, and Ti. This study allowed a detailed assessment of the elemental composition and bioaccessibility of essential and non-essential elements in animal meats and their PBMA. The use of the INFOGEST 2.0 protocol combined with ICP-OES and ICP-MS techniques proved to be an effective method for analyzing the bioaccessibility of elements at both high and low concentration in complex food materials. This method provided fundamental information for understanding the nutritional quality of these food matrices.

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ICP Spectrometric Study of Macro- and Micronutrient Homeostasis in Soybean Cultivated with Gold Nanoparticles

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Inductively coupled plasma (ICP) based techniques are powerful tools for investigating plant ionomics[1], enabling the simultaneous and sensitive determination of essential macro- and micronutrients. In this study, ICP OES and ICP-MS were employed to assess the effect of gold nanoparticles (AuNPs) on nutrient homeostasis in soybean plants. Seedlings were cultivated under controlled photoperiod and temperature conditions[2], and two treatments were carried out: control (without AuNPs) and AuNPs (100 μg L^{-1}). The ionomic profile of soybean plants was obtained for macronutrients (Ca, Mg, and S), micronutrients (B, Cu, Fe, Mn, and Zn), and Au. The results showed that Au was detected in roots (1.7 mg kg^{-1}), with no translocation to aerial tissues. Additionally, ICP analysis revealed significant changes in nutrient distribution, regarding macronutrients Mg increased by 52% in roots, while Ca and S remained stable. Conversely, Fe concentration increased by 17% in roots, whereas Zn, Cu, and Mn decreased in stems and roots. Complementary physiological evaluations demonstrated that AuNP exposure enhanced root branching and elongation, leading to increased fresh biomass (24% in leaves, 20% in stems, and 33% in roots), without visible tissue damage. Principal component analysis (PCA) (Figure 1), obtained from the ICP dataset, confirmed distinct separation between treatments. Finally, ionomic analysis using ICP techniques revealed how AuNP-induced alterations in macro- and micronutrient homeostasis of soybean plants. These findings reinforce the relevance of spectrometric approaches to advance understanding of effects and plant-nanomaterial interactions.

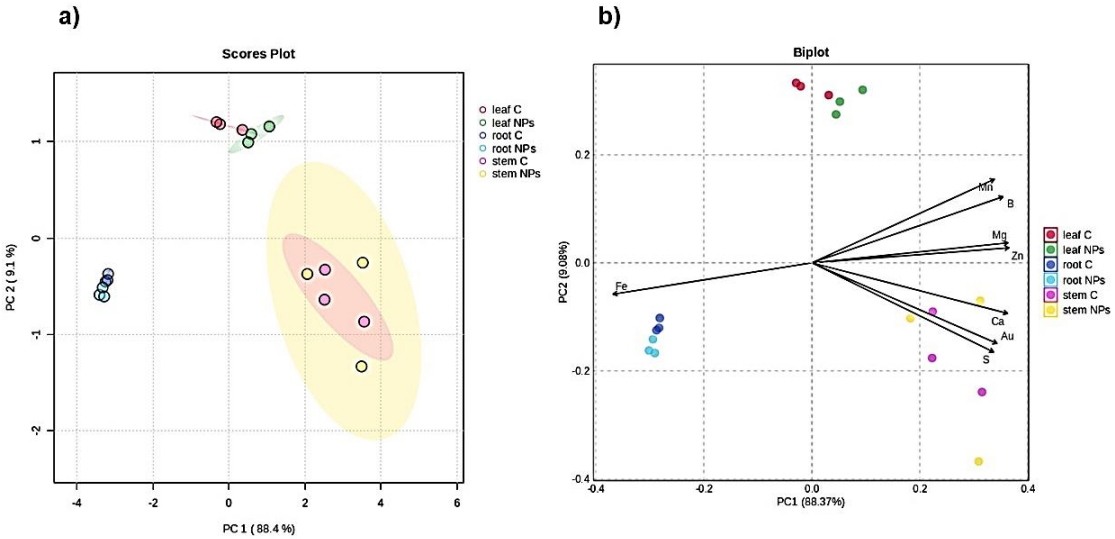

Figure 1. PCA of control vs. AuNPs-treated soybean compartments (leaf, stem, root), using macro (Ca, Mg, S), micro (B, Cu, Fe, Zn, Mn), and Au variables. Score plot (a) and loading plot (b)

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Enrichment of toxic elements in degraded plastic straws from the coastal marine environment with vegetation, Espírito Santo, Brazil

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Plastics are composed of polymers and intentionally added substances (IAS), such as additives, as well as non-intentionally added substances (NIAS), such as catalyst residues or monomers that did not completely react during the polymerization process. This composition provides plastics with a wide range of properties, contributing to their extensive application in the automotive, construction, healthcare, agriculture, and packaging sectors.[1] However, the excessive production and application of plastics, combined with inadequate solid waste management, especially of single-use items such as straws, bags, and packaging, have resulted in the presence of these materials in different ecosystems. In the environment, plastics undergo degradation processes that alter their physicochemical properties, intensifying the leaching of additives containing numerous toxic chemical elements (As, Cd, Co, Cr, Pb) due to the rupture of the polymer chain, as well as pores and cracks, which increase the surface area available for interaction with the medium. On the other hand, degradation processes can form oxygenated functional groups on the surface of plastics, which increase charge, hydrophilicity, and polarity and affect interactions with pollutants in the surrounding environment, including chemical elements.[2,3] In view of this, this study aimed to quantify Al, Ba, Cd, Co, Cr, Pb, Ti, and Zn in degraded plastic straws and compare the results with virgin samples. For this work, samples of visibly degraded plastic straws were collected in restinga areas, from six beaches located in Vila Velha and three beaches located in Vitória, Espírito Santo, Brazil. The samples were characterized as polypropylene by Fourier-transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR), and bands were observed in the region between 1650–1850 cm^{-1}, characteristic of carbonyl groups, and bands in the area between 3200–3600 cm^{-1}, attributed to hydroxyl groups, indicating that the straws were undergoing degradation. Morphological characterization by scanning electron microscopy (SEM) was also carried out, and showed that degraded straws have several cracks and fractures on the surface, while virgin straws have a smooth surface. Subsequently, the samples were digested with 4.0 mL of HNO_3 (68% m m^{-1}), 1.0 mL of HCl (37% m m^{-1}), and 0.2 mL of H_2O_2 (30% v v^{-1}) in a microwave radiation oven. The analytes were determined by inductively coupled plasma mass spectrometry (ICP-MS) with He as collision gas. Analytical performance parameters were assessed. Calibration curves showed coefficients of determination greater than 0.999 for all analytes. To verify the accuracy of the method, the certified reference material ERM-EC680m was used, and the agreement values ranged from 90 to 107% for Al and from 80 to 110% for the other analytes. The concentrations obtained for degraded straws were high, especially for Pb, which ranged from (35 ± 1) µg g^{-1} to (245 ± 59) µg g^{-1}. In contrast, for virgin straws, Pb was quantified only in one white sample, with a value of (0.210 ± 0.016) µg g^{-1}. These results suggest that degradation favors the increase in elemental concentrations due to the greater capacity for interaction between degraded plastics and chemical contaminants.

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Single-event analysis of discrete entities using microwave-induced nitrogen plasma–mass spectrometry

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ICP-MS has become a standard for (ultra)trace elemental analysis due to its excellent sensitivity and multi-element capabilities. However, its widespread use is hampered by spectral interferences—especially in the low mass range (<81 amu)—primarily arising from Ar-based polyatomic ions, such as ArO^+ and Ar_2^+, which compromise the accurate quantification of key elements like Fe and Se.[1] Over the years, improvements such as collision/reaction cells and sector-field configurations have helped mitigate these interferences, albeit often at the cost of instrument complexity and increased operational burden.The microwave-induced nitrogen plasma (MINP) source, sustained by microwaves at atmospheric pressure and using nitrogen as the plasma gas, offers a fundamentally different plasma environment. Nitrogen is not only more economical (40-60%) and readily available than Ar, but also avoids the generation of problematic Ar-based interferences. While MINP had been previously applied in optical emission and bulk mass spectrometry,[2] its implementation in single-event detection had not yet been demonstrated.

This study pioneers the application of MINP-MS in single-event mode for real-time, high-throughput characterization of NPs, cells, and MPs. The evaluation began with Fe_2O_3 NPs monitoring the ^{56}Fe nuclide, with a limit of detection of 8.6 ag for Fe, equivalent to a particle size threshold of 19 nm—surpassing the detection capabilities of quadrupole-based ICP-MS systems. Size distribution results obtained by SP-MINP-MS for Fe_2O_3 NPs (20–70 nm) matched closely with transmission electron microscopy (TEM) and dynamic light scattering (DLS), confirming the method's accuracy.

For Se, despite its high ionization energy, metallic SeNPs (150 and 250 nm) were reliably quantified by monitoring ^{80}Se. A calibration curve constructed using SeNP standards yielded excellent linearity ($R^2 = 0.9994$). This approach was further extended to single-cell analysis, using Se-enriched yeast (SELM-1 CRM) as a model. A transport efficiency-independent calibration strategy was employed, relying on SeNPs to determine Se content per cell. The results showed strong agreement with data from conventional SC-ICP-MS, with average Se masses of ~65 fg per cell, validating the performance of SC-MINP-MS for biological systems.

Additionally, the instrument's capability to handle large, low atomic number particles was demonstrated *via* the analysis of polystyrene (PS) and polytetrafluoroethylene (PTFE) MPs. These MPs (2.5–3.0 µm) were quantified by monitoring $^{12}C^+$ signals and applying a calibration strategy using citric acid as a standard. The resulting size distributions closely matched nominal sizes, reinforcing the system's robustness for micrometer-sized polymeric materials. Event durations ranging from 470 to over 900 µs were consistent with literature values for single-entity ICP-MS and correlated well with particle size.

These findings establish single-event MINP-MS as a promising analytical platform for analyzing discrete entities. It provides significant advantages over conventional Ar-based ICP-MS, including reduced interferences, lower operational cost, and comparable or superior sensitivity for analytes such as Fe and Se. By avoiding the limitations of Ar-based plasmas and enabling accurate quantification across a wide range of particle types and sizes, MINP-MS in single-event mode opens new avenues for high-resolution, interference-free elemental analysis at the individual entity level.

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RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY
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ASSESSMENT OF ELEMENTAL BIOACCESSIBILITY IN EDIBLE INSECTS USING PLASMA-BASED TECHNIQUES

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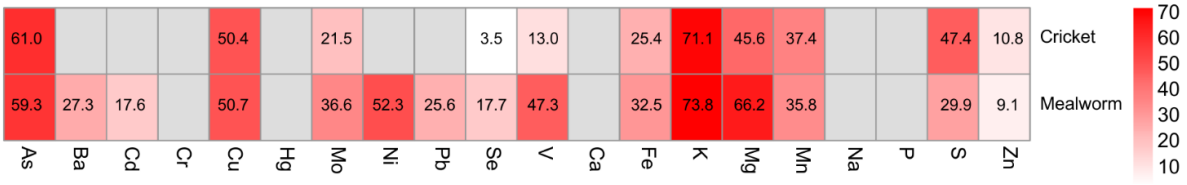
Edible insects have received growing attention as sustainable and innovative food sources due to their high nutrient content, lower demand for natural resources, and reduced environmental impact compared to conventional livestock [1,2]. However, their widespread adoption necessitates detailed knowledge of mineral composition and potential risks associated with toxic elements [3]. In this study, the total content and bioaccessible fraction of macro- and micronutrients were determined, as well as metallic contaminants, in *Acheta domesticus* (crickets) and *Tenebrio molitor* (mealworms). Dried samples were ground using a mortar and pestle, and subjected microwave-assisted digestion (MWAD) with diluted acid to determine the total concentration. The bioaccessibility was evaluated using an *in vitro* gastrointestinal procedure [4] under controlled temperature (37 ºC), which was, in short: i-) oral phase, involving 2.0g of the food sample plus amylase and a pool of inorganic salts at pH=7; ii-) gastric phase, which is done at pH=3 during 120 min using HCl, enzymes (mainly pepsin and mucin), other organic compounds (such as urea, glucose and albumin) and salts; iii-) intestinal phase, performed at pH=7 during 120 min using enzymes (mainly pancreatin, lipase, and bile extract), urea, albumin and salts. After centrifugation the supernatant is separated and mineralized using MWAD. The elemental analysis was performed using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma tandem mass spectrometry (ICP-MS/MS). Calibration curves exhibited excellent linearity ($R^2 > 0.99$) and low detection limits (0.04-120.4 ug/L for ICP OES and 2.7-437.9 ng/L ICP-MS). Method accuracy was confirmed using a certified reference material (TORT-3), with recoveries ranging from 95–105%. Results showed high levels of potassium and magnesium (7237.3-8774.3 mg/kg for K and 1022.4-1966.2 mg/kg for Mg) as the major components, while iron and zinc (53.8-66.6 mg/kg for Fe and 151.1-123.0 mg/kg for Zn) were the principal micronutrients. Toxic elements, including arsenic, cadmium, lead, and mercury, were detected at low concentrations, with mercury frequently below the limit of quantification. Bioaccessibility ranged from 9% to 73%, with As, Cu and K presenting values above 50% for both insects. The analysis of P, Na, and Ca in the simulated digestive fluids proved challenging due to the addition of these salts at relatively high concentrations to ensure the sensitivity of the spectrometric methods. This represents a clear methodological limitation, as such conditions can introduce interferences. Crickets provide higher bioaccessible S, Mn, Zn, and As, whereas mealworms offer greater total Mg, K, and Fe, but with variable bioaccessibility, highlighting species-specific nutritional and safety profiles. These findings underscore the nutritional value and safety of consuming these insects, highlighting the robustness of plasma-based analytical techniques and sample preparation strategies for multi-element analysis in complex food matrices.

Figure 1. Bioaccessibility (%) of elements in edible insects



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IDENTIFICATION OF PEDOLOGICAL GROUPS IN TOPSOIL (0-20 cm) USING ETRs VIA MACHINE LEARNING

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The aim of this study was to create a topsoil classification system using Rare Earth Elements−REEs via machine learning with Python. The classification system will show functional soil groups according to the differential weathering of REE-bearing minerals, the selective mobilization of light and heavy REEs, interactions with soil mineral phases (oxides, hydroxides, clay minerals), redox processes affecting Ce and Eu, and active biogeochemical processes. With practical applications in digital mapping, automatic soil classification, and environmental monitoring. A total of 145 soil samples (0−20cm) representing two different types of parent materials (igneous and metamorphic) were microwave-digested following EPA Method 3051A. For digestion, each 0.2 g soil sample was treated with 7.5 mL concentrated nitric acid (65% *v*/*v*, ultrapure) and 2.5 mL concentrated hydrochloric acid (37% *v*/*v*, ultrapure). Pseudo-total REE content in soils was determined using an inductively coupled plasma mass spectrometer (Thermo Scientific™ iCAP Q ICP-MS, Germany, Bremen). Method accuracy was verified using IAG UoK Loess reference material, which showed excellent recovery for light REEs (89–94%) and lower recovery for heavy REEs (47–100%). Method detection limits (10× standard deviation of blanks, n = 12) ranged from 0.002 $mg \cdot kg^{-1}$ (Lu) to 0.588 $mg \cdot kg^{-1}$ (Ce). All analyses were conducted at the Environmental Studies Center of São Paulo State University (CEA, UNESP, Rio Claro, Brazil). A total of 27 units between rare earth elements (La−Lu) and proxies ($LREE_N/HREE_N$, ∑LREE, ∑HREE, ∑REE, δEu, δGd, δCe, La_N/Yb_N, La_N/Sm_N, La_N/Gd_N, Sm_N/Yb_N, Gd_N/Yb_N, and Gd_N/Lu_N) were considered. Principal component analysis was performed. Dimensional reduction was applied to the data matrix (145 × 27)[1], with component selection based on the Kaiser criterion. PC1 explains 41.1% of the total variance of the data and PC2 explains 24.0% of the total variance. The groups were identified after the application of the optimized K-means algorithm[2] in the PC1-PC2 coordinate clustering space, and determination of the optimal K by elbow method and silhouette analysis (K = 6 clusters). The REEs in the six groups were identified by the follow characteristics: (**1**) **purple**: (n = 25) total REEs preserved, La_N/Yb_N ratios close to source rock, minimal Ce/Eu anomalies, incipient weathering (A/C horizons); (**2**) **blue**: (n = 27) moderate weathering, incipient REEs mobilization, beginning of fractionation, slightly negative Eu anomaly, B horizon in formation; (**3**) **green**: (n = 51) advanced weathering, significant fractionation, well-developed B horizon; (**4**) **yellow**: soils LREEs enriched, mobilization of HREEs, active redox processes; (**5**) **pink**: (n =3) soils with preserved mafic heritage, relatively stable HREEs; (**6**) **light yellow**: (n=0) soils with extreme felsic signature, possible contamination or unique processes, extreme signatures, multiple anomalies: simultaneous Ce, Eu, Gd. Outside regional standards. This analysis reveals six distinct pedogenic environments characterized by different degrees of pedological evolution, REE mobility, geochemical signatures of the parent material, and active biogeochemical processes. Each of the six groups represents a functional soil type with specific geochemical processes for REEs. These results can be integrated with other physical-chemical soil data (e.g., Fe, Mn, Al, Ca/Mg, mineralogy), geological and pedological maps, topography, and the geomorphological evolution of the terrain. Also, special application in the identification of soils that present B horizon with accumulation of ion-adsorbed clay[3].

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EVALUATION OF RP-DLLME FOR FURTHER ALKALINE AND ALKALINE-EARTH METALS DETERMINATION IN CRUDE OIL ATMOSPHERIC AND VACUUM RESIDUES BY ICP-OES

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The presence of alkali and alkaline earth metals in heavy crude oil fractions, such as atmospheric residue (AR) and vacuum residue (VR), can significantly impact refining operations. These elements act as catalytic poisons, deactivating acid sites, reducing both the activity and useful life of catalysts used in processes such as hydroprocessing and catalytic cracking[1,2]. Furthermore, these metals contribute to scale formation and equipment corrosion, especially under high-temperature conditions. In this context, the adoption of accurate analytical methods for determining these elements in Crude Oil Atmospheric (AR) and Vacuum Residues (VR) becomes essential[1,2]. However, some drawbacks are observed for conventional methods used in crude oil digestion for further Ba, Ca, K, Mg, Na, and Sr determination, such as the wide concentration range of these analytes, contamination-related issues, and the limited sample amount for closed systems[3]. In order to overcome these problems, in the present work, the reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) method was developed for further Ba, Ca, K, Mg, Na, and Sr determination in crude oil AR and VR by inductively coupled plasma optical emission spectrometry (ICP OES). The RP-DLLME method is based on the analytes extraction from the organic phase (oil sample) to an aqueous phase using a dispersant/extractant (isopropyl alcohol/HNO_3) mixture. The microwave-assisted wet digestion (MAWD) method using concentrated HNO_3 and analytes determination by ICP OES was applied to obtain the reference values (based on the recommended by the method of the American Society for Testing and Materials D7876:13/2018[4]). Barium, Ca, K, Mg, Na, and Sr determination was performed using an inductively coupled plasma optical emission spectrometer with axial view (Optima 4300 DV, PerkinElmer, United States) after RP-DLLME and MAWD methods. Some operational parameters were evaluated: *i*) the type of solvent used for solubilizing the crude oil AR and VR (acetic anhydride, acetic acid, vaseline, toluene, and kerosene), *ii*) the use of a dispersant solvent (isopropyl alcohol), *iii*) sample mass (1.0 to 10.0 g), *iv*) concentration of the extractant solvent (0.5, 1.0, and 2.0 mol L^{-1} HNO_3), and *v*) centrifugation time (5 to 20 min). Optimal results were achieved using 5 g of crude oil AR and VR dissolved in 5 mL toluene, a solvent mixture containing 500 µL of isopropyl alcohol and 500 µL of 2.0 mol L^{-1} HNO_3, at 75 °C, and 20 min of centrifugation. No statistically significant difference (*t*-test, 95% confidence level) was found between the results obtained by the RP-DLLME method and the reference values (MAWD). Owing to the high sample mass (5 g), diluted solutions, and low blank values, the method provided very low limits of quantification (ranging from 10 to 40 ng g^{-1}) for all analytes. The proposed RP-DLLME method can be considered a simple and rapid sample preparation approach for the determination of alkaline and alkaline earth metals at trace levels in crude oil AR and VR. In addition, the RP-DLLME method aligns with green chemistry principles by using relatively simple instrumentation, reducing time and concentrated acid consumption, and minimizing environmental impact during sample preparation.

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ESTIMATION OF THE MEASUREMENT UNCERTAINTY IN ICP-MS TIMBER ANALYSIS

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The inductively coupled plasma mass spectrometry (ICP-MS) technique provides high sensitivity and multielement capabilities, making it an important tool in analytical chemistry[1]. Despite its strengths in quantitative analysis, the reliability of results relies on the appropriate estimation of measurement uncertainty. This study aimed to apply the principles of the GUM (Guide to the Expression of Uncertainty in Measurement)[2] to systematically identify and quantify the main sources of uncertainty in ICP-MS analysis. Both top-down and bottom-up approaches, based on quality control procedures and experimental design, were used to assess uncertainty in the analysis of wood samples. The bottom-up approach considered individual sources of uncertainty during the conversion of counts per second into mass fractions, while the top-down approach estimated uncertainty empirically from replicate measurements. For this study, a tropical wood reference material with certified values for twenty-four chemical elements was used. The material was produced at the Radioisotopes Laboratory of CENA/USP, and the reference values were established following the guidelines of ISO Guide 35:2017. For both the top-down and bottom-up approaches, 30 replicates from the same bottle of reference material were evaluated. Analytical portions of 250 mg were weighed into PTFE vials and subjected to microwave-assisted acid digestion with 4.5 mol L^{-1} HNO_3 and 9.8 mol L^{-1} H_2O_2 at 200 °C and 1800 W and the elements Ba, Cr, Sr and Sm were determined using a triple quadrupole inductively coupled plasma mass spectrometer. These elements were selected based on their concentration ranges, covering major, minor and trace levels, to evaluate the influence of elemental concentration on the final measurement uncertainty. An Ishikawa diagram was used to identify potential sources of uncertainty, such as, bias of the analytical balance, deviations in volumetric equipment, variation in the dilution factor, dry/wet mass ratio, internal standardization, and calibration curve parameters. These factors were quantified and incorporated into a functional measurement model for the bottom-up approach. Expanded uncertainty was calculated using a coverage factor of k = 2, corresponding to a confidence level of approximately 95%. Two factors were identified as having the greatest influence on uncertainty: the standard deviation of counts per second and the intercept of the calibration curve. The intercept, which represents the instrument response in the absence of the analyte, had a direct impact on method sensitivity, particularly for analytes at low concentrations. The standard deviation of the signal reflected intrinsic measurement variability due to environmental fluctuations and instrumental noise, contributing significantly to the overall uncertainty. A small standard error in the intercept led to underestimation of uncertainty, amplifying minor variations in calibration and compromising analytical accuracy. The results indicated that the estimated uncertainty accounted for the uncertainty inherent in the reference material for Ba, Cr, Sr and Sm, demonstrating that the method reliably captured the total variability of the measurements. Furthermore, a consistent inverse relationship between analyte concentration and uncertainty was observed. These findings highlight the critical influence of key analytical parameters on accurate uncertainty estimation in ICP-MS. A rigorous evaluation and incorporation of factors such as signal variability and calibration characteristics are essential to minimize underestimation and enhance the overall robustness and reliability of analytical results.

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Enhanced Selenium Uptake and Translocation in Golden Flaxseed Under Hydroponic Cultivation

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Selenium agronomic biofortification is a promising strategy to increase selenium content in crops and livestock, thereby helping to address global micronutrient deficiencies. To optimize plant growth and evaluate the uptake and distribution of selenium and other metal(loid)s, well-controlled experimental conditions are essential. In this study, a hydroponic cultivation system was employed to investigate the optimal conditions for selenium biofortification in flaxseed (*Linum usitatissimum* L.). Total selenium was quantified by ICP-MS using itrium as internal standard, after evaluation of some figures of merit. It was developed a full 2^2 factorial design with a central point, and the independent variables were: concentrations of Se^{4+} (as Na_2SeO_3) and Hoagland's nutrient solution. The levels of the variables are presented in Table 1. Additionally, three control experiments were performed using 5%, 7,5% and 10% Hoagland solution without selenium exposure (cultivation blanks). The response variables evaluated included plant length, mean biomass per plant, and total selenium content in the roots (R), stems (S), and leaves (L). Statistical analyses were conducted using *Statistica*® version 10.0 (StatSoft, 2011). Flaxseed germination was carried out on moistened germination paper for four days, until the radicles reached a length of approximately 1 cm. The seedlings were transferred to 600 mL plastic pots (n = 2, with 15 plants per pot) and cultivated in Hoagland's nutrient solution supplemented with Se^{4+} in different concentrations [1,2] (Table 1). The cultivation period was 15 days, with solution changes occurring every 3 days. After the cultivation period, the plants were measured and separated into R, S, and L. Then, they were dried to a constant mass and weighed. Dried samples were submitted to microwave acid-digestion using distilled concentrated HNO_3, plus H_2O_2 and H_2O. Total selenium was quantified by ICP-MS (^{78}Se and ^{82}Se), matrix effect, spiked sample tests (n = 3, 3 levels), accuracy (NIST 2976), limits of detection (LOD) and quantification (LOQ) were evaluated. Recovery tests from lower to higher levels were (96 ± 19)%, (91 ± 2)% and (91 ± 6)%, while for NIST 2976 was (98 ± 6)%.The best results were obtained with ^{82}Se and matrix effect was not observed. The LOD and LOQ were 24 µg g^{-1} and 76 µg g^{-1}, respectively. The generated response surface plots indicated that lower concentrations of both selenium and Hoagland's nutrient solution were associated with increased plant length and biomass accumulation. Selenium quantification, particularly in experiments 1 and 2, revealed approximately a threefold increase in selenium translocation to the stems and leaves of plants cultivated with 5% Hoagland solution. Additionally, the control experiments demonstrated that plants grown in 7.5% Hoagland solution exhibited the greatest length and biomass among of all tested conditions. Based on these results, 7.5% Hoagland solution was selected as the optimal nutrient concentration. In accordance with the objectives of this study, decreasing the concentration of the nutrient solution promoted larger plant growth and increased selenium translocation.

Table 1 – Variables and levels in a 2^2 full factorial with triplicate at the central point.

Experiments	[Se^{4+}] *µmol L^{-1}*	[Hoagland] *(%)*
Experiment 1	(+): 84 µmol L^{-1}	(+): 10%
Experiment 2	(+): 84 µmol L^{-1}	(-): 5%
Experiment 3	(-): 12 µmol L^{-1}	(+): 10%
Experiment 4	(-): 12 µmol L^{-1}	(-): 5%
Central point (CP) n = 3	(0): 48 µmol L^{-1}	(0): 7,5%

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EVALUATION OF SOIL PHOSPHORUS AVAILABILITY USING HANDHELDLIBS

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Efficient P management is essential for agricultural sustainability. Although abundant in soils, much of the P occurs in unavailable forms, either adsorbed to organic matter or co-precipitated with Al, Fe, and Ca. To compensate for this low availability, phosphate fertilizers are frequently applied; however, excessive use increases costs and can lead to environmental impacts.[1] Thus, the determination of the available P fraction (labile P) is crucial for guiding appropriate nutrient replenishment. Traditional methods, however, have limitations, as they require large volumes of hazardous reagents, generate waste, are time-consuming, and are prone to errors.[2] In this context, Laser-Induced Breakdown Spectroscopy (LIBS) emerges as a promising alternative, enabling fast multi-element analyses with minimal sample preparation and no waste generation. Furthermore, portable instruments, such as handheld LIBS (hLIBS), allow for direct in-field determinations.[3] In this study, we evaluated a method for determining labile P from spectra acquired using an hLIBS system (SciAps Z-903) on 60 soil samples with different textures and nutrient contents. Data processing consisted of applying a natural logarithm (ln) transformation to both reference values of labile P and spectral intensities, followed by vector normalization to standardize variable magnitudes and enhance convergence of the ElasticNet algorithm. Variables were preselected based on spectral lines with high relative intensity and transition probability, assigned to P, Al, Ca, Fe, C, and N, including adjacent wavelengths. Hyperparameter optimization was performed using nested cross-validation (k-fold, k = 5), with 13 wavelengths ultimately selected by the model. Final calibration was validated by Leave-One-Out Cross Validation, yielding a strong correlation between predicted and reference labile P values (R = 0.80) with RMSE = 0.51. The results demonstrate that the combined use of hLIBS and machine learning enabled fast, robust estimation of labile P without chemical reagents. Proper preprocessing and careful variable selection were critical for model performance, highlighting the potential of this approach for soil analysis. Notably, variables associated with P immobilization, particularly Al lines, contributed significantly to labile P prediction. The use of portable systems broadens the applicability of the method, offering prospects for direct in situ analyses, cost reduction, and optimized nutrient management in agricultural systems.

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Estimation of health risks associated with cadmium, mercury, and lead exposure from foods of the Brazilian Amazon

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The Amazon Basin supports diverse food systems rooted in traditional knowledge, yet growing anthropogenic pressures, particularly illegal gold mining, are increasing the release of trace elements into aquatic and terrestrial ecosystems, with implications for food safety and public health. This study quantified non-essential elements (cadmium, Cd; lead, Pb; mercury, Hg) and essential elements (magnesium, Mg; chromium, Cr; manganese, Mn; iron, Fe; copper, Cu; zinc, Zn; selenium, Se) in five categories of foods typical of the Brazilian Amazon: Brazil nuts and sweets, spices, vegetables/preserves, flours, and fish/seafood. Twenty-nine samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). Non-carcinogenic risk was evaluated for Cd, Pb, and Hg using hazard quotients (HQ) and the aggregate hazard index (HI). Elemental concentrations varied across food groups. Brazil nuts showed the highest Se concentrations (11624.83 ± 395.55 µg kg^{-1}), while fish/seafood exhibited the highest Hg concentrations (4702.62 ± 373.48 µg kg^{-1}). Multivariate analyses (PCA, Pearson correlation, and hierarchical clustering) revealed clear patterns of elemental co-occurrence. **Figure 1** shows median HQs for Cd, Hg, and Pb were <1 in plant-based categories, whereas fish/seafood risk was dominated by Hg (median HQ_Hg = 2.349). Hazard quotients and HI values for fish/seafood exceeded reference thresholds, indicating potential health risks for frequent consumers. In contrast, plant-based foods had lower concentrations of non-essential elements and negligible non-carcinogenic risk. These findings underscore the need for sustained monitoring, risk communication, and environmental enforcement to reduce contaminant releases associated with illegal gold mining, while safeguarding the nutritional and cultural value of Amazonian diets.

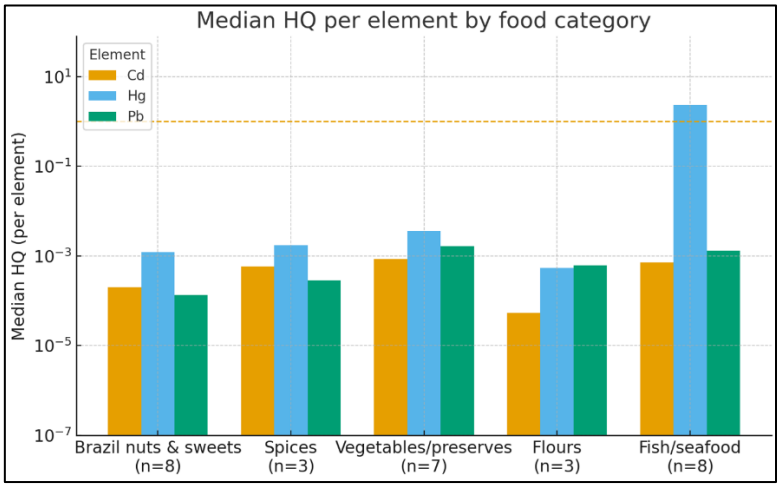

Figure 1. Median HQ for Cd, Hg, and Pb by food category (log scale). The dashed line indicates HQ=1. In fish/seafood, Hg dominates the risk contribution; in plant-based categories, all three elements show median HQs well below 1.

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MULTIVARIATE OPTIMIZATION OF MICROWAVE-ASSISTED DIGESTION PARAMETERS FOR ELEMENTAL ANALYSIS OF HONEY SAMPLES

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Honey is a complex matrix for elemental analysis due to its wide variability in composition and high organic matter content, composed mainly of sugars such as fructose and glucose[1]. Therefore, proper sample preparation is a crucial step to ensure standardization and reliable results in elemental determinations. This study aimed to optimize the acid decomposition of honey using microwave-assisted digestion, targeting elemental analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The influence of nitric acid concentration and pre-digestion on the efficiency of the process was evaluated, with the goal of minimize both residual carbon and acidity levels. A full factorial experimental design (n=3) was applied, varying nitric acid (HNO_3) concentrations (2.00, 3.59 and 7.00 mol L^{-1}) and pre-digestion (without and 2 h), using three honey samples from *Apis mellifera* with different colors[2]. Sample masses of 250 mg of honey were weighed into polytetrafluoroethylene (PTFE) vessels and subjected to pre-digestion using concentrated nitric acid in the digestion tubes. After pre-digestion, variable volumes of ultrapure water and 2.0 mL of 30% hydrogen peroxide (H_2O_2) were added. For 2.00, 3.59 and 7.00 mol L^{-1} HNO_3, the respective volumes of concentrated nitric acid were 1.0, 1.8 and 3.6 mL, along with 5.0, 4.2 and 2.5 mL of ultrapure water. Digestion was carried out using a microwave system following a program with temperature of 195º C and power of 1800 W. Residual acidity was determined by acid-base titration, using 10 mL of sample, 1 mol L^{-1} NaOH as titrant and phenolphthalein as indicator. Residual carbon was quantified by inductively coupled plasma optical emission spectrometry in radial view using a calibration curve in the 0 - 5000 mg/L range. The results were evaluated using the global desirability function, complemented by analysis of variance (ANOVA) to define the best condition. Statistical analysis (ANOVA) showed that only acid concentration has significant influence ($p = 0.0029$), while pre-digestion time was negligible ($p = 0.7096$). The condition yielding the highest global desirability ($D_{global} = 0.776$) involved the use of 2 mol L^{-1} HNO_3 and 2 h of pre-digestion, with low residual acidity (1.67%) and good carbon removal efficiency (1791 mg/L). However, the same acid concentration without pre-digestion also showed satisfactory performance ($D_{global} = 0.689$), with residual carbon of 2062 mg/L and residual acidity of 1.76%, making it a viable and more practical option. Higher acid concentrations, such as 3.59 and 7 mol/L, resulted in lower desirability indices ($D_{global} = 0.601$ and 0.250, respectively), mainly due to increased residual acidity, which may increase blank values and require subsequent sample dilution before analysis.

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Evaluation of the use of HBF_4 in sugarcane and forage sample preparation procedures for elemental determination by MIP-OES

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Elemental analyses of agronomic samples require several pretreatment steps, which are one of the main sources of error. Sample preparation is usually necessary to convert solid samples into a solution, which in many cases involves acid decomposition in a closed system with microwave heating. However, matrices containing high silicon content, such as sugarcane and *Brachiaria brizantha*, are challenging to mineralize due to the strong interaction between the Si bond and the carbon in organic matter. During the digestion of these samples, it is common to use hydrofluoric acid, which is highly reactive and complexing and requires the addition of high concentrations of boric acid to prevent the formation of insoluble fluorides and attacks on the glass and quartz accessories present in the equipment[1,2,3]. In this study, the use of tetrafluoroboric acid was evaluated in the preparation of samples for the determination of Ca, K, Mg, P, Si, and Fe by microwave-induced plasma optical emission spectrometry (MIP-OES) in a set of sugarcane leaves (*Saccharum* spp.) and *Brachiaria brizantha*. The samples were microwave-assisted acid digestion using a mixture of HNO_3 + H_2O_2 + H_2O in a ratio of 3:2:3 with and without the addition of 0.2 mL of HBF_4 [2]. After digestion, the solutions were diluted to 30 mL with ultrapure water. The results obtained with HBF_4 presented recoveries, ranging from 91 to 114% related to sugarcane samples previously determined by energy-dispersive X-ray fluorescence (ED-XRF)[2,4] and a reference material (*Brachiaria Brizantha* cv Marandu, RM-Agro E1001a). All analytes had adequate limits of detection (LOD), with relative standard deviations (RSD) < 2%. The results obtained using HBF_4 were compared with those obtained without HBF_4, and significant differences were observed for Si and P (Student's t-test at a 95% confidence level). The obtained results demonstrate that HBF_4 can be used for sample preparation of plant materials with high silicon content, replacing HF. Furthermore, the application of the methodology using tetrafluoroboric acid also demonstrates significant effectiveness in determining other nutrients present in the analyzed matrix.

Keywords: plant tissues, tetrafluoroboric acid, sample digestion

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INFLUENCE OF PARTICLE SIZE IN THE DIRECT SEWAGE SLUDGE ANALYSYS BY LASER-ASSISTED TECHNIQUES

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Sewage sludge (SS), a byproduct of wastewater treatment, is a valuable material for use as fertilizer due to its high content of organic matter and nutrients. Its use is aligned with the UN's Sustainable Development Goals (SDGs), promoting a circular economy. However, for this purpose, rigorous quality control is imperative. Direct analysis of SS is possible using laser-assisted techniques such as Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma Optical Emission Spectroscopy (LA-ICP OES). Despite their advantages, there are challenges to overcome. As these are microanalytical techniques, the intrinsic heterogeneity of SS influences sampling representativeness and atomization efficiency, which degrades the precision and accuracy of the analytical results[1]. This research investigates the influence of particle size of a candidate SS reference material (RM) on its direct analysis by LIBS and LA-ICP OES. The candidate SS RM was dried, ground and sieved to obtain two particle size fractions: ≤ 50 µm and > 150 µm. All portions were analysed by ICP OES after acid decomposition to obtain reference values, which indicated absence of analyte segregation. For laser assisted techniques, samples were pelletized, mapped and analysed. The mapping revealed some small areas of heterogeneous distribution of Cr, Cu, and Mg at micro-scale. For quantification, Slope Ratio Calibration (SRC) was used[2] and no significant effect of particle size on accuracy between fractions was observed. In contrast to the point-to-point mapping ablation mode, quantitative analysis was performed using a raster mode. This method corrected for minor variations in the analytical signal, yielding relative errors of approximately 15% for the studied analytes (e.g. Cr) when compared with ICP OES results. In conclusion, this work establishes that despite small micro-scale heterogeneities arising from different particle size, reliable quantitative results can be achieved with LIBS and LA-ICP-OES. The application of an SRC calibration strategy alongside raster mode sampling was crucial for improving the reliability of this RM for future direct solid analyses by laser-assisted methods.

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Evaluation of wet digestion procedures for lithium determination in geological samples by atomic spectrometry

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The growing demand for Technologically Critical Elements (TCEs) stems from their essential role as resources for developing more efficient and environmentally friendly technologies. Among these, lithium stands out due to its relevance in batteries, electronics, and energy storage systems.[1] In nature, Li occurs incorporated into the crystalline structures of minerals and rocks at minor or trace levels within physico-chemically complex matrices containing refractory phases, which make sample preparation particularly challenging. Accordingly, establishing a reliable method for lithium determination in such matrices is crucial for both environmental monitoring and resource evaluation.[2,3] In this context, this study aimed to develop a method for the determination of lithium in porous metamorphic rocks by atomic spectrometric techniques using acid digestion.[4] Five acid-digestion procedures were evaluated under two heating systems—microwave-assisted digestion (MWAD) and a conductively heated digestion system (CHDS)—employing concentrated mineral acids (nitric, hydrofluoric, and hydrochloric acids) as well as boric acid, ascorbic acid, and water. Method accuracy was assessed by analyzing the Basalto de Ribeirão Preto reference material (BRP-1) and through analyte recovery tests, in addition to a preliminary study employing laser-induced breakdown spectroscopy (LIBS). X-ray fluorescence (XRF) and X-ray diffraction (XRD) identified quartz as the predominant phase, confirming the need for HF in all digestion procedures. Lithium determination by LIBS yielded a preliminary estimate of 1.1% (m m^{-1}), with high variability (±8.2%). Quantification of the analyte by inductively coupled plasma optical emission spectrometry (ICP-OES), flame atomic absorption spectrometry (FAAS), and inductively coupled plasma mass spectrometry (ICP-MS) indicated contents of approximately 1.0% with relative standard deviation (RSD) below 15% for all techniques. Although limits of detection and quantification were satisfactory—ranging from 1–100 mg kg^{-1} and 1–340 mg kg^{-1}, respectively—it was not possible to quantify the analyte in the reference material with adequate confidence using any of the techniques and sample-preparation procedures, because the informational value for BRP-1 is 7 mg kg^{-1}. Recoveries obtained via standard-addition tests fell within the limits established by AOAC International. Overall, further studies using more suitable reference materials are warranted to ensure precision and accuracy at more satisfactory levels, supporting the development of robust methods for lithium determination in complex geological matrices.

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[CNPq; FAPES; SEBRAE; CAPES; GRAMAZINI; UFES; LEA; LabPetro]

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Multivariate Optimization of an Acid-Free Sonochemical Method for the Determination of Metals in Complex Matrices

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The increasing demand for environmentally sustainable analytical methods has driven the development of alternative sample preparation strategies that can reduce or eliminate both the use of hazardous reagents and the generation of toxic waste[1]. In this work, we report a sustainable analytical approach for the determination of trace metals (Cd, Cr, Cu, Fe, and Zn) in complex biological samples using an acid-free sonochemical wet extraction method (AFSE). Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for element determination, and multifactorial analysis was used to investigate the effect of hydrogen peroxide (H_2O_2) concentration as a key parameter in the analyte extraction process. In total, three important variables were evaluated: (*i*) H_2O_2 concentration (0-32% v/v), (*ii*) sonication time (1-90 min), and (*iii*) extraction temperature (15-100 °C). Five certified reference materials (CRMs) and a commercial sample of fish were used to evaluate the method's performance. AFSE results were also compared with those from microwave-assisted acid digestion (MAD) of the same samples. The optimal AFSE conditions were defined as: (*i*) 25% v/v H_2O_2, (*ii*) 50 min of sonication at 44 kHz, and (*iii*) an extraction temperature of 60 °C. Under these conditions, analyte recoveries exceeded 75% for all elements evaluated. The quadratic regression model explained 89% of the data variability (R^2 = 0.89), with an adjusted R^2 of 0.94. No statistically significant differences were observed between AFSE and MAD results ($p > 0.05$). Excellent linearity across the 0-100 μg L^{-1} range for all elements ($R^2 > 0.999$), and low limits of detection (LOD) and quantification (LOQ) confirm the method's adequacy for trace element determination: Cd (LOD/LOQ: 0.5/1.6 μg L^{-1}), Cr (LOD/LOQ: 0.6/2.1 μg L^{-1}), Cu (LOD/LOQ: 0.6/1.8 μg L^{-1}), Fe (LOD/LOQ: 0.4/1.4 μg L^{-1}), and Zn (LOD/LOQ:1/3.6 μg L^{-1}). The method has also proved to be robust, enabling accurate determinations with sample masses as low as 20.0 mg. When applied to a commercial fish sample, concentrations of Cu, Fe, and Zn were determined as 0.67 ± 0.11, 10.74 ± 0.97, and 17.21 ± 1.86 mg kg^{-1}, respectively. These values are consistent with those obtained with MAD. Cadmium and Cr levels were below the method's LOD for this sample. Overall, the results demonstrate that AFSD is a technically sound and ecofriendly alternative for trace metal determination in biological matrices, providing an analytical performance that is comparable to the conventional and robust MAD method, while significantly reducing chemical consumption and environmental impact.

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Laser-Induced Breakdown Spectroscopy: Advancing Calibrating Materials for Elemental Analysis of Liquid Samples

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The Laser-Induced Breakdown Spectroscopy (LIBS) technique has stood out due to its significant advances in multielemental analysis of solid samples, often requiring minimal sample preparation. In recent years, the application of LIBS to liquid samples has gained increasing attention, as it enables the extension of LIBS well-established advantages in solid analysis to the liquid samples. The Molecular and Atomic Spectroanalytical Group (LEMA-UFABC), in collaboration with other research groups, has been actively engaged in the development of methodologies for converting liquid-to-solid, with the aim of facilitating LIBS analysis through the production of calibrating materials and extending its application to liquid matrices. Using lignin as a solid substrate, a method combining thin film microextraction (TFME) and LIBS was developed, involving the deposition of thin lignin films via dip coating[1]. Paraffin wax[2] and beeswax[3] were also employed as substrates for metal incorporation and subsequent elemental analysis of liquid samples with diverse characteristics, such as waters from different sources, alcoholic beverages, mineral oils, and cosmetic products. In other studies, Matte photographic paper was used for the preparation calibrating materials, which were successfully applied in the elemental determination of a wide range of matrices including natural waters, nail polishes, and printer inks[4,5]. More recently, the use of edible biopolymers has been explored for the preparation and application of calibrating materials. It is noteworthy that all proposed methodologies considered not only the analytical performance but also the abundance, cost-effectiveness, and environmental sustainability of the solid substrates, favoring materials with low hazard potential. Lastly, various calibration strategies were investigated, ranging from conventional approaches such as external and internal standard calibration to more recent strategies like slope ration calibration (SRC). The aim of this work is to present selected methods carried out by LEMA-UFABC, in collaboration with other research groups, which focus primarily on the preparation of calibrating materials and the elemental analysis of liquid samples using the LIBS technique.

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Enhancing LIBS performance with silver nanoparticles synthesized on paper by Ring-Oven

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The search for more sensitive, sustainable, and straightforward analytical alternatives has been increasing in the academic and scientific fields, particularly regarding the determination of elemental chemical composition. This demand arises from the fact that environmental, pharmaceutical and food samples, among others, are often analyzed using high-cost techniques that require substantial sample preparation to minimize chemical interferences. In this context, Laser-Induced Breakdown Spectroscopy (LIBS) offers advantages such as multielemental capability and non-destructive analysis, despite the challenges related to the direct determination of metal ions in liquid matrices. The characteristics of LIBS are also synergistic with the effects generated by the incorporation of nanoparticles into the system, mainly due to their signal-enhancing ability derived from unique optical and electronic properties, which result in greater sensitivity and lower detection limits.[1] This effect is commonly exploited by depositing liquid samples and nanoparticle suspensions onto solid substrates, such as paper. In contrast, the present work proposes the use of the Ring-Oven (RO) technique for in situ synthesis of nanoparticles, reducing reagent consumption, while simultaneously concentrating both nanoparticles and analytes into a small colored area formed on the filter paper in the shape of a ring. Although rarely applied, the RO represents a simple and efficient method in which liquid samples deposited onto filter paper migrate by capillarity toward the edge as the solvent evaporates under heating, resulting in an analyte-enriched ring that can be directly analyzed by LIBS.[2] Moreover, the reduced reagent consumption of this method also decreases waste generation, thereby promoting the principles of green chemistry. Several synthesis strategies using RO were evaluated, successfully achieving the in-situ formation of silver nanoparticles (AgNPs), as confirmed by scanning electron microscopy (SEM) images. Reducing agents such as ascorbic acid (Figure 1a) and stannous chloride (Figure 1b) were evaluated. During LIBS measurements, the filter paper was fixed on a rotating platform, allowing the accumulation of 120 non-overlapping laser pulses (Nd: YAG Q-switched, Brilliant Quantel B, 1064 nm, 20 Hz, 5 ns) across the entire circumference of the ring. The emitted radiation was collected with a 5-mm diameter lens and focused onto the tip of a 105 µm optical fiber, which guided the light to an echelle polychromator (Andor Technology) coupled to an ICCD camera (Star DH734, Andor Technology). The emission spectra revealed a significant enhancement of the emission signals for Al (396.15 nm), Ba (493.41 nm), Cr (428.97 nm) and Cu (324.76 nm), with a signal increase of ca. 10x. The results obtained from the synergic effects between the pre-concentration step promoted by the RO and the presence of AgNPs attest both the efficiency of the in situ synthesis and the robustness of the analytical strategy. The clear improvement in signal intensity highlights the potential of the proposed approach to overcome traditional limitations of LIBS, providing higher sensitivity and competitiveness in terms of detection limits. Furthermore, the integration of these techniques demonstrates the feasibility of a simple, sustainable, and high-performance procedure, reinforcing the relevance of RO combined with metallic nanoparticles for advanced applications in analytical spectroscopy.

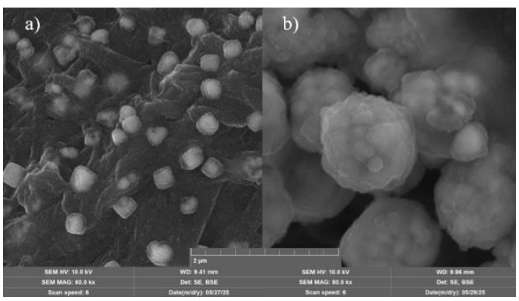

Figure 1: AgNPs synthesized by RO.

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Illuminating the copper industry: How LIBS and hyperspectral imaging are transforming mining analytics and processes

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Copper is a critical material for the global decarbonization of energy sources, enabling the generation, transmission, and electrification of mobility. To meet the growing global demand, improving the efficiency and sustainability of copper production is essential, particularly through real-time analytical assessment. Traditional atomic spectroscopy techniques, though reliable, are often laborious, contaminating, time-consuming, and costly, and they lack the capability for online, real-time monitoring.

In this context, our research group has developed Laser-Induced Breakdown Spectroscopy (LIBS)–based analytical methods specifically designed for the copper industry. These innovations enable rapid, in situ analysis of elemental and mineralogical compositions at multiple stages of production, from mineral exploration to metallurgical operations, like grinding, flotation, smelting, and electrorefining.

We combine stand-off LIBS, hyperspectral LIBS, hyperspectral imaging (HSI), and machine learning (ML) to achieve comprehensive analytics in the copper industry. The setups presented here provide quantitative analysis of valuable elements (Cu, Mo, Ag, Au) and penalizing species (As, Pb, Zn, S, Fe), along with the identification of mineralogical phases and the generation of 2D elemental and mineralogical maps. These methods have been applied to diverse samples, including drill cores, rock powders, copper concentrates, electrorefining residues, and elemental analysis of aerosols. Stand-off LIBS monitoring of Cu, O, and S in molten phases during the desulfurization stage of smelting is presented. This approach enables real-time control of process chemistry, supporting optimized operation, improved energy efficiency, and reduced environmental impact.

Our results demonstrate how light-based technologies, driven by LIBS and HSI, are transforming the analytics in the copper industry, bringing the vision of real-time, intelligent mining closer to reality.

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EPA 3051A performance for sample preparation in a conductively heated digestion system closed vessels for determination by ICP OES

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Spectrometric methods such as inductively coupled plasma optical emission spectrometry (ICP OES) or inductively coupled plasma mass spectrometry (ICP-MS) rely on sample introduction systems based on liquid solutions.[1] For this, sample preparation using microwave-assisted digestion is a step in elemental analysis laboratory routine. Many methods for sample preparation have been developed, tested and stablished for a wide variety of samples, aiming for a precise and exact determination.[2] The conductively heated digestion system closed vessels (CHDS) was proposed in 2014 and has been successfully applied to different matrices digestions.[1] The United States Environmental Protection Agency (EPA) has a collection of accredited methods for environmentally relevant samples, such as sediments, sludge and soils that requires microwave-assisted digestion. These samples are of relative complexity, and to accomplish total decomposition it is often required the use of a mixture of acids, additional decomposition steps and harsh conditions. As an alternative, extraction or partial decomposition methods are proposed and validated, such as EPA 3051A, aiming to determine more labile elements presents in matrix. This method consists of using 500 mg of sample with concentrated HNO_3 (10 mL) or a mixture of HNO_3 (9 ml) and HCl (3 ml), in a closed-vessel microwave-assisted heating, for 10 minutes, at 175 ºC. Although effective, microwave systems are often cumbersome and expensive. CHDS instrument is mounted in a digestion cabinet resistant to acid fumes with venting systems and comprises an aluminum block with 24 slots equipped with a temperature control terminal. Digestion is performed in quartz tubes with a capacity of 45 mL that are sealed with PTFE lids equipped with built-in breakable safety disks designed for 28 bar maximum pressure. So far, the digestor has been proven as a versatile and affordable option for sample preparation aiming at elemental determination.[1] Therefore, this work aims to investigate the performance of conductively heated digestion system closed vessels (Simplify system, Vert Technologies) in the EPA 3051A method for sample preparation of reference materials and determination of As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb and Zn by inductively coupled plasma optical emission spectrometry (ICP OES). To assess the effectiveness of the proposed method, certificated reference materials were used, especially those which the certificate presented leached values using EPA 3051A. The reference materials used were: Western Phosphate Rock (NIST SRM 694), Trace Elements in Multi-Nutrient Fertilizer (NIST SRM 695), and New Jersey Soil (NIST SRM 2706). Sample mass of 250 mg was treated with a mixture of HNO_3 (2.25 ml) and HCl (0.75 ml) in the 3:1 proportion. The heating program consisted of a ramp heating rate of 10 ºC min^{-1} to a hold of 210 ºC, for 10 minutes. The vessels were allowed to cool to room temperature. After heating, the mixture was transferred to a 50 mL tube, and the final volume was made up to 25 mL. For the multielemental determination, an ICP-OES instrument was used, model ICAP-7000 (Themo Fisher Scientific). Results showed a good agreement for NIST SRM 695, with recovery varied from 80% (Co) to 110% (Cd). For NIST SRM 2706 recoveries were lower, ranging from 70% (Ca) to 99% (Cd), except for Ni and Mn that showed recoveries higher than those expected. The proposed digestion system based on conductively heated wet digestion in closed vessels showed to be a reliable alternative for sample preparation using EPA 3051A method for elemental determination by plasma-based techniques.

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RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY
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DETERMINATION OF INORGANIC CONTAMINANTS IN E-LIQUIDS FROM ELECTRONIC NICOTINE DELIVERY SYSTEMS USING ICP-MS

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Recognized as a chronic condition driven by nicotine dependence, smoking remains the leading cause of preventable disease and death worldwide. A wide range of tobacco-derived products is commercially available, with conventional cigarettes being the most widely consumed globally. In recent years, however, the tobacco industry has diversified its product portfolio, with increasing interest in Electronic Nicotine Delivery Systems (ENDS). Commonly referred to as e-cigarettes or vapes, these battery-powered devices deliver nicotine through the vaporization of liquid refills (e-liquids) contained in their cartridges[1]. Although the sale of ENDS is prohibited in Brazil under RDC Nº 855/2024, illegal commercialization persists, exposing users to a complex mixture of irritating, toxic, and carcinogenic compounds. Numerous harmful substances have been reported in these products, including heavy metals, which pose significant health risks to users. The selection of contaminants in this study, arsenic (As), cadmium (Cd), lead (Pb), nickel (Ni), mercury (Hg), and chromium (Cr), was based on safety criteria established by RDC Nº 896/2024, which regulates tobacco-derived products and sets technical requirements for their control. This study aimed to develop and validate an analytical method using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the determination of these metals in e-liquids used in ENDS. Sample preparation involved microwave-assisted acid digestion. To determine the optimal digestion conditions, recovery tests were conducted under varying parameters, including digestion time, temperature, and solvent concentrations. The quantification of As, Cd, Pb, Hg, and Ni was performed using ICP-MS in standard mode, while the determination of Cr employed the Kinetic Energy Discrimination (KED) mode to minimize spectral interferences. The selected methodology was validated in accordance with ISO/IEC 17025 and the guidelines established by INMETRO. After validation, six e-liquid samples provided through a partnership between INCQS/Fiocruz and the Brazilian Federal Revenue Service were analyzed. The validated methodology demonstrated compliance with regulatory standards for linearity, accuracy, and precision. Only three of the six inorganic contaminants studied were found at quantifiable concentrations in all the analyzed e-liquid samples. The levels of Cd, Pb, and Ni were below the limit of quantification (LOQ), which was set at 0.005 $\mu g.g^{-1}$ for Cd and Pb and at 0.025 $\mu g.g^{-1}$ for Ni. In contrast, average concentrations of 0.029 $\mu g.g^{-1}$ (0.015 to 0.068 $\mu g.g^{-1}$) for As, 0.608 $\mu g \cdot g^{-1}$ (0.31 to 1.20 $\mu g.g^{-1}$) for Cr, and 0.052 $\mu g \cdot g^{-1}$ (0.022 to 0.100 $ug.g^{-1}$) for Hg were detected. The variation in concentrations observed may be attributed to the different origins of the e-liquid samples, which could vary in composition, flavors, and manufacturers, thus directly influencing contaminant levels. The low concentrations or absence of Cd, Pb, and Ni may be attributed to the use of synthetic nicotine in the production of these e-liquids, as synthetic nicotine does not carry the metal contaminants typically found in nicotine derived from tobacco leaves. Given the known occurrence of metal leaching from devices, further studies on the vapors produced by ENDS are essential for more representative comparisons. Despite some limitations, this study provides valuable data that supports the ongoing discussion.

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Property values assignment for organic coffee leaves reference material

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Brazil is the main producer and exporter of Arabica coffee in the world, with a total of 1.84 million hectares for the production of 37 million bags, of which 32% were exported to 126 countries in the first quarter of 2025[1]. To ensure the effectiveness of mineral supplementation and produce high-yield of high-quality coffee, foliar diagnosis is required. The quality of the results and equipment calibration depend, among other factors, on the use of standards similar to the matrix of the sample being analyzed. To this end, certified reference materials (CRMs) are developed, whose physical, chemical, or biological properties are rigorously characterized using highly accurate metrological analytical techniques. These materials have certified values accompanied by their associated uncertainties[2]. To develop the CRM-Agro Coffee Leaves reference material, approximately 30 kg of *Coffea arabica* L. cv. Catuaí Vermelho (IAC 99) leaves were collected from a nationally certified organic farm in the municipality of Ibiraci, Minas Gerais, Brazil. The leaves were ground in a mill with titanium knives and a ball mill with agate chamber, obtaining a particle size of 178 µm, and packaged in 210 amber polyethylene bottles containing 25 g each. Ten bottles were used for characterization. For the within-bottle homogeneity study, one bottle was selected and 10 analytical portions collected. For the between-bottle homogeneity study, 10 bottles were sampled in triplicate. For the transport stability study, they were subjected to 99% humidity and 40°C in an oven for 30 days. In the long-term stability study, materials were evaluated under storage conditions for a period of 2 years. Analyses performed by inductively coupled plasma mass spectrometry (ICP-MS) and neutron activation analysis (NAA) used 200 mg analytical portions. In the ICP-MS analysis, microwave digestion with 6 ml HNO_2 and 2 ml H_2O_2 was performed. For NAA, the material was irradiated in the IEA-R1 nuclear research reactor, of the Institute of Energy and Nuclear Research, of the Brazilian Nuclear Energy Commission (IPEN/CNEN)[3], São Paulo, SP. For analytical quality control, the reference materials SRM1515 Apple Leaves, IAEA 336 Trace and Minor Elements in Lichen and CRM-Agro C1005a Sugar Cane Leaves were used. The reference value assignment for the chemical elements was performed based on the average of the characterization and studies of within-bottle and between-bottle homogeneity, transport and long-term stability, and the uncertainty was calculated by the Top-Down method, with the variance of the average of the homogeneity and stability studies[2]. Furthermore, the Horwitz uncertainty was calculated. This is a widely used empirical method that estimates expected analytical uncertainty based on analyte concentration. Elements found in low concentrations in the sample are expected to have greater associated analytical uncertainty. The relationship between the observed uncertainty and the Horwitz uncertainty is expressed by the Horrat index. The coffee leaf reference material was considered homogeneous and stable for its intended use. Reference values were obtained for the elements B, Ba, Br, Ca, Ce, Cs, Cu, Fe, K, La, Mn, Mo, Na, P, Rb, Sc, Sm, Sr, and Zn, with a Horrat index > 0.97, indicating that the analytical techniques used to assign the reference values present smaller analytical errors than those theoretically expected according to the Horwitz model.

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Tracing Copper Fungicide Uptake and Distribution in Pea Plants and Soil Using ^{65}Cu Isotope Labeling

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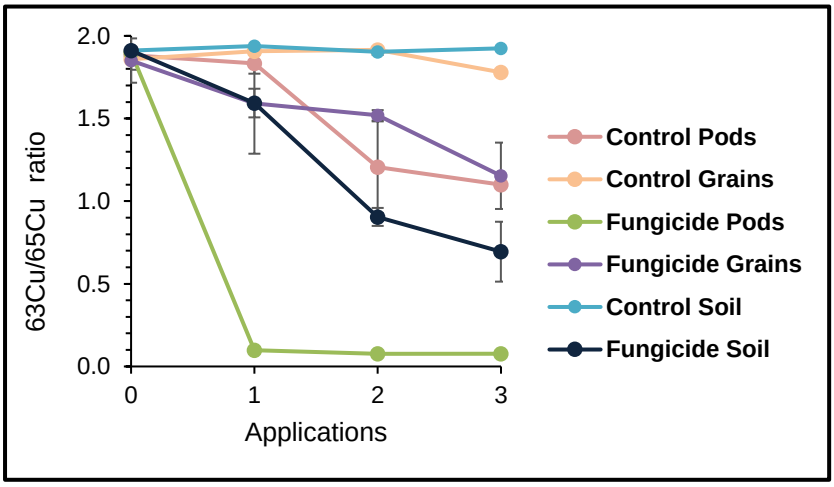
Copper-based fungicides are commonly used in grain farming to prevent yield losses and undesirable changes in organoleptic properties. However, the ingestion of these compounds can pose significant health risks to humans and animals when exposed through the oral route of absorption. To evaluate whether copper from foliar-applied fungicides can be absorbed and translocated to edible plant tissues, this study investigates the mobility of copper from a copper oxychloride fungicide using ^{65}Cu as a stable isotope tracer. A greenhouse system was established to grow peas *(Pisum sativum L.)* and simulate agricultural fungicide applications. The ^{65}Cu-labeled copper oxychloride fungicide was synthesized in-house and fully characterized by X-ray diffraction (XRD), Raman spectroscopy, and Fourier-transform infrared (FTIR) spectroscopy. Three applications of the fungicide (0,073g of total copper) were performed in a greenhouse pea growing system, while a control system received ultrapure water. After each application, surface soil, pods, and grains were collected, dried, ground, and digested. Total copper concentrations were measured via ICP OES, and $^{63}Cu/^{65}Cu$ isotopic ratios were analyzed using ICP-MS. Trends in isotopic ratio and total copper accumulation are visualized through the time series below, indicating the fungicide's mobility and its accumulation in plant tissues and soil.



Samples exposed to the copper fungicide exhibited markedly reduced $^{63}Cu/^{65}Cu$ isotopic ratios, indicating the uptake of the ^{65}Cu tracer. Pod samples from the treated system showed a sharp decrease, especially after the first application. In the control grains, isotopic ratios stayed consistent throughout the experiment, reflecting the absence of direct contact with the fungicide. Conversely, grains from the treated system showed a consistent decrease in isotopic ratio values throughout the three applications. This pattern suggests a possible mechanism for absorbing or transferring copper isotopes from the pods to the grains, indicating the potential for internal contamination of edible plant tissues, even when the fungicide is applied externally. A similar trend was observed in the topsoil: while isotopic ratios remained constant in the control soil, the treated soil showed a consistent decrease after each application. These findings indicate that the copper fungicide is not only absorbed by aerial plant parts but also accumulates in the soil over time. Altogether, the use of ^{65}Cu isotope tracing proved highly effective in assessing the systemic mobility, transfer, and environmental persistence of copper-based fungicides under controlled greenhouse conditions.

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[BAM, CAPES, CNPQ, FAPESP]

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Development and Validation of an ICP-MS Method for Uranium Analysis in Urine: Support for the Individual Monitoring Program for Occupational Exposure

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CNEN NN 3.01 regulation establishes the mandatory implementation of an individual monitoring program for occupationally exposed individuals (OEI) with the aim of ensuring radiological protection of workers in nuclear facilities through the assessment of internal and external exposure[1]. Internal exposure and incorporation are major concerns due to the direct irradiation of internal organs by alpha and beta radiation, which increases the risk of cellular damage and cancer development[2]. Once absorbed, approximately 98% of uranium is excreted in urine, however, the remaining 2% can persist in the kidneys and bones for extended periods[3]. Conventional dosimeters are not able to measure incorporation, so bioassays or in vivo counting are essential. Therefore, urine analysis is one of the most effective ways to evaluate the incorporation of radionuclides as uranium. This study explored one of the most robust techniques for uranium determination: inductively coupled plasma mass spectrometry (ICP-MS). This technique is robust due to its high sensitivity, analytical throughput and simplicity of sample preparation compared to other techniques used for the same purpose, such as alpha spectrometry. Urine samples were therefore collected and submitted to dilution (1:20 v/v) with 2% nitric acid prior to ICP-MS analysis. The calibration method involved the use of uranium standards with concentrations ranging from 10 to 40 ng/L, with the continuous introduction of ^{115}In as the internal standard. This methodology was validated in accordance with Inmetro's DOQ-CGCRE-008 guideline[4], yielding results with low quantification limits in the range of 10 ng/L (ppt) and recovery rates ranging from 75.5% to 113.2%. This enables the implementation of a new analytical method to support Ipen's program, thereby strengthening the safety of radiological protection for OEIs.

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SILVER QUANTIFICATION IN PERSONAL PROTECTIVE MASKS: A SUSTAINABLE STRATEGY USING LA-ICP-MS

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Silver and silver nanoparticles (AgNPs) are widely used for their antimicrobial properties in personal protective masks and became essential during the COVID-19 pandemic due to their potential to reduce viral transmission. However, their increasing use raises concerns regarding potential impacts on human health, animal health, and the environment, concerns that align with the One Health concept. Therefore, sensitive and sustainable analytical methods are increasingly required for the quality control of such products[1]. This study aimed to optimize Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) for the determination of total silver content in protective masks and to compare its performance with conventional methods, such as microwave-assisted acid digestion followed by ICP-MS analysis. Personal protective masks (n=2), composed of polyester and cotton of different colors were purchased from commercial establishments in Rio de Janeiro. Blanks comprised 100% cotton, lint-free fabric. The same fabric was used to prepare the calibration curve for the LA-ICP-MS analysis. The masks were cut into 1 cm^2 quadrants to ensure that the analyzed pieces had homogeneous areas. For total silver determination, the masks were subjected to microwave-assisted acid digestion. The digested samples were analyzed using an ICP-MS, model NexION 300D, Perkin Elmer. For direct analysis, an ICP-MS spectrometer model 8900 Triple Quadrupole ICP-QQQ, Agilent coupled to a Nd:YAG laser ablation system, was used. To evaluate Green Analytical Chemistry (GAC), the AGREE program was employed, which uses 12 parameters to calculate a "greenness" index, facilitating comparison between methodologies based on environmental and safety criteria such as reagent use, energy consumption, analysis time, and waste generation[2]. The LA-ICP-MS technique was optimized by adjusting the parameters of energy (40–80%), spot size (40–120 µm), and ablation speed (5–50 µm s^{-1}), aiming to improve ablation efficiency and analytical quality. The ideal energy was 60%, with a spot size of 120 µm and an ablation speed of 50 µm s^{-1}. The frequency was maintained at 20 Hz to ensure reproducibility. Signal normalization was performed using ^{13}C as an internal standard to compensate for variations in the ablation rate and improve result accuracy. For validation, NIST 612 reference material was used, despite the difference in matrix compared to the fabric. Three ablations were performed under optimized conditions, showing good reproducibility (%RSD < 15%). The limit of quantification of LA-ICP-MS was 5 mg L^{-1}, higher than the conventional ICP-MS detection limit of 2.5 µg L^{-1}, which limits the application of LA-ICP-MS for samples with low silver concentrations. After optimization, the samples were analyzed by LA-ICP-MS, with ablations performed in randomly distributed zones on the fabric surface, carried out in a line. The comparison between LA-ICP-MS and conventional ICP-MS (after microwave digestion) showed that both techniques are suitable for quantifying ionic silver. Sustainability evaluation using the AGREE software demonstrated superior environmental performance for LA-ICP-MS due to its lower waste generation and reduced chemical usage, despite slightly higher energy consumption. Overall, LA-ICP-MS presents itself as a promising, efficient, and greener alternative for the quality control of silver-containing health products, supporting safer and more sustainable analytical practices.

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VALIDATION OF AN ANALYTICAL METHOD FOR THE DETERMINATION OF NUTRIENTS AND CONTAMINANTS IN FISH FROM THE LOWER SÃO FRANCISCO RIVER USING PLASMA TECHNIQUES.

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Analytical validation is an important tool that enables, through the systematic evaluation of a method via experimental tests, the assurance of the reliability and reproducibility of the obtained results, providing evidence that the specific requirements for its intended use are met. The Lower São Francisco (BSF) region plays a vital role in socioeconomic development and the preservation of local culture. However, the impacts of human activities can lead to the accumulation of harmful substances, such as potentially toxic elements, in aquatic organisms[1,2]. Continuous monitoring of water parameters, fish fauna, and flora is crucial for assessing environmental impacts, identifying reliable bioindicators, ensuring food safety, and supporting sustainable management policies[3]. In this experiment, the development and validation of an appropriate analytical methodology for determining inorganic nutrients and contaminants in fish collected from the BSF were carried out. Analyses were performed using optical emission spectrometry with microwave-induced plasma (MIP OES) and inductively coupled plasma mass spectrometry (ICP-MS). The validation parameters and acceptance criteria were defined according to the characteristics of each analyte. Therefore, the optimal digestion conditions (using diluted acid)[4] and determination procedures were established, including the evaluation of detection (LOD) and quantification (LOQ) limits, linearity, precision, and accuracy, using certified reference materials and addition-recovery tests. Fe, Zn, Cr, Cu, V, Ni, Co, Mo, Mn, Se, Sr, As, Cd, Hg, and Pb were determined by ICP-MS, while Ca, K, Mg, and P were determined by MIP OES in 136 samples collected from two weather stations over 12 months. For the first time, the mineral profile of fish from the BSF was obtained, indicating satisfactory nutrient levels in accordance with daily consumption recommendations and contaminant levels below the limits established by legislation. The parameters evaluated during validation (linearity, selectivity, accuracy, and precision) were suitable for determining the analytes within the criteria set by regulatory agencies ANVISA (National Health Surveillance Agency) and INMETRO (National Institute of Metrology, Quality, and Technology).

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[CNPq, CAPES, BNDES (BRSAqua)]

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Green ultrasound-assisted NADES extraction for multielement determination in tea leaves by ICP spectrometry

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Tea (*Camellia sinensis*) is one of the most consumed beverages worldwide, and monitoring potentially toxic and essential elements in tea leaves is crucial for food safety and human health. Conventional multi-element analysis typically relies on acid digestion, which requires hazardous reagents and extensive processing, posing environmental and operational challenges. Natural deep eutectic solvents (NADES) offer a green alternative, being biodegradable, non-toxic, and efficient for the extraction of target elements. When combined with ultrasound-assisted extraction (UAE) and optimized through response surface methodology, NADES-based methods enable reproducible, high-performance, and sustainable sample preparation, aligning with Green Analytical Chemistry (GAC) principles. In this study, a UAE-NADES method was developed for the determination of toxic (As, Cd, Pb) and essential (Cu, Fe, Mn, Zn) elements in tea leaves using ICP-OES and ICP-MS. The NADES, composed of choline chloride, oxalic acid, and water (1:1:1 molar ratio), was prepared on a hot plate and exhibited high extraction efficiency. Optimal conditions were achieved with a 40-minute extraction time, 80 °C, and 3.00 mL of solvent. Method performance was evaluated with certified reference materials, with recoveries ranging from 73% to 107% and relative standard deviations <10.0%. The limits of quantification (LOQ, mg kg^{-1}) were 0.021 (As), 0.019 (Cd), 0.86 (Cu), 9.70 (Fe), 3.23 (Mn), 0.062 (Pb), and 2.12 (Zn). Application to tea leaf samples showed concentrations (mg kg^{-1}) of 0.021–0.130 (As), 0.024–0.523 (Cd), 6.67–18.03 (Cu), 50–714 (Fe), 56–3203 (Mn), 0.063–1.02 (Pb), and 17.2–62.6 (Zn). The estimated daily intake (EDI, mg/day) from a daily tea consumption of 11.4 g was calculated and compared with the recommended dietary intake (RDI) values set by the Brazilian Health Regulatory Agency (ANVISA).[1,2] EDI values ranged from 0.03–0.19 (Cu), 0.01–2.71 (Fe), 0.21–33.50 (Mn), and 0.07–0.65 (Zn), underscoring their nutritional and toxicological significance. The UAE-NADES method yielded results comparable to reference methods and proved to be simple, efficient, safe, and cost-effective, while aligning well with GAC principles (AGREE: 0.68; AGREEprep: 0.58). These results highlight the potential of UAE-NADES as a sustainable alternative for multielement analysis in complex food matrices, addressing both environmental and consumer safety concerns.

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[CAPES, FAPES, CNPq, UFES]

Microcrystalline cellulose beads for separation and speciation of Gd(III) and Gd-Chelate in water

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Gadolinium-chelates (Gd-chelates) have been widely used as based contrast agent with clinical magnetic resonance imaging (MRI). The usual dose is 0.1 mmol per kg of the patient. Gd-chelates are hydrophilic, thermodynamically stable and kinetically inert, is administered intravenously and is rapidly eliminated intact primarily through the kidneys into the urine. It is now well-established that the species of Gd(III) is partially retained in vivo and is toxic. Gd(III) is also retained in the brain, bone, skin, and other tissues in patients with normal renal function. In patient with renal disease, the retention of Gd-chelate is associated with nephrogenic systemic fibrosis disease.[1] Extensive use has led to increased Gd levels in industrialized parts of the world, adding to natural occurrence and causing environmental and health concerns.[2] Separation of the Gd chelates was achieved with high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). For detection, various methods were employed, including UV vis absorbance and fluorescence spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and inductively coupled plasma mass spectrometry (ICP-MS).[3] In this work a method for separation of Gd(III) from Gd-chelate in water sample base on selective adsorption of Gd(III) onto microcrystalline cellulose beads (MMC-beads) and determination by ICP OES. For MCC-beads preparation, a mixture of 7% (w/v) of NaOH plus 12% (w/v) of urea was added to 5% (w/v) of microcrystalline cellulose and kept at 10 ºC, under magnetic agitation (200 rpm) for 20 minutes; after this solution was dripped in 2 mol/L HCl as coagulant media, using a peristaltic pump. For column packing, 300 mg of dry MCC-beads (d ~ 500 µm) were mixed to 10 mL of deionized water and added to the polypropylene column (0.8 cm internal diameter) and porous polyethylene frits (0.8 cm diameter; > 1 µm pore size). The column was packaged only with the action of gravity. A volume of 20 mL of water passed through out of the column and after washed with water, the Gd(III) adsorbed was desorbed with 2 mL of HCl 1 mol/L and analyzed by CP OES. Analysis of tap water, river water and dam water, without and with addition of 5 µg/L of Gd(III), 5 µg/L of Gd-chelate and a mixture of 5 µg/L of Gd(III) + 5 µg/L of Gd-chelate Gd(III) were done using the proposed column system. The concentrations of Gd(III) in waters samples was below to the LOD (4 µg/L). Good recoveries of added Gd(III) was obtained for tap water (101±1%), river water (95±3%) and for dam water (98±5%) demonstrated accurate quantification, after separation using the proposed MCC-beads as adsorbent. For separation of Gd(III) and Gd-chelate in the water samples, recoveries range from 92±4% to 102±5%. Overall, the results demonstrated the efficiency of MCC-beads for separation and speciation of Gd(III) from Gd-chelate from natural water samples. In conclusion, these results of non-chromatographic method allowed rapid assessing of toxic specie of Gd(III), predicting potential risks of these element in water sources.

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Preparation of a Calibration Material for Application in Laser-Induced Breakdown Spectroscopy (LIBS)

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LIBS is a multielement analytical technique applicable to solid, liquid, and gaseous samples. However, due to its microsampling nature and the requirement for matrix matching, arising from the laser–sample surface interaction, one of the main challenges in routine quantitative LIBS analysis is the lack of suitable calibration materials.

The aim of this work was to develop a calibration material using photographic paper as a solid substrate. For this purpose, the paper was immersed in a multielemental solution containing the metals Al^{3+}, Co^{2+}, Cr^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+}, along with the complexing agent (trisodium salt of 1,8-dihydroxy-2-(4-sulfophenylazo)-3,6-naphthalenedisulfonic acid, SPADNS), forming ion pairs with dodecyltrimethylammonium bromide (DTAB) for efficient retention on the solid substrate.

The extraction conditions (pH, SPADNS and DTAB concentrations, paper area, and ultrasonic bath conditions) were optimized using Fractional Factorial Design and Central Composite Rotatable Design. From this study, the optimized conditions were: 1.6×10^{-2} mol L^{-1} SPADNS, 3.2×10^{-3} mol L^{-1} DTAB, phosphate buffer at pH 8.0, paper area of 9.0 cm^2, and ultrasonic bath 37 kHz, 100% power, for 30 min at 40 ºC. The LIBS instrumental parameters (laser energy, number of accumulated pulses, delay, and integration time) were optimized univariately, and the best conditions were: laser energy of 150 mJ, 7 accumulated pulses, 2.5 µs delay, and 13 µs integration time[1].

With the optimized extraction conditions and instrumental parameters, calibration curves were obtained. The linear response ranges were 0.50–10.0 mg L^{-1} (Al, Cr, Mn, and Zn), 1.0–10.0 mg L^{-1} (Co), and 0.50–5.0 mg L^{-1} (Cu), with precision ranging from 4.2% to 28%. Using internal and external standard calibration strategies, the efficiency of the calibration material was demonstrated through spiking and recovery tests in certified reference materials of freshwater (Cu, Cr, and Zn), wastewater (Al and Cr), and blood serum (Al, Cr, Mn, and Zn), employing the extraction strategy[1].

For non-aqueous liquid samples, such as colored nail polishes (Al, Cu, and Mn), printer ink (Cu), and mineral oil Conostan® (Cr, Cu, and Mn), analysis could be performed by simple deposition onto the matte paper surface, without the need for prior preparation. The results were consistent with those obtained by ICP OES after digestion and with the certified values of Conostan®. Recoveries of the spiked analytes ranged from 81% to 123%, and relative errors compared to certified values were between 0.40% and 25%, confirming the effectiveness of the calibration material for the determination of Al, Cr, Cu, Mn, and Zn in samples with very distinct characteristics[1].

The developed calibration material is low-cost, since extraction on matte paper with 10.0 mL of the metal complex solution allows the production of at least four calibration units. Therefore, the results highlight its potential for the determination of these metals in complex samples, such as printer ink, nail polish, and mineral oil, without the need for prior preparation, establishing it as a promising strategy for LIBS applications.

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DILUTED ORGANIC ACIDS AS GREENER EXTRACTANTS FOR TRACE METAL ANALYSIS IN BIODIESEL AND FEEDSTOCKS BY ICP–OES

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Animal fats and vegetable oils are usual feedstocks for biodiesel production, offering a renewable alternative to fossil fuels. However, their complex chemical composition represents a challenge for trace metal analysis, which is needed for quality control and environmental issues. Metals such as Ca, Mg, Cu, Al, and Fe may remain in biodiesel as a result of the catalytic process and the raw material itself, and above regulation limits (5.0 mg kg^{-1} for Ca and Mg) can cause corrosion and blockage of engine components[1,2]. Inductively coupled plasma optical emission spectrometry (ICP–OES) is the recommended technique for elemental analysis, however, the high lipid content from these samples requires time-consuming microwave-assisted acid digestion (MW–AD), typically using concentrated acids and oxidants (e.g. HNO_3 and H_2O_2), and the amount of residual carbon may be critical for ICP–OES determinations. As a greener alternative, formation of stable metal complexes with organic acids, such citric (CA) and tartaric (TA) acids, has been exploited for e.g. contaminated soil[3] and lithium-ion batteries[4], but the approach was not exploited for biodiesel samples. This work aims to develop a greener sample preparation procedure for the determination of metals in biodiesel by ICP–OES, using diluted organic acids as extractants. Reference samples (pork lard and biodiesel) previously digested with MW–AD (1.0 mL HNO_3, 3.0 mL of 30% v/v H_2O_2, and 4.0 mL of water), using an Ethos 1600 (Milestone, Italy) microwave, with a heating program consisting of a temperature ramp to 240 °C in 40 min followed by a 40 min hold, were analyzed by ICP–OES (iCAP 7400 Duo, Thermo Scientific, USA) and used for the univariate optimization of the extraction procedure. Effects of acid concentration, sample mass, acid volume, extraction time, and temperature were evaluated. The optimized condition that provided the highest recoveries was 1.5 mL of sample, 3.0 mL of 2.0 mol L^{-1} organic acid solution, heating at 90 ºC for 30 min in water bath, followed by a 7-fold dilution of the aqueous phase. Analytical curves using multielement standard (Al, Cd, Cr, Cu, Mo, Ni, P, Pb, V, Mg, Ca, P, Si, Al, Na, Mn, Zn, and Fe) were prepared using Y and Ga as internal standards in CA and TA media. In this study, CA and TA demonstrated significant potential as green alternatives for metal extraction from pork lard, particularly for Ca, Mg, Al, Mn, Zn, and Fe with extraction efficiency ranging from 80±3% to 87±3% (CA) and 79±4% to 94±5% (TA), whereas Na was extracted exclusively with TA (79±2%). In biodiesel, the results were consistent for Ca, Mg, and Al with extraction efficiency between 96±4% to 107±1%. Recoveries in biodiesel samples spiked with an organometallic multielement standard demonstrated absence of matrix effects: Ca (79±4% to 83±5%), Mg (78±3% to 95±3%), Al (84±2% to 84±3%), Na (102±8%), Mn (91±1% to 99±3%), Zn (86±1% to 96±4%), Ti (84±1% to 91±4%), V (89±1% to 98±4%), Cr (79±1% to 78±3%), Ni (91±1% to 96±3%), Cu (80±1% to 90±3%), Cd (86±1% to 92±3%), Pb (83±1% to 82±5%), Mo (83±1% to 86±4%), and Fe (82±2% to 88±6%), except for P and Si (below 50% for CA e TA) and Na for CA. Accuracy was confirmed by comparison with MW-AD, showing agreement at the 95% confidence level. This sample preparation method aligns with green chemistry principles, with citric and tartaric acids demonstrating higher greenness compared to conventional MW–AD (AGREEprep = 0.64 (proposed procedure) vs. 0.28 (MW-AD)). These findings confirm the feasibility of using diluted organic acids as sustainable extractants, reducing energy demand and reagent consumption while ensuring reliable elemental analysis of biodiesel and fat-rich feedstocks.

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INVESTIGATION OF PREDICTOR PARAMETERS FOR P DETERMINATION IN SOIL BY SD-LIBS

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The quantitative determination of P in soils is essential for both environmental and agronomic studies. Conventional methods, however, often require sample preparation steps involving hazardous reagents and additional chemical inputs during quantification. This contrasts with the growing demand for clean analytical approaches, aligned with the principles of green chemistry, which aim to minimize or eliminate post-analysis waste. Thus, developing new strategies for P determination represents not only a scientific challenge but also an opportunity to advance more sustainable, safer, and efficient methodologies.[1] In this context, Laser-Induced Breakdown Spectroscopy (LIBS) has emerged as a promising alternative, enabling rapid, direct analyses with minimal sample preparation.[2] Moreover, recent studies have demonstrated that coupling LIBS with a spark discharge (SD) system can significantly enhance the detection of P atomic lines in fertilizer analysis.[3] Building on this, the present study conducted a preliminary investigation of predictor variables for P determination in soils as a basis for future calibration models. Twenty soil samples with different textures were analyzed. Reference concentrations of P were obtained after conventional sample preparation and determination by spectrophotometry[4]. In parallel, homogenized samples were pressed into pellets and analyzed by SD-LIBS under argon flow. Spectra were normalized using the argon atomic emission line at 420.06 nm. In the initial stage, ten variables were selected: three atomic emission lines of P (213.61, 214.91, 253.60 nm) and seven PO molecular emission bands (246.35, 246.40, 246.45, 246.61, 247.79, 324.86, 327.40 nm). Linear correlations, evaluated using Pearson's coefficient (R), showed no significant association for most variables, except for the bands at 324.86 nm (R = 0.54) and 327.40 nm (R = 0.50). These findings highlight the potential of molecular fragment-related variables in constructing linear calibration models. In addition, the combined contribution of variables was assessed by multiple linear regression (MLR), considering all possible two- and three-variable combinations. A systematic analysis in Visual Basic for Applications was performed, generating 165 MLR models, which were evaluated by 10-fold cross-validation to assess generalization performance. Pearson correlation coefficients from the predictions were then ranked. The results showed that the highest linear correlations were consistently obtained when combining the P atomic emission line (253.60 nm) with PO molecular bands (246.45, 246.61, 246.35, and 327.40 nm), either in two- or three-variable models. These outcomes emphasize the joint relevance of both atomic and molecular emission features for P prediction in soils, by linear models.

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Development of a spectrometric analytical platform for studying selenium nanoparticles in environmental contexts

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Analytical characterization of nanoparticles and understanding their transformation in complex environmental matrices requires complementary and robust spectroscopic tools capable of capturing the physicochemical changes at the single-particle level. This study demonstrates an integrated multi-spectrometric platform to comprehensively characterize selenium nanoparticles (SeNPs) and elucidate their behavior and interactions with soil constituents and cadmium ions.

SeNPs were synthesized via microwave-assisted green protocols, and subsequently exposed to soil fractions differing in composition and salinity. In addition, the Chernozem soils, with and without Cd contamination, were amended with orange juice-derived SeNPs to assess environmentally relevant transformations.

A multi-spectrometric analytical platform combined three advanced techniques to capture complementary dimensions of SeNPs behavior. Single particle inductively coupled plasma mass spectrometry (SP ICP MS) enabled the monitoring of the size and size distributions of core SeNPs and their particle number concentration, while capillary electrophoresis coupled to ICP MS (CE-ICP MS) provided the separation and detection of SeNP-ligand conjugates and the investigation of the surface coating dynamics. Single particle microwave plasma optical emission spectrometry (SP MWP OES) delivered element-specific spectral fingerprints, enabling time-correlated emission detection of selenium, carbon, and cadmium, thereby revealing organic surface coatings and direct Se–Cd associations at the particle level. For SeNPs, the size detection limits (LOD_{size}) were estimated to be 52 nm in SP MWP OES and about 30 nm in SP ICP MS depending on the sample type and ionic background. Spectrometric signatures demonstrated that sulfur- and nitrogen-rich soil fractions enhanced SeNP stability, whereas high salinity promoted aggregation. Reduced extractable Cd concentrations in SeNP-amended soils, combined with Se–Cd co-detection signals, confirmed decreased Cd mobility.

The proposed analytical platform demonstrates that integrating multiple spectrometric techniques provide a comprehensive spectral profile of nanoparticles, correlating their physicochemical stability or transformations with environmental processes. This approach highlights the capability of advanced spectroscopy to monitor nanoparticle behavior in complex soil matrices and supports the potential application of SeNPs as sustainable fertilizers and Cd immobilizers.

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In Vitro Bioaccessibility and Bioavailability of Metals in Fish from a Mining Region of Minas Gerais, Brazil: Human Health Risk Assessment

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In recent years, the continuous contamination of Brazilian river tributaries by toxic metals, resulting from anthropogenic activities (especially mining) and associated environmental disasters, has become a major concern in the country[1]. Mining tailings dams collapsing in Mariana (2015) and Brumadinho (2019), both in the state of Minas Gerais (MG), are emblematic examples of environmental tragedies that released large quantities of toxic metals into local river basins[2]. In this context, assessing the bioaccessibility and bioavailability of metals in fish caught in the Rio Doce basin (which received most of the waste associated with the 2015 and 2019 events) is essential to assess the risks to human health, especially for exposed riverine populations. This study systematically investigated the bioaccessibility and bioavailability of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in samples of fish (*Paralichthys brasiliensis*) obtained from a street market in Mariana, MG. The analytes were determined by inductively coupled plasma mass spectrometry (ICP-MS), and the method's accuracy was evaluated using a certified reference material (Mussel Tissue, NIST SRM 2976). The bioaccessible fractions of metals found (mg kg^{-1} / %) were Cd (0.028 / 61%), Co (0.049 / 61%), Cr (0.304 / 57%), Cu (0.144 / 11%), Fe (11.51 / 52%), Mn (0.223 / 38%), Ni (0.110 / 36%), Pb (0.226 / 47%), and Zn (12.49 / 53%). The bioavailable fractions (mg kg^{-1} / %) were Cd (0.011 / 4%), Co (0.022 / 7%), Cr (0.124 / 3%), Cu (0.038 / 2.7%), Fe (3.513 / 16%), Mn (0.015 / 2.6%), Ni (0.022 / 7%), Pb (0 / 0%), and Zn (4.366 / 18%). Monte Carlo simulations with 10,000 iterations were used to assess the risks to human health for different age groups (children and adults) based on each element's estimated daily intake (EDI)[3], hazard quotient (THQ), and carcinogenic risk (CR)[4]. EDI values calculated for Cd, Co, Cr, Ni, and Pb were within the provisional tolerable daily intake limit ($<10^{-5}$ mg kg^{-1}). The total toxic effect (TTHQ, which combines all elements) remained below 1, indicating a non-significant risk, while CR values remained within the acceptable range (10^{-6} to 10^{-4}). However, a probabilistic analysis ($p < 0.05$) of the CR results revealed that children are more vulnerable to carcinogenic effects due to exposure to Cd, Co, Cr, Ni, and Pb. In contrast, low THQ and CR probabilities were calculated for adults, indicating a lower vulnerability of this group considering the concentrations observed in this study.

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Green approach for the preparation of oily samples: multielement determination via ICP OES after extraction induced by emulsion breaking

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Determination of the contaminants in oily matrices is essential for quality control, since, the oils high consumption and production generally lead to contamination during the refining process, or other factors that can increase the concentration of toxic agents and unwanted components in the oil, such as metals. Because oils are complex matrices, direct analysis is difficult, and therefore, sample preparation is necessary to determine the concentration of such contaminants. Established methods in analytical chemistry, such as acid digestion and dilution in organic solvents, require significant energy expenditure and the use of toxic solvents. Therefore, alternative methods that are less harmful to the environment are desirable. Green Analytical Chemistry (GAC) emerges as an ally in evaluating analytical methods, considering criteria such as toxic waste generation, energy efficiency, solvent/reagent safety, and analyst safety [1].

In this context, the aim of this work was to develop an analytical method combining extraction induced by emulsion breaking (EIEB) [2] with the ICP OES technique for the determination of Cd, Cr, Cu, Ni, Ti, and V in mineral, edible, and essential oil samples, and biodiesel reference material.

The emulsion was first formed in different media (1.0 mL) [3]: (i) Triton X-114 (2% w/v) and HNO_3 (3% v/v); (ii) Triton X-114 (2% w/v), HNO_3 (3% v/v), and 1-butanol; (iii) Triton X-114 (2% w/v), HNO_3 (3% v/v), and 2-propanol; (iv) HNO_3 (3% v/v) and 1-butanol; and; (v) HNO_3 (3% v/v) and 2-propanol. Emulsion formation of 1.0 g of sample in the different media occurred through vortex mixing, and breakdown was assessed by heating, centrifugation, and the addition of HNO_3 or deionized water. Metals were determined in the aqueous phase using ICP OES, and extraction capacity was assessed using an organometallic standard (Conostan®).

Based on the results obtained, the selected compromise condition was the addition of 1.0 mL of a mixture of TX-114 (2% w/v) and HNO_3 (3% v/v), followed by vortexing for 60 seconds and emulsion breaking by heating at 90 °C for 15 minutes. When compared to a previous study developed by the research group [3], this approach enabled an increase in analytical frequency. The efficiency of the proposed method was evaluated by spiking all samples with different concentrations of Conostan® (60, 120, and 240 μg kg^{-1}). The recovery results varied depending on the oil matrix: an average of 90% for mineral oil; 83–106% for biodiesel; approximately 89% for eugenol; and between 70% and 95% for lavender and lemon oils. The edible oil samples exhibited the most variable recovery percentages. Using the standard addition curve, it was possible to determine the metal concentrations in most samples. For instance, the concentration determined for the biodiesel reference material (B-100 soy-based SRM 2772 – NIST) was agreed (102%) with informed value (20 μg kg^{-1}).

These results demonstrate the potential of EIEB as a sample preparation method, with recovery rates ranging from 80% to 110% for most metals studied across various oil matrices. It is important to highlight that the entire method was optimized using mineral oil as the base matrix, yet it proved effective for oil samples with distinct characteristics.

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ACCURATE DETERMINATION OF ALKALINE AND ALKALINE-EARTH ELEMENTS IN CRUDE OIL BY ICP-OES AFTER MICROWAVE-ASSISTED EXTRACTION

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Alkaline and alkaline-earth elements are usually found in the aqueous fraction of crude oil emulsions, as inorganic salts. The presence of these elements in crude oil may cause poisoning, corrosion, and salt deposits on pipes and towers of distillation, even at low concentrations.[1,2] In this way, accurate methods for further alkaline and alkaline-earth elements determination in crude oil are required. However, some drawbacks are observed for conventional methods for crude oil digestion for further Ba, Ca, K, Mg, Na, and Sr determination, such as the wide concentration range of these analytes, the problems related to contamination and sample projection, as well as the limited sample amount for closed systems. To overcome these problems, extraction with diluted solutions, or even water, can be used. When combined with the use of auxiliary energy sources, such as microwaves, this approach presents a promising alternative to conventional decomposition methods. In the present work, the microwave-assisted extraction (MAE) method was developed for further Ba, Ca, K, Mg, Na, and Sr determination in crude oil by inductively coupled plasma optical emission spectrometry (ICP-OES). A microwave-assisted sample preparation system (Multiwave 3000, software version v2.02, Anton Paar, Austria) equipped with eight high-pressure quartz vessels (internal volume, maxima temperature, and pressure of 80 mL, 280 °C, and 80 bar, respectively) was used for the MAE method. The microwave-assisted wet digestion in a pressurized digestion cavity (MAWD-PDC) using concentrated HNO_3 and analyte determination by ICP-OES were applied to obtain the reference values. For the MAWD-PDC method, a high-pressure microwave-assisted digestion system (Multiwave 7301, Anton Paar, Austria) equipped with five quartz vessels (80 mL), with maximum temperature and pressure of 265 ºC and 160 bar, respectively, was used. Barium, Ca, K, Mg, Na, and Sr determination was performed using an inductively coupled plasma optical emission spectrometer with axial view (Perkin Elmer, modelo Optima 4300DV, Shelton, EUA) after MAE and MAWD-PDC methods. To assess the analytical, environmental, and practical requirements of the methods used for alkaline and alkaline-earth elements determination in crude oil, the White Analytical Chemistry (WAC) metric was employed.[3] The following parameters for MAE were evaluated: *i*) crude oil mass (1 to 10 g), *ii*) water volume (6 to 20 mL), which was used as extractor solvent, *iii*) temperature (100 to 240 °C), and *iv*) extraction time (1 to 30 min). Under optimized conditions, no statistical difference (*t*-test, confidence level 95%) between the results obtained by the MAE method and the reference values was observed. Due to the use of a high sample mass (10 g) and water as the extraction solution, the quantification limits were very low (ranging from 0.001 to 0.1 μg g^{-1}, for Ba and Na, respectively). The proposed MAE method can be considered a simple and fast tool for sample preparation of crude oil for further alkaline and alkaline-earth metals determination at low concentrations. In addition, the MAE method and ICP-OES determination proved to be a good option for the simultaneous determination of Ba, Ca, K, Mg, Na, and Sr in crude oil, achieving higher scores in analytical, environmental, and practical criteria. In this way, the MAE method can be used as an accurate alternative method for routine analysis in the petroleum industry.

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Determination of potentially toxic elements in sweeping dust from Early childhood education center in Florianópolis, Brazil by ICP-MS.

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Air quality is a major global public health concern, with children representing one of the most affected groups. In Brazil, wildfires and urban expansion exacerbate the presence of dust and suspended particles[1], which can even reach school environments. Such dust may serve as a source of potentially toxic elements (PTEs) and organic compounds. Children aged 0–5 years are particularly vulnerable due to their greater proximity to the ground and higher respiratory rates relative to body weight, which increase both ingestion and inhalation of contaminants. These exposures can impair neurological development and contribute to chronic diseases[2]. Because of the complexity of the dust matrix, composed of particles of varying sizes (≤100 µm), specific sample preparation was required for pollutant determination. This study aimed to optimize the preparation of dust samples collected by manual sweeping from indoor and outdoor environments of two early childhood education center in Florianópolis, Santa Catarina, Brazil, during April and May 2025. The samples were subjected to both bulk and microwave-assisted digestion to compare and evaluate the effectiveness of the techniques. The optimized methodology employed 10–100 mg of sample, 3 mL of HNO_3, 2 mL of H_2O_2, 1 mL of HCl, 1 mL of HF, and 300 mg of H_3BO_3. The method performance parameters demonstrated satisfactory linearity, with detection limits ranging from 0.1 to 6.7 µg g^{-1}, quantification limits from 0.2 to 20 µg g^{-1}, and relative standard deviations (RSD) below 5%. Accuracy was validated using certified reference materials (BCR-723 and NIST 1648e), achieving >95% agreement at the confidence level for Pb, Cd, Ni, V, Zn, Sb, As, Co, Cu, and Al. Recovery tests yielded satisfactory values (80%–116%) for these 10 analytes, as well as for six additional analytes (Cr, Hg, Mo, Ag, Sn, and Ti). The optimized procedure is currently being applied to dust samples collected from daycare centers for chemometric evaluation, with the goal of assessing differences in exposure between environments and institutions. Quantifiable levels of Pb, Cd, Hg, Ni, Zn, Sb, Co, and Cr have already been detected in real samples from early childhood education center. These findings demonstrate that applying ICP-MS to daycare dust is a promising strategy for evaluating PTEs in school environments, thereby supporting exposure assessment and risk analysis in children.

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[UFSC, CNPq, TAC e CAPES]

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Bioaccessible Metals in Uruguayan Sea lettuce: Dietary Contribution and Cooking Effects via MP AES

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Seaweeds are considered a potential superfood due to their rich chemical composition, which includes antioxidants, vitamins, and essential minerals. It is well known that seaweeds can bioaccumulate essential and toxic elements; therefore, they represent a potential source of elements with both nutritional and toxicological relevance.

Recent studies show that sea lettuce (*Ulva sp.)* from the Uruguayan coast is rich in iron (Fe) and arsenic (As), and has considerable total amounts of other elements such as chromium (Cr) and manganese (Mn). To evaluate its nutritional value and food safety, it is essential to evaluate the absorbed amount of these elements after seaweed ingestion. Since *in vitro* bioaccessibility is a better approximation to the absorbed amount than total content, our research group applied this approach to estimate this parameter and its possible health implications.

In this context, this work aimed to determine the *in vitro* bioaccessibility of the aforementioned elements in *Ulva sp.* collected on the Uruguayan East Coast, and its variation with typical cooking processes (raw, boiling, stir-frying, and seasoned with garlic and with onion), to evaluate their contribution to the recommended dietary allowance (RDA) of essential elements, and assess the compliance of arsenic with international regulations related to seaweeds.

The in vitro method was based on the INFOGEST protocol. Briefly, 1g of the sample was accurately weighed and shaken for 2 minutes with 2.0 mL of saliva-simulated solution (0.7 g of α-amilase in 100.0 mL of ultrapure water) at 37°C. Then, 5.0 mL of the gastric-simulated solution (0.3 g of pepsin and 0.05 g of lipase dissolved in 1.0 mL of HCl 12 mol L^{-1}, filled to 100.0 mL with ultrapure water, pH 1.2) was added, and the mixture was shaken at 37ºC for 2 hours. Then, 5.0 mL of intestinal simulated solution (0.2 g of bile salts dissolved in a solution containing 0.5 g of pancreatin dissolved in 8.0 mL of NaOH 0.2 mol L^{-1}, filled to 100,0 mL, pH 6.8) was added, and the mixture was shaken for another 2 hours at 37ºC. Finally, the mixture was centrifuged at 4000 rpm for 10 minutes, and bioaccessible and residual fractions were separated. Mass balances were performed to evaluate the accuracy of the *in vitro* method. Analytical determinations were performed by Microwave Plasma Atomic Emission Spectroscopy (MP AES) and MP AES coupled with hydride generation (HG MP AES) for arsenic. The analytical methods were previously validated.

Mn was the element with the highest bioaccessibility, with a mean of 58.2%, despite its relatively low total concentration. However, their contribution to RDA was the lowest, representing only 3.3% for men (M) and 4.2% for women (W), considering a 50 g portion of fresh seaweed. Cr and Fe presented significantly lower bioaccessibilities, with means of 27.2% and 21.5%, respectively. Nevertheless, their contribution to RDA was considerably higher, 17% (W) and 12% (M) for Cr, 7% (W) and 15% (M) for Fe, promoting Uruguayan *Ulva* as a potential source of these elements. Arsenic bioaccessible fraction could not be determined since it was lower than the limit of quantification (0.04 mg kg^{-1}, dry basis), representing a bioaccessibility lower than 0.9% and suggesting safety regarding this parameter. Regarding the cooking effect, an ANOVA test confirmed that Cr bioaccessibility increased significantly ($p < 0.05$) after boiling at 100ºC for 5 minutes. Fe presented a bioaccessibility significantly different from boiled at 100ºC for 5 minutes or stir-fried at 120ºC for 5 minutes with a proportion of 4:1 seaweed:olive oil, but no differences were found with raw seaweed. Mn bioaccessibility did not present statistical differences with different cooking processes. Concerning seasoning, adding onion in a proportion 20:1 seaweed:onion, increased iron bioaccessibility from 18.8% to 21.2%. On the other hand, adding garlic in the same proportion decreased chromium bioaccessibility from 30.7% to 25.3%.

Overall, *Ulva sp.* from Uruguay seems to represent a promising nutritional ingredient with low toxicological risk.

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Determination of heavy metals in water, sediments, and vegetation by ICP-OES in the Bitzales area (Tabasco, Mexico)

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River systems in Mexico and worldwide are of high ecological and social relevance and require high-quality analytical data to quantify heavy metals and metalloids across environmental matrices such as water, sediments, and vegetation; in 2018, the mortality of nearly 50 Caribbean manatees (*Trichechus manatus*), an endangered species [1], in the Bitzales area (Macuspana, Tabasco, Mexico) prompted integrated monitoring of these matrices to assess environmental conditions [2]. This study validates an inductively coupled plasma–optical emission spectrometry (ICP-OES) method for routine multi-matrix monitoring in the Bitzal River (Macuspana, Tabasco, Mexico), enabling robust temporal and cross-matrix comparisons. In 2024, ten sites comparable to those sampled in 2018 were revisited. Elemental determinations were performed by ICP-OES (PerkinElmer Avio 500); water was analyzed directly, whereas sediments and plant tissues were oven-dried (70 °C, 24 h), homogenized (grinding for vegetation; disaggregation/sieving for sediments), and digested by microwave-assisted acid digestion (Milestone MLS-1200; 9 mL HNO_3 + 3 mL H_2O_2 for vegetation; 9 mL HNO_3 + 3 mL HCl for sediments). Method development encompassed wavelength selection, evaluation/correction of spectral and chemical interferences, and matrix-specific plasma optimization. For calibration were used certified multielement standards, and QA/QC included procedural blanks and replicates; certified reference materials were analyzed (Orchard Leaves CRM, Cat. #CRM-OL, in 4% HNO_3; NIST® SRM® 2711a Montana Soil II). Data were processed in Syngistix for ICP-OES. Instrumental and method detection limits were estimated from per-element standard deviations and achieved (waters, mg L^{-1}): Al 0.0003, Ba 0.00003, Li 0.0003, Mn 0.00003, Ni 0.0003, Sr 0.0003; (vegetation, mg kg^{-1}): As 0.0006, Ba 0.0006, Cd 0.0003, Cr 0.0003, Li 0.0003, Ni 0.0006, Mn 0.00003, Sr 0.0003, V 0.0012; (sediments, mg kg^{-1}): As 0.0003, Ba 0.0006, Cd 0.0009, Cr 0.0003, Ni 0.0003, Pb 0.0015, V 0.006. Concentrations were reported as mg L^{-1} (waters) and mg kg^{-1} (solids). Mean concentrations (descending) were: waters—Sr (0.270) > Ba (0.027) > Al (0.009) > Ni (0.007) > Li (0.005) > Mn (0.004); vegetation—Mn (1272.241) > Sr (73.876) > Ni (50.020) > Ba (42.281) > Cr (39.663) > V (37.925) > Li (5.424) > As (2.803) > Cd (0.222); sediments—V (1473.286) > Cr (290.429) > Ba (269.403) > Ni (239.648) > Pb (7.868) > As (6.753) > Cd (0.314). The patterns are consistent with anthropogenic inputs and variable environmental conditions; together with per-element spike recoveries >70%, the validated ICP-OES workflow yields accurate, comparable, and traceable data suitable for seasonal environmental monitoring and rigorous temporal and cross-matrix assessments of heavy metals and metalloids.

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Concentration of chemical elements in the visceral mass of oysters (crassostrea virginica) from Puerto Ceiba, Paraíso, Tabasco México using ICP-OES after microwave digestion

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The oyster is characterized as a filtering organism, making it vulnerable to contamination of the aquatic environment, where the presence of various pollutants, such as hydrocarbons and heavy metals, is a significant factor in determining the safety of this species[1]. That is why it is essential to conduct studies to quantify the presence of heavy metals in these foods[2]. Tourist-gastronomic route Puerto Ceiba-El Bellote in the municipality of Paraíso, Tabasco, is characterized by its great tourism and gastronomy, but also by the high activity of the oil industry[3]. Due to the above, in this work, the determination of metalloids and heavy metals in oysters from farms near the gastronomic tourist corridor was carried out. In June 2023, 60 oyster samples were collected from three points at Mecoacan Lagoon (Transformando Mecoacan, Boca los Angeles y Puente Ilusión y Ceiba). The samples have been treated with microwave digestion Millestone MLS 1200 MEGA. Concentration was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)[4]. Mexico has the NOM-242 for the concentration of As, Cd, Hg, and Pb[5]. The Mexican NOM does not establish limits for Cr, Cu, Mn, Ni, and Zn; instead, the concentrations were compared with international regulations. To ensure a quality analysis, a certified dogfish liver reference material (DOLT-5) was tested and compared with concentrations obtained from oyster tissue samples. The levels of Cr (2.687 ± 0.34 mg kg-1), Cu (464.68 ± 68 mg kg-1), Mn (54.54 ±1.3 mg kg-1), Ni (5.097 ±0.010 mg kg-1) and Zn (668.98 ± 98 mg kg-1) exceed the maximum limits established by FAO/WHO (0.1 mg kg-1 for Cr, 10 mg kg-1 for Cu, 0.40 mg kg-1 for Mn, 5 mg kg-1 for Ni and 100 mg kg-1 for Zn)[6]. The determined amount of these metals was higher than that reported in other national and even regional investigations.

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REVEALING SOIL TOTAL ORGANIC CARBON WITH HANDHELD LIBS AND MOLECULAR SIGNATURES

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The soil carbon cycle plays a central role in global warming, making the accurate assessment of Total Organic Carbon (TOC) a critical step in developing effective climate change mitigation strategies.[1] Traditional TOC analysis methods are often time-consuming, costly, prone to errors, and environmentally unsustainable due to extensive sample preparation and significant consumption of chemical reagents.[2] This study presents an innovative, rapid, and reagent-free methodology for the direct quantification of TOC in soils, employing portable handheld Laser-Induced Breakdown Spectroscopy (hLIBS). The method exploits molecular emissions from C_2 and CN fragments, generated from the decomposition of soil organic matter, enabling fast, simple, and accurate TOC determination. A total of 53 soil samples were analyzed. Each sample was compressed into pellets and examined using a compact LIBS system (hLIBS, SciAps Z-903). For each sample, three pellets were prepared, resulting in 192 spectra per sample, which were subsequently normalized using the intensity of an ionic argon emission line at 349.06 nm. The dataset was divided into two subsets: 39 samples for model calibration and 14 samples for independent validation. During the variable selection step, 20 emission wavelengths were chosen, with their peak intensities used as input variables. Among these, 12 wavelengths corresponded to molecular emission bands of CN and C_2 (358.12, 385.60, 386.58, 387.83, 388.67, 413.22, 414.32, 466.80, 468.26, 469.18, 474.32, and 516.79 nm). Additionally, eight supplementary wavelengths showing strong linear correlations with TOC ($R > 0.6$) were also selected (350.19, 351.24, 356.21, 359.63, 359.79, 360.11, 360.18, and 362.40 nm). A Partial Least Squares Regression (PLS) model was then fitted using eight principal components, with data standardized prior to modeling. The developed model demonstrated excellent calibration performance (Rcal = 0.9553) and a mean absolute error (MAE) = 0.2547%. When applied to the validation set, the model maintained satisfactory predictive capability, yielding a Pearson correlation coefficient (Rval) = 0.793 and an MAE = 0.3795%. Overall, the findings demonstrate that hLIBS is a promising technique for TOC determination in soils, providing rapid, accurate, and minimally destructive analyses that can be performed *in situ*. The proposed analytical approach represents an attractive solution to support sustainable soil management strategies and the development of effective practices for enhancing carbon sequestration.

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NANOPARTICLES OR NANOEMULSIONS? BIOACCESSIBILITY OF IRON FROM MILK FORTIFIED WITH NANOSTRUCTURES

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One of the major public health concerns is iron-deficiency anemia, a condition characterized by reduced hemoglobin levels in the blood, often caused by a deficient intake of bioavailable iron. Among the strategies to combat anemia and other nutritional deficiencies, the World Health Organization[1] recommends fortifying staple foods, such as wheat and maize flours, rice, and salt, with vitamins and essential elements. However, iron fortification in other staple foods, such as milk and its derivatives, is challenging. Commonly, iron salts are employed as iron fortifiers. Nevertheless, the presence of ionic iron (Fe^{2+} or Fe^{3+}) affects milk quality and stability and provides a low fraction of bioaccessible iron, making the fortification less effective than desired. On the other hand, the use of nanostructures may provide a better way to encapsulate and deliver iron in a more bioavailable form for the human organism, potentially increasing its absorption. Thus, in this work, two nanostructures, Fe(III) oxo-hydroxide nanoparticles (NPs) and a nanoemulsion (NE) prepared with Ferriprotoporphyrin IX Chloride (heme iron, hemin) as organic phase and whey protein as emulsifier, were evaluated as alternative iron fortifiers for bovine milk. A value of 30% of the recommended daily intake (RDI) of Fe, which is 14 mg Fe/day[2], was used for fortification of 200.0 mL of UHT milk, providing 4.2 mg of Fe. Besides the nanostructures of iron, ferrous sulfate, and ferric pyrophosphate, the two most common iron fortifiers were also used. The bioaccessibility was assessed by applying the standardized *in vitro* digestion method INFOGEST 2.0[3] to the milk with and without iron fortifiers, and the results were compared. The total iron contents and its bioaccessible fractions were determined by inductively coupled plasma optical emission spectrometry (ICP OES) after acid decomposition. The iron from the unfortified milk exhibited no bioaccessible fraction in our assays, indicating that the total contents of Fe in this matrix are not available for intestinal absorption, corroborating the fact that dairy foods are not considered good sources of Fe in the diet, which justifies the necessity of fortification. In the milk fortified with ferrous sulfate and ferric pyrophosphate, Fe presented bioaccessible fractions of 22 ± 3 % (w/w) and 4 ± 1 % (w/w), respectively. In the samples fortified with the oxo-hydroxide Fe NPs, a bioaccessible fraction of 38 ± 2 % (w/w) was obtained, whereas in the samples fortified with NE of heme iron and whey protein, Fe bioaccessibility was estimated at 66 ± 3 % (w/w), exhibiting improved bioaccessibility. In this way, the most effective iron fortifier was the nanoemulsion, indicating that this type of nanostructure is promising for the fortification of dairy food.

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EVALUATION OF INORGANIC ELEMENTS IN CARBOHYDRATE GELS BASED ON JENIPAPO AND BANANA FOR ENDURANCE ATHLETES

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Athletes can benefit from carbohydrate gels to improve physical performance, especially during long-term exercise[1]. Findings show that serum and urinary concentrations of inorganic elements can change during endurance activities, possibly due to increased demand on skeletal muscle and tissue damage[2]. Therefore, the aim of this study was to compare the levels of inorganic elements in different formulations of nutritional gels and in a commercial gel for endurance athletes. The project was approved by the Research Ethics Committee of the State University of Ceará (UECE) (Nº 4.866.034). The process for producing a carbohydrate energy gel for exercisers and the carbohydrate energy gel product have been filed under patent number BR 10 2023 021.438 0. The gels were formulated in the laboratory from the fruits of jenipapo (*G. americana* L.) and banana (*Musa* spp.), demerara sugar, glucose syrup and agar-agar gum in fixed quantities. The gels have the following proportions in relation to the concentrated clarified jenipapo and banana juices: gel with 50% of each fruit, gel with 70% jenipapo and 30% banana, and gel with 90% jenipapo and 10% banana. For comparison purposes, a commercial gel containing maltodextrin, simple sugars, mineral salts, antioxidants, preservatives and artificial colors was included. The three formulations showed the same sensory acceptance profiles, as well as the same physicochemical parameters and composition as the commercial gel analyzed[3]. The samples were subjected to acid digestion, for this, approximately 0.16 g of sample was mixed with 5 mL of 65% w w^{-1} HNO_3 in a digestion block at 120 °C for 4 hours, and the resulting digest was diluted to a final volume of 50 mL with ultrapure water. The elements were determined using inductively coupled plasma optical emission spectrometry (ICP-OES). The data were analyzed using one-way analysis of variance (ANOVA) to compare the element contents among the four gel formulations, followed by Tukey's multiple comparison test (GraphPad Prism 8). Student's t-test was applied to compare the element contents between two groups (banana and jenipapo). As a result, all the gel formulations showed significant differences ($p < 0.001$) in Ca, Fe, K, Na and P content, showing that composition strongly influences mineral availability, since jenipapo showed significantly higher concentrations of Ca, Fe, K, Na compared to banana ($p < 0.001$). The gels containing fruit showed higher concentrations of K and P when compared to the commercial gel, elements directly associated with muscle function[4] and energy production in the body[5], respectively. They also contained higher levels of Fe and Ca, minerals of recognized physiological relevance, since Fe participates in oxygen transport in the body[2] and Ca plays an essential role in muscle and cardiac performance[6]. There was a significant difference between the fruit-based gels and the commercial gel regarding the concentrations of the evaluated elements, suggesting that the mineral profile of fruit-based gels may favor their use in sports.

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Optimization of sample preparation for multielemental determination in soybeans by ICP-MS

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Sample preparation is a critical step in chemical analysis, directly influencing the accuracy, precision, and reproducibility of results. Furthermore, the adoption of optimized preparation protocols, such as minimizing the use of toxic reagents, reducing the volume of waste, and using energy efficiently, contributes to safe, economical and sustainable analyses. The present study aimed to optimize the drying, grinding and chemical processing of soybeans for multielement analysis by inductively coupled plasma mass spectrometry (ICP-MS). Particle size is a factor that can significantly affect the homogeneity of a material[1]. The grinding step was evaluated in two different equipments: a ball mill model MM-500 Control (Retsch) and a rotor mill model ZN-300 (Retsch), with titanium components. Three grinding methods were established: (A) grinding in a ball mill with 2.0 cm diameter balls, resulting in particles of varying sizes (4 mm to 500 µm); (B) grinding in a ball mill with 0.9 cm diameter balls, resulting in particles smaller than 1 mm; and (C) grinding in a rotor mill operating at 16,000 rpm with a 250 µm sieve opening. The material analysis was structured to evaluate two factors independently: the three grinding methods and two analytical portions (250 mg and 500 mg), totaling six treatments, each analyzed in triplicate. The samples were subjected to microwave-assisted acid digestion, with 250 mg and 500 mg weighed into polytetrafluoroethylene (PTFE) tubes and treated with 3 mL of nitric acid (HNO_3, 65%), 2 mL of hydrogen peroxide (H_2O_2, 30% w/w) and 3 mL of deionized water[2]. Digestion was carried out in a Milestone ETHOS UP system, operating at a constant power of 1800 W. The resulting solutions were analyzed in an Agilent 8900 ICP-MS/MS mass spectrometer, allowing the quantification of 32 elements: As, B, Ba, Ca, Cd, Ce, Co, Cs, Cu, Er, Eu, Fe, Ga, Gd, Hg, Ho, K, Mn, Mo, Nd, Ni, P, Pb, Rb, Sb, Sm, Sr, Tb, V, W, Y and Zn. The results indicated no significant interaction between the mass and grinding type factors, which allowed the isolated evaluation of the main effects. For 250 mg samples, a statistically significant difference was observed between at least two particle sizes for the elements Ca, Fe, Ga, P, Rb and V. For 500 mg samples, a larger number of elements showed significant variation depending on the grinding type: B, Ca, Ce, Er, Eu, Fe, Ga, Gd, Ho, Mn, Nd, Ni, P, Rb, Sm, Tb and V. The increase in the number of differential elements observed in the samples with greater mass can be attributed to the lower relative variability, which affects the sensitivity of the tests. Grinding type C presented significantly different results from those obtained with grindings A and B, confirming that particle size has an influence, especially when the analytical portion uses lower mass. In the direct comparison between the 250 mg and 500 mg, significant differences were identified for As, B, Cd, Ga, Hg, Ho, Pb, Sb and W. However, the low concentration of these elements implies greater heterogeneity, as predicted by the Horwitz uncertainty, which explains the statistically significant differences observed. In general, the 500 mg provided more stable and reproducible results. Nevertheless, the data obtained from 250 mg were considered comparable, as long as type C grinding was used.

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Eco-friendly sample preparation using Deep Eutectic Solvents for the analysis of bivalve mollusks samples by MIP-OES

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Sample preparation is a critical step in analytical chemistry[1], often involving hazardous, high-value reagents and compromised purity. Despite the advances made, further improvements are necessary to develop more sustainable approaches that align with the principles of green sample preparation. Therefore, this study investigated the use of deep eutectic solvents (DES) in extraction methods for analyzing bivalve mollusks as an alternative sample preparation for the elemental determination of Ca, K, Mg, Na, and P via plasma techniques. DES was prepared by combining choline chloride (ChCl), various carboxylic acids and sugars in different molar ratios (1:1, 1:2, and 1:3). The hydrogen bond donors used were acetic acid (AA), formic acid (FA), malonic acid (ML), malic acid (MA), oxalic acid (OX), and xylitol (XY). These solvents were used to extract the analytes from a commercial bivalve mollusk sample, whose mass fraction had been previously determined using microwave-assisted acid digestion as a reference method. Experimental conditions were optimized using the solvent formed by OX (1:2 molar ratio), and a Doehlert design was employed for the extractant solvent volume and extraction time. For this, a thermostatic bath with stirring at 90 °C was used, followed by centrifugation to separate the extract from the bottom body, followed by a 1 mL aliquot of extract being replenished with 9 mL of 1% HNO_3, and subsequent elemental determination by microwave-induced plasma optical emission spectrometry (MIP-OES). Method performance was evaluated based on the % recovery relative to reference values. Optimization of extraction time (min) and solvent volume (mL) allowed the determination of the most favorable conditions, resulting in a robust statistical model ($R^2 > 0.97$). The optimal conditions were 2.5 mL of DES and an extraction time of 30 min, which provided a high % recovery for all analytes. According to the Cochran test, the method showed adequate linearity, being homoscedastic for all analytes in a linear range from 0 to 14 mg L^{-1}. The limits of quantification obtained for P, Ca, K, Mg, and Na were 331, 13.7, 6.32, 0.53, and 14.7 mg L^{-1}, respectively. The method's reliability was verified using the reference materials oyster tissue (NIST 1566b) and fish tissue (E3002A), producing recoveries between 90% and 107% for the evaluated analytes (n = 3). The method's repeatability was adequate (n = 3), with relative standard deviations < 9.0%. The developed method demonstrates adequate performance in sustainability assessment using the analytical greenness metric for sample preparation (AGREEprep)[2], achieving a score of 0.67. This experiment indicates that DES is a viable and greenness alternative for the elemental analysis of bivalve molluks, offering greater efficiency and sustainability in sample preparation. Also, contributing to the achievement of the United Nations Sustainable Development Goals 12, 13, and 15.

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DETERMINATION OF GEOGRAPHIC MARKERS IN WOOD BY LIBS WITH SINGLE-POINT CALIBRATION

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Wood traceability plays a crucial role in combating illegal logging, ensuring compliance with environmental regulations, and supporting sustainable forest management and trade certification systems. Reliable analytical strategies are required to verify geographic origin and authenticity, as conventional documentation can be easily falsified. In this context, chemical fingerprinting of wood emerges as a powerful approach to provide robust and objective traceability. Laser-Induced Breakdown Spectroscopy (LIBS) is a versatile multi-elemental analytical technique that enables solid sample analysis with minimal or without sample preparation. Although these features make it attractive for environmental and biological studies, calibration is challenge due to matrix effects and the scarcity of suitable reference materials. In this context, single-point calibration has proven to be a viable alternative for semi-quantitative determinations[1], as it reduces the reliance on certified reference materials and broadens the applicability of LIBS to complex matrices. In this study, woods from one hundred trees were analyzed by LIBS without any previous treatment and elements with potential as markers of geographic origin were determined by single point calibration, taken four wood samples of different densities previously analyzed by ICP-OES as reference standards. The measurements were performed in a Q-switched Nd:YAG laser (Brilliant, Quantel, 1064nm), with a lens-to-sample distance of 18.5 cm, 100 mJ laser pulse energy, 3.0 µs delay time, 13.0 µs integration time, and 250 laser pulses. Under these experimental conditions, several relevant elements were determined: 7±2–27±2 $mg \cdot kg^{-1}$ (Sr), 28±7–123±18 $mg \cdot kg^{-1}$ (Ba), 0.3±0.1–1.4±0.13 $mg \cdot kg^{-1}$ (Sb), 13.8±5–148±20 $mg \cdot kg^{-1}$ (Si), 2±1–8±1 $mg \cdot kg^{-1}$ (Al), 7±1–36±4 $mg \cdot kg^{-1}$ (Zn), 7± $mg \cdot kg^{-1}$–20±2 (Pb), 0.14±0.03–0.37±0.03 $mg \cdot kg^{-1}$ (Cu), 0.2±0.01–1.4±0.3 $mg \cdot kg^{-1}$ (Mn), 214±39–1053±172 $mg \cdot kg^{-1}$ (Mg), and 1.24±0.23–3.4±1.1 $mg \cdot kg^{-1}$ (Fe). K-means algorithm revealed significant interactions among the elements, forming clusters. A positive correlation between Ba and Sr (PC1: 59%; PC2: 41%) was observed, modulated by soil pH (5.5–6.0). Variations in Mg uptake were associated with differential absorption of Ba and Sr (PC1: 45%; PC2: 31%), possibly reflecting competition among alkaline-earth cations for root transporters, as reported in the literature[2]. The interactions among Ba, Sr, and Mg underscore the role of Mg not only as a nutrient but also as a potential regulator of ionic dynamics in soil–plant systems. Higher Sb and Si amounts (PC1: 69%; PC2: 30%) were associated with variations in Ba availability, reflecting the differential mobility of these elements in highly weathered tropical soils, although additional investigations are necessary to confirm this correlation. The observed correlation between Mg and Fe highlights the critical role of Mg in photosynthesis (PC1: 58%; PC2: 42%), as a central component of chlorophyll that may indirectly modulate Fe demand through leaf redox processes[3]. Additionally, the competition between Cu and Pb (PC1: 59%; PC2: 41%) indicates the sharing of root transporters, suggesting that competing elements can influence the relative uptake of metals, reflecting the adaptive capacity of plants in metal-rich or contaminated soils. These results indicate that the integration of LIBS with single point calibration provides an effective strategy for the semi-quantitative determination of trace elements in wood, providing relevant insights for geographic traceability.

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Feasibility of the SP-ICP-MS Technique for Microplastic Analysis

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It is estimated that plastic waste accounts for 60 to 80% of marine litter, directly impacting aquatic ecosystems. The degradation of these materials under UV light generates microplastics (MPs), defined as plastic particles smaller than 5 mm, and nanoplastics (NPs), with dimensions smaller than 100 nm. MPs can be classified as primary (intentionally manufactured at this size) or secondary (resulting from the fragmentation of larger plastic debris). These particles have the potential for bioaccumulation, translocation within organisms, and association with toxic metals such as lead (Pb) and copper (Cu). Recent studies have reported the presence of MPs and NPs in seawater, freshwater, sediments, soils, air, and they have even been detected in the placenta and breast milk. Despite their detection in various matrices, the analysis of MPs and NPs presents a significant challenge for quality control laboratories due to the wide range of sizes, shapes, and chemical compositions of these particles. Fourier-transform infrared spectroscopy (FTIR), Raman microscopy, and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDX), which allow for the identification of polymer composition and structure. In addition to these techniques, single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) has emerged as a promising approach for application in routine laboratories. The aim of this study was to optimize the SP-ICP-MS technique for the detection and characterization of microplastic particle size, targeting its application in environmental samples, such as lagoon and seawater. Parameters such as flow rate, dwell time, and scan time were optimized to achieve the best analytical response. Suspensions of polystyrene (PS) microparticles with diameters of 1, 2, and 3 µm were used. Samples were diluted in ultrapure water after 1 minute of sonication, and only glassware was used to minimize contamination. Detection was based on the carbon element. Although carbon is not traditionally determined by ICP-MS due to its high detection limits, advances in the technique and the optimization of critical parameters have made this approach feasible. In this study, ^{13}C was selected, with a required acquisition frequency higher than 100 Hz. While the transport efficiency (TE) for nanoparticles typically exceeds 8% when using concentric nebulizers and cyclonic spray chambers, TE for microplastics is reported to be below 2% in the literature. The optimized parameters resulted in a dwell time of 200 µs, flow rate of 0.18 mL/min, TE of 2.9%, and a size detection limit (LOD_size) of 1 µm. The results are promising and indicate the feasibility of the SP-ICP-MS technique as a screening method for the rapid detection of microplastics in products of sanitary interest.

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THE EFFECT OF CASHEW NUT CONSUMPTION ON SELENIUM LEVELS IN THE BLOOD OF ADOLESCENTS WITH OBESITY

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Diet is essential for maintaining adequate selenium (Se) status and preventing metabolic and inflammatory complications[1]. In obesity, serum Se levels exhibit alterations compared to those of individuals with normal weight, which may be associated with adverse health outcomes[2]. This study aimed to evaluate the effects of cashew nut consumption on Se fractionation in blood samples and glutathione peroxidase (GPx) activity in 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 counseling during the study. Anthropometric, dietary, and biochemical parameters (Se and GPx) were assessed at the beginning and end of the study. The elements were analyzed in plasma and erythrocyte fraction by inductively coupled plasma–mass spectrometry with a reaction cell (DRC-ICP-MS). The groups were compared using the parametric test of mixed-design ANOVA for repeated measures with Bonferroni post hoc correction in time 0 and after 12 weeks (T12). The significance level was set at $p < 0.05$. The results are represented in Table 1.

Table 1. Characterization of variables in the CON and the CASN, according to intervention time.

Elements	CON (n=25)		CASN (n=38)		p (T0)	p (time and group)
	T0	T12	T0	T12		
GPx, U gHb^{-1} ¥	57.81 (33.00)	49.66 (32.25)	42.38 (28.97)	32.98 (19.59)	**0.019**	0.861
Se, µg L^{-1} ¥						
Plasm	75.24 (11.29)	90.93 (16.95)	75.48 (10.97)	81.12 (19.02)	0.921	0.158
Erythrocyte	132.95 (47.97)	121.37 (46.03)	110.10 (28.53)	155.21 (31.18)*	**0.029**	**<0.001**

Abbreviations: CASN, cashew nut group; CON, control group; T0, initial time; T12, final time; Se, selenium; GPx, glutathione peroxidase. ¥ transformed variables in natural logarithms. * Intragroup analysis showed a *p* -value of less than 5%.

The results suggest that cashew nut consumption for 12 weeks may contribute to improving Se status at the cellular level in adolescents with obesity, since significant differences were observed in the erythrocyte fraction. However, this change was not reflected in GPx activity, which may be related to the short intervention period or to the lower sensitivity of this selenoprotein to Se nutritional status. Chemical speciation methods for investigating selenoproteins in fractions are essential to understanding the biochemical mechanisms of Se in obesity. However, this work provides essential information about cashew nut consumption. Speciation experiments are being conducted by the group to better understand these mechanisms.

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Influence of altitude on the elemental profile of specialty coffees from Minas Gerais

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Minas Gerais stands out as the main Arabica coffee-producing hub in Brazil, bringing together edaphoclimatic conditions and cultural practices that confer unique sensory characteristics to the beans produced. Within this context, specialty coffees gain prominence, defined as those that achieve a minimum score of 80 points on the Specialty Coffee Association (SCA) scale, evaluated by attributes such as aroma, flavor, uniformity, and acidity, in addition to the absence of defects. The state of Minas Gerais concentrates important coffee-growing regions, such as Matas de Minas and Sul de Minas (Atlantic Forest biome) and Cerrado Mineiro and Chapada de Minas (Cerrado biome), which present different altitude ranges. The altitude at which coffee is cultivated has different effects on its chemical composition[1] and is among the factors influencing coffee quality[2], as it affects the physiological development of the plant and, consequently, its sensory profile[3]. Therefore, this study aimed to evaluate the influence of altitude on the elemental profile of specialty coffees produced in Minas Gerais. A total of 66 specialty coffee samples from the 21st Minas Gerais Coffee Quality Contest, held in Belo Horizonte in 2024, were provided by the Minas Gerais Technical Assistance and Rural Extension Company (EMATER-MG) and the Regional Coffee Growers Cooperative in Guaxupé (Cooxupé). The samples were prepared at the Radioisotopes Laboratory – CENA/USP through standardized lyophilization and grinding methods. Elemental determination was carried out by triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS), after microwave digestion using HNO_3 and H_2O_2. Analytical quality was assessed with certified reference materials NIST SRM 1515 Apple Leaves, CRM-Agro 1007a Green Coffee, and CRM-Agro 1006a Soy Flour. For statistical analysis, the data were classified into three altitude categories: low (<600 m; n = 12), medium (600–1000 m; n = 27), and high (>1000 m; n = 27). The assessment of associations between altitude and the elemental profile, as well as multivariate variation, was verified by Spearman correlation and MANOVA. Fourteen chemical elements were determined: B, Ba, Ca, Ce, Cs, Co, Cr, Cu, Fe, K, Mn, Mo, Rb, and Sr. The results indicated significant correlations for Cr ($\rho = 0.345$, $p = 0.0045$), Sr ($\rho = 0.333$, $p = 0.0063$), Mn ($\rho = 0.324$, $p = 0.0080$), K ($\rho = -0.305$, $p = 0.0127$), Rb ($\rho = 0.304$, $p = 0.0130$), Fe ($\rho = -0.292$, $p = 0.0173$) and Ba ($\rho = 0.254$, $p = 0.0394$), suggesting that these elements are directly associated with altitude variation. MANOVA confirmed significant differences in chemical composition among the altitude categories (Wilks' $\lambda = 0.474$, $p = 0.0446$). These results demonstrate that altitude exerts a relevant influence on the elemental profile of the coffees analyzed, particularly with respect to Cr, Sr, Mn, K, Rb, Fe, and Ba.

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ELEMENTAL PROFILE AND CHEMOMETRICS FOR GEOGRAPHICAL TRACEABILITY OF HONEYS FROM PANTANAL AND CERRADO BIOMES

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The honey of *Apis mellifera* bees presents a chemical composition directly influenced by flora and environmental conditions of the region of origin. The elemental profile can act as a natural marker for authentication and geographical traceability purposes. Spectrometry techniques combined with chemometric methods are promising tools to explore this profile, allowing the differentiation of honeys from different localities, contributing to product valorization, fraud prevention, and the strengthening of the regional beekeeping sector. This work aims to evaluate the elemental profile of honeys from Pantanal and Cerrado biomes in the state of Mato Grosso do Sul, targeting their geographical identity[1,2]. A total of 35 honey samples were collected in various cities to better represent the reality of production in this state of Brazil. The samples were stored in a temperature and humidity-controlled environment. An aliquot of 300 mg of honey was weighed into PTFE capsules. Two milliliters of concentrated nitric acid (69%) were added, and a pre-digestion was carried out for 2 h. Then, 1 mL of hydrogen peroxide (30%) and 5 mL of ultrapure water were added. The samples were subjected to microwave-assisted digestion (Millestone ETHOS UP) at 195 °C and 1800 W. The digests were diluted to 25 mL with ultrapure water and subsequently analyzed by inductively coupled plasma mass spectrometry (ICP-MS), using calibration curves for Cu, Fe, Mn, Zn, Cr, Ba, Sr, As, Cd, Ni, V, Pb, and Se in the concentration range of 1-500 µg/L, and by inductively coupled plasma optical emission spectrometry (ICP-OES), with calibration curves for Ca, K, Na, Mg, S, P, Mn, Fe, Ba, Cu, and Zn in the concentration range of 0.005-500 mg/L. Certified reference materials (NIST 1549 Non-Fat Milk Powder and CRM-Agro C1004a Tomato Pulp) were employed for analytical quality control. Multivariate statistical tools such as analysis of variance (ANOVA), hierarchical cluster analysis and dissimilarity were applied to the elemental profile of honey samples to identify patterns of similarity and differentiation among them. Significant differences in mass fractions of Ca, K, Mg, Mn and Fe were observed among the honey samples. The applied multivariate tools highlighted clear patterns of dissimilarity and differentiation between the samples, indicating the potential of elemental profile of honeys for geographical traceability.

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Determination of the content of chemical elements in dogfish using NADES and quantification by MIP OES and ICP-MS

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Fish are one of the main sources of protein consumed by humans. However, they may undergo bioaccumulation of metals in their organs, and the concentrations of these metals tend to be higher than those found in the environment in which they live[1]. In order to determine the concentration of metals in these samples, elemental analysis is required, which involves a crucial sample preparation step. Normally, acidic decomposition is performed using HNO_3, $HClO_4$, etc that may be harmful to both the environment and human health. Thus, there is great interest in the development of new solvents considered "green," aiming to replace those associated with high toxicity, flammability, and volatility[2]. In this context, the Natural Deep Eutectic Solvents (NADES) can be considered, which present advantages such as low toxicity, simple preparation, improved sustainability, and biodegradability. These solvents are formed through hydrogen bonding between a donor compound and an acceptor compound. That said, the objective of this work was to determine the content of essential and potentially toxic trace elements in dogfish samples obtained from commercial markets through the use of NADES. A solvent based on citric acid:xylitol:water was synthesized in molar ratios of 1:1:2 and 1:1:10 using a domestic microwave oven. The solvent was subsequently characterized by FTIR, ^{1}H NMR, ^{13}C NMR, and NOESY, showing satisfactory results. Afterwards, solubilization of the dogfish samples was performed using the domestic microwave. In this step, approximately 1 g of sample was weighed in quartz vessels following the addition of 5 g of eutectic solvent. The total solubilization of the sample was obtained by applying 40% of the nominal power of the microwave (800 W) for 4 minutes. The samples were quantitatively transferred to volumetric flask and made up to 15 mL with deionized water. The samples were stored at 4ºC. The resulting extracts were analyzed for their elemental content using ICP-MS (As, Ba, Cd, Cs, Cr, Co, Fe, Li, Mn, Ni, Se, Sr, and V) and MIP OES (Mg, Na, and K). Microwave-assisted closed-vessel acid decomposition with HNO_3 + H_2O_2 was used for comparison with NADES, and the latter proved to be a satisfactory method for the quantification of chemical elements such as As and Fe in fish samples. On the other hand, As concentrations in the analyzed samples were ranging from 9.6 µg g^{-1} to 15.0 µg g^{-1}, demonstrating that consumption of the studied fish may pose a risk to the population. Arsenic is a potentially toxic trace element that can cause effects ranging from stomach irritation and diabetes to death[3]. Additionally, PCA, HCA, and Kohonen self-organizing maps were employed for clustering samples collected from different locations. Finally, and importantly, it was estimated that analyses using NADES reduce environmental impact by approximately 70% compared to the use of HNO_3 in the sample preparation step.

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ASSESSMENT OF THE RELATION BETWEEN TOXIC ELEMENTS CONTENT AND OROFACIAL PAIN IN TEMPOROMANDIBULAR DISORDER (TMD) PATIENTS

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Toxic element exposure through different contaminated sources is an issue that poses a threat to human health, as they are recognized as being a major cause of many illnesses, thus contributing to the development of various diseases and worsening symptoms such as pain.[1,2] Temporomandibular joint dysfunction (TMD) is a multifactorial condition that affects the temporomandibular joint, causing orofacial pain that can be associated with biological, emotional, and environmental causes.[3] Therefore, this study aimed to evaluate the relationship between the content of toxic elements in plasma samples and orofacial pain in patients with TMD. Sixty-five patients were evaluated. The content of As, Cd, Cr, Hg, and Pb was quantified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). For this, the plasma sample was diluted 20 times using a solution of 2% v v^{-1} HNO_3 and 0.02% v v^{-1} Triton X-110. The data were analyzed by quantitative statistics, with the Mann-Whitney test, considering “p” less than 5%, using the SPSS software. The final data is shown in table 1.

Table 1: Toxic elements and pain level association. (Mean (SD), n =3)

Toxic Element	Concentration (SD) ↔	Moderate pain (SD) ↔	Severe pain (SD) ↔	p-value
As (µg L^{-1})	71.9 (6.4)	70.8 (6.7)	73.6 (5.7)	**0.037²**
Cr (µg L^{-1})	630 (32)	615 (30)	652 (33)	0.632²
Hg (µg L^{-1})	90.8 (5.9)	94.3 (7.2)	85.8 (3.3)	0.646²
Pb (µg L^{-1})	10.5 (2.2)	8.72 (1.36)	13.0 (3.1)	0.698²

The values were significant for As (p = 0.037); However, non-significant results were obtained for Cr, Hg, and Pb, while Cd concentration was below LOQ. Thus, it is concluded that only arsenic was associated with the severity of orofacial pain. This finding in individuals with higher pain levels can be sustained by the capacity of this element in increasing inflammation and oxidative stress, which can worsen pain sensibility and TMD progression [2,3].

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Seasonal evaluation of inorganic contaminants in sediments of river affected by mining rejects

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In 2015, a catastrophic dam collapse at an iron ore mine in Mariana, Brazil, led to one of the Brazil's worst environmental disasters. The incident caused extensive environmental, social, and economic damage, including widespread contamination of the Doce River Basin. Since such contamination can greatly affect the mobility and availability of metal(loids) over an unknown period, regular monitoring of the contaminants in the river sediments is of great importance[1]. In this sense, this study aimed to quantify the concentration of inorganic contaminants in sediment samples from the Doce River Basin collected over a two year period. The samples were collected at 15 sampling points along the Doce River. Additionally, sediments from the Santo Antônio River, which was not affected by the dam collapse, were collected at 6 sampling points, and used as reference (total of 21 sampling points). Samples were collected from the depositional margins of the rivers twice a year (in April and October) from 2023 to 2024, totalling 4 collections over two years, and stored at -20 °C until analysis. Prior to sample preparation, the samples were defrosted, dried under air flow, milled and sieved at 2 mm. The U.S. EPA 3051A[2] standard method was chosen as sample preparation method, as this acid extraction provides insight into the metal(loids) that may become available in the environment. The extraction was performed using an Ethos One microwave system (Milestone, Italy), using 500 mg of sample and 12 mL of reverse *aqua regia* as extractant. The determination of As, Cd, Cr, Cu, Hg, Mn, Pb, U, V and Zn in the extracts was carried out by inductively coupled plasma mass spectrometry using an Agilent 7700 spectrometer (Agilent Technologies, Japan), operating with a collision cell by kinetic energy discrimination and in standard mode. Rhodium was employed as internal standard. The method was validated according to the National Institute of Metrology Standardization and Industrial Quality of Brazil regarding linearity, accuracy, limits of detection and quantification, working range and sensitivity, and was considered adequate for the intended objectives. For accuracy determination, standard addition experiments were performed at two levels and resulted in recoveries between 80 and 120% for all analytes. The data were evaluated considering the maximum allowed limits by the Brazilian National Environmental Council (CONAMA 454/12 resolution)[3]. Moreover the geoaccumulation index (I_{geo}) and the enrichment factor (EF) of each element were calculated to establish the possibility of sediment contamination. The results were compared across sampling points and collections, and Principal Component Analysis was employed to evaluate possible patterns. It was observed that dry and rainy seasons did not have a major influence on analyte concentration throughout the two-year study. Furthermore, many sampling points presented As, Cr and Pb values above the maximum limit established by CONAMA 454/12 over the monitored period, which may indicate persistent contamination. Finally, the I_{geo} and EF suggest contamination by Mn, Cr, and As, which may still be residues from the 2015 dam collapse. In this sense, further studies regarding the mobility and potential bioaccumulation of these contaminants are necessary to develop solid strategies for environmental monitoring and remediation.

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[FAPEMIG APQ-00208-19, RENOVA, CNPq, UFMG]

X-ray, Raman, Mössbauer, SIMS, and nanoSIMS Techniques

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EVALUATION OF METALLIC ALLOYS IN ELECTRONIC NICOTINE DELIVERY SYSTEMS USING X-RAY FLUORESCENCE SPECTROMETRY

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Electronic Nicotine Delivery Systems (ENDS) are classified by the Brazilian Health Regulatory Agency as smoking products and are prohibited from being manufactured, distributed, and sold in Brazil under RDC Nº 855/2024. Since their introduction to the market, the use of ENDS has significantly increased, especially among adolescents and young adults, with an estimated total of more than 68 million users reported in 2020. Alongside this growth in users, the number of studies focusing on these products has also increased, including investigations into the composition and contaminants of e-liquids, the vapors generated, consumption patterns, among others. ENDS consist of two main components: the device itself, comprising a battery and a cartridge, and a liquid refill, known as e-liquids. The device is responsible for providing energy and generating heat to vaporize the e-liquid stored inside the cartridge[1]. A current concern is whether the contact between the e-liquid and the device materials during heating may lead to the leaching of inorganic elements from the alloys into the vapor inhaled by users. The objective of this study was to evaluate the different components of ENDS devices and verify their compliance with current legislation, as well as to identify the presence of contaminants that may pose health risks. The analyzed devices, provided through a partnership between INCQS/Fiocruz and the Brazilian Federal Revenue Service, were classified as third-generation devices. These devices, known as Mods, allow for greater vapor production and a more intense user experience. Two samples from one brand (samples A and B) and one sample from another brand (sample C) were analyzed. The devices were identified, cataloged, and disassembled, with all parts in contact with the e-liquid separated for analysis. A total of 29 parts were analyzed using Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF), conducted in collaboration with the National Institute of Metrology. In samples A and B, stainless steel SS-304 and Nichrome V were identified, while only stainless-steel SS-304 was found in sample C. Nichrome, composed primarily of Ni and Cr, may contain other elements depending on the alloy type and is widely used as a heating element, consistent with its use in device coils. SS-304, composed of Cr, Ni, Fe, Mn, and other elements, is a highly versatile alloy commonly used in various products due to its corrosion and heat resistance. Other elements found in the samples included Fe, Cu, Zn, Ba, and Cl. These elements may pose health risks depending on their concentration and route of exposure. The presence of contaminants, especially Pb and Cd, found in the alloys of all analyzed devices raises concerns about user safety and health, as these metals are not permitted in such products. Pb and Cd are known for their toxicity and may pose serious health risks, particularly when leached into the vapor inhaled during device use. The detection of these contaminants is concerning due to the potential for user exposure, highlighting the need for further evaluation of the leaching of these elements into the inhaled vapor to better understand the health risks associated with the use of these devices.

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Application of X-ray fluorescence and visible/near-infrared spectroscopy for classification of commercial pet foods

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The pet food market typically categorizes products into quality tiers (standard, premium, special premium and super premium), which differ in ingredient quality, nutritional value and price. However, these categories lack legal definitions and objective classification criteria[3]. Among the spectrometric techniques, X-ray fluorescence spectrometry (XRF) and visible/near-infrared spectroscopy (Vis-NIR) are attractive to pet food analysis due to their non-destructive feature, minimal sample preparation requirement and high sample throughput. In addition, the techniques provide complementary data: XRF quantifies elemental composition (e.g., Ca, P, Fe, Zn)[1], while Vis-NIR may be used to determine organic constituents such as crude protein, ether extract, and crude fiber[2].Therefore, this study evaluated the potential of XRF and Vis-NIR to distinguish between super premium and lower-tier products, aiming to support the development of an objective classification tool.

Moreover, the study investigated the potentialities of the techniques to discriminate products by manufacturer, life stage (puppy, adult, senior), and by the presence of genetically modified (GM) ingredients. Analytical strategies to verify such information are important for ensuring labeling compliance and food safety.

Classification models were developed using partial least squares discriminant analysis (PLS-DA). The declared label information for manufacturer, quality tier, life stage, and GM status was used as the reference data (Y-dependent variables), with the full XRF and Vis-NIR spectra serving as the predictor variables (X-independent variables). A total of 120 samples were used for calibration and 78 independent samples for validation.

Validation results demonstrated that both techniques were effective in discriminating super premium from lower-tier products, achieving high classification accuracies of 87% with XRF and 83% with Vis-NIR. Consequently, these spectroscopic techniques can be used for verifying pet food quality tiers.

Classification by manufacturer (XRF: 64%; Vis-NIR: 58%) and life stage (XRF: 68%; Vis-NIR: 69%) were more challenging, largely due to imbalanced class sizes. Sensitivity was highest for dominant classes but poor for underrepresented ones, indicating the need for strategies to mitigate class imbalance in a future study.

The techniques showed high accuracy in discriminating products "GM-free" from others (XRF: 86%; Vis-NIR: 85%). However, a closer look to additional factors is required before drawing a conclusion. The "GM-free" label is often found on super-premium and grain-free products. Therefore, it is difficult to determine if the discrimination is driven by the genetic modification status itself or by other compositional differences (e.g., the absence of certain ingredients like corn and soybean).

Ultimately, XRF and Vis-NIR can be potentially applied as objective analytical tools for verifying pet food quality tiers and label information. Their adoption could provide rapid measurements to support quality control and regulatory practices in the pet food industry. Future research should explore larger and more balanced datasets, data fusion, as well as advanced chemometric strategies, to further improve classification performance.

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INTEGRATION OF SOLID PHASE EXTRACTION AND EDXRF: NICKEL DETERMINATION USING DMG-MODIFIED COTTON FABRIC

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Considered the 24th most abundant metal in the Earth's crust, nickel is used as a component of various metal alloys due to its ability to confer thermal and corrosion resistance to the alloy.[1] The metal is present in several industrial products, such as rechargeable batteries, coins, pigments, and low-cost jewelry.[2] Despite its wide application, nickel exposure can cause damage to human health due to its toxicity at high concentrations.[1,2] In addition, it is estimated that about 20% of the world's population is sensitive to this metal, which is a cause of allergies and contact dermatitis.[1] A variety of techniques are available for the determination of nickel, with flame atomic absorption spectroscopy (FAAS) serving as a representative example. Nonetheless, this technique exhibits certain limitations, particularly when the analyte is present at trace levels. To address this limitation, solid-phase extraction proves to be a highly efficient strategy which, when coupled with alternative materials, represents a cost-effective approach to sample preparation. However, SPE procedures coupled with FAAS as the detection technique require an elution step, which results in a slight dilution of the analyte and increases the risk of introducing errors. In this context, energy-dispersive X-ray fluorescence spectroscopy (EDXRF) can be employed as a detection technique following SPE procedures, thereby eliminating the need for an elution step.[3] Thus, the aim of this work is the determination of nickel ions in synthetic sweat samples after contact with jewelry, in order to evaluate the release of this ion from such materials, which could lead to the development of allergic reactions in users, using EDXRF combined with solid-phase extraction on cotton fabric. For SPE, cotton fabric discs (2 cm in diameter) impregnated with 100 µL of 0.1 mol L^{-1} dimethylglyoxime were placed in a 3D rotary device. The extraction conditions were previously optimized, using 30 mL of Ni(II) ion solution at pH 8, with an extraction time of 20 minutes. Nickel solutions were prepared from jewelry samples leached in synthetic sweat solution for seven days, at concentrations ranging from 0.3 to 3 mg L^{-1}. The extraction efficiency of nickel ions by the dimethylglyoxime-impregnated fabric was about 75% (1.806 mg g^{-1} of Ni(II)) under the optimal extraction conditions. After analyte extraction, the sorbent phase was subjected to determination by EDXRF using a Shimadzu EDX 7000 spectrometer. The cotton fabric was placed directly into the equipment, under vacuum atmosphere and a 10 mm collimator, with an analysis time of 2 minutes per sample. The calibration curve obtained for the leached jewelry matrix showed good linearity (R^2 = 0.99168) and sensitivity (slope = 46.586), indicating that the EDXRF technique can be used for the determination of nickel ions in jewelry after solid phase extraction, without the need for analyte elution, thus simplifying the quantification of the analyte of interest. Accuracy and precision tests of the method are under development, as well as the evaluation of nickel in other aqueous matrices by EDXRF.

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Hyphenated/ Multimodal Techniques

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Gold nanoparticles on transgenic soybean callus cultivation: Speciomics analysis using multimodal techniques (HPLC-ESI-HRMS-ICP-MS/MS)

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The use of nanoparticles (NPs) in combination with in *vitro* plant production represents a valuable tool in the field of biotechnology and aligns well with the agriculture 4.0 concept [1]. In this study, different concentrations of AuNPs (10, 100 µg/L, and 10 mg/L) were applied to transgenic soybean callus (Roundup Ready – carrying the *cp4-epsps* gene, obtained via *Agrobacterium sp*., and Intacta – carrying the *Cry1Ac* gene) to evaluate the metabolic responses under controlled stress conditions. The study was performed integrating cutting-edge techniques (multimodal techniques – LC-ESI-HRMS-ICP-MS/MS) [2] for speciomics analysis, which involves the characterization of chemical species in the sample through omics-based [3], as showed in Figure 1. The results revealed the presence of diverse metallobiomolecules containing chemical elements such as Cu, Fe, Mg, Mn, Ni, S, P and Zn, as well as other secondary metabolites, totalizing more than 400 compounds. Furthermore, differences were observed between the two transgenic varieties, with both known and unknown metabolites being identified depending on the concentration of AuNPS added. Most of the metabolites identified are linked to tolerance or sensitivity to nanoparticle-induced stress. This work enhances the understanding of metallic nanoparticle effects in plants and offers insights for environmental risk assessment, the development of safe biotechnological applications, and the identification of potential new metabolites.

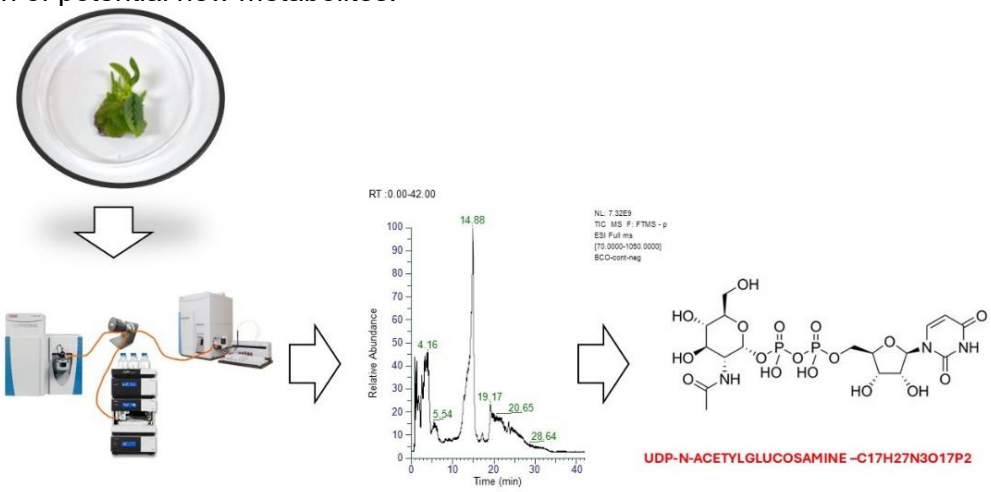

Figure 1. Chromatograms obtained simultaneously in HILIC-LC-ESI-HRMS-ICP-MS/MS and biomolecules containing heteroatoms from soybean callus sample with 10 mg/L of AuNPs.

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AF4-UV-MALS-ICP-ToF-MS analysis gives insight into the possible mechanism of silica nanoparticles, such as a mitigator agent of Hg in the soybean plant

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Using silica nanoparticles (SiO_2NPs) has emerged as an eco-friendly, non-invasive, low-cost, and safe strategy, particularly for mitigating heavy metal-induced oxidative stress in plants [1]. However, the mechanism of action requires further investigation, especially concerning plant–nanoparticle interactions. The objective of this work was to employ hyphenated/multimodal techniques, such as AF4-UV-MALS-ICP-ToF-MS, to evaluate the interactions between SiO_2NPs and Hg in contaminated soil, and HPLC-ICP-MS/MS-ESI-MS/MS to investigate metabolite variations without species-specific standards [2]. The SiO_2NPs used in this study ranged from 20 to 30 nm in size. Applying AF4-UV-MALS-ICP-ToF-MS provided valuable information on the potential mechanisms by which SiO_2NPs mitigate Hg contamination. The fractogram correlating Hg and Si signals, obtained from ICP-ToF-MS and AF4-MALS, showed overlapping signals at the same retention time, suggesting the adsorption of Hg ions by silica nanoparticles, as demonstrated in Figure 1.

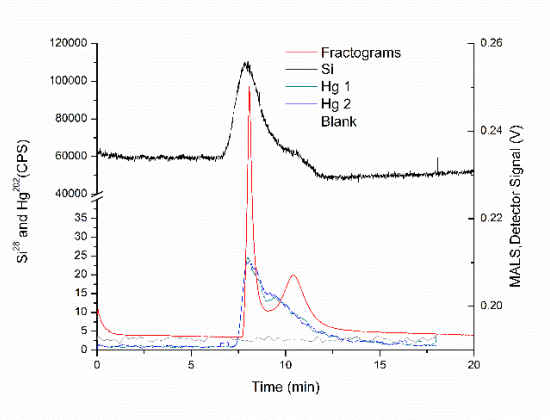

Figure 1: Fractogram of root extract, correlation between the silicon and mercury signals.

The overlap of Hg and Si signals in soybean roots suggests that Hg is immobilized in the roots, thereby minimizing the contaminant's translocation to the plants' aerial parts[3]. Although the presence of Hg, Na_2SiO_3, and SiO_2NPs may be altering the metabolites, the root samples revealed a clear distinction between the control and Hg-treated groups, with a clustering trend observed between the NP + Hg samples and the control group, highlighting the beneficial effects of silica in mitigating Hg contamination in soybean plants.

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Photochemical Vapor Generation of Fluorine Coupled to Indirect Detection by ICP-MS/MS

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Fluorine (F) is an environmentally relevant element due to its involvement in persistent and toxic organofluorine compounds such as PFAS, but its trace-level determination poses significant analytical challenges. Although inductively coupled plasma mass spectrometry (ICP-MS) is the preferred method for trace/ultratrace elements determination, direct measurement of total F concentrations remains difficult using Ar-based plasmas. The first ionization potential of F (17.4 eV) is higher than that of Ar (15.8 eV) and intense polyatomic ion interferences occur at *m/z* 19. Triple-quadrupole ICP-MS/MS can partially overcome these limitations by monitoring plasma-formed metal-fluoride ions such as $[^{138}Ba^{19}F]^+$, enabling sub-ppm determination[1]. Photochemical vapor generation (PVG) is an alternative sample introduction technique that can achieve significantly higher introduction efficiency than conventional nebulization. It has been successfully applied to halogens by generating volatile CH_3X species[2]. Pioneering work using GC-MS as an offline detector demonstrated the PVG feasibility for F by forming gaseous CH_3F via vacuum-ultraviolet irradiation of dilute acetic acid with Cu^{2+} as the mediator, although the yield was low (<1%)[3]. Subsequent studies further verified this process, yet the efficiency improvement remained insufficient[4]. This is undoubtedly related to the lack of suitable instrumentation for online monitoring of F, which precludes proper PVG optimization. This motivated us to combine PVG with the indirect F detection using ICP-MS/MS.

The preliminary results of the ongoing experiments will be presented. First, the conditions of ICP-MS/MS (Agilent 8900) with conventional nebulization were optimized for indirect F detection, using the signal to noise ratio as the key metric. This included verifying that $[BaF]^+$ is the most suitable polyatomic ion for indirect F determination, optimizing the reaction/collision cell settings using O_2, He, and/or H_2 to maximize $[BaF]^+$ selectivity, and optimizing sampling and transport of $[BaF]^+$ from the plasma to the detector. Second, the most suitable configuration for coupling PVG with ICP-MS/MS was determined. The samples were introduced to a thin-film flow-through photoreactor using a flow injection mode of operation. A Ba solution at a concentration of 50 mg L^{-1} in deionized water, with Re as the internal standard, was nebulized to the spray chamber of ICP-MS/MS. The gas phase from the generator was introduced downstream of the spray chamber using an ultra-high matrix introduction accessory. This configuration ensured a constant supply of Ba into the plasma and even enabled the estimation of the PVG efficiency by comparing its sensitivity to that of solution nebulization, according to a previous protocol[5]. Third, the PVG feasibility was convincingly verified using both acetic and propionic acid in the medium, with 60 mg L^{-1} of Cu^{2+} as the mediator. Data of subsequent experiments devoted to testing the various acid mixtures, the irradiation time, and some other transition metal ions added as mediators (e.g., Cd^{2+}, Co^{2+}, and Fe^{2+}) will be included.

In summary, the proposed PVG-ICP-MS/MS was shown to allow for the detailed optimization of PVG conditions for F. This outcome is promising for achieving more sensitive and robust total F determination in various environmental matrices in the near future.

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Trends and New Approaches

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PHOTOACOUSTIC SPECTROSCOPY IN AMMONIA MONITORING

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Greenhouse gas (GHG) detection is crucial for monitoring activities such as deforestation, land use, and energy emissions. Among the monitored compounds, ammonia (NH_3) stands out, whose volatilization is the main form of nitrogen loss present in urea used as fertilizer. Urea is widely used in agriculture due to its high nitrogen content, low cost, and ease of application[1,2]. However, the efficiency of using this fertilizer in the soil is significantly compromised by the loss of ammonia through volatilization and the leaching of nitrates. Photoacoustic spectroscopy (PAS) stands out for its high sensitivity, wide linear dynamic range, and online measurement capability[3]. In this study, PAS was used to monitor NH_3 volatilization in urea-treated soils. The experiment was conducted under controlled conditions, using three soils with distinct physical characteristics (clay, medium, and sandy) that received different doses of urea. The clay soil showed the lowest NH_3 volatilization, exhibiting a 69% higher urea-binding capacity than the other soils evaluated. In contrast, the sandy soil showed the highest NH_3 volatilization, indicating lower urea retention due to its high porosity. A relative standard deviation of less than 12% was obtained for replicates for both the different dosages and the different soil physical characteristics throughout the experimental period, indicating adequate precision for the study. The medium-textured soil showed smaller deviations between measurements, both in terms of repeatability and reproducibility. The choice of soil type and fertilizer dosage is crucial for minimizing NH_3 volatilization and increasing the utilization of agricultural inputs. The results indicated that PAS is suitable for this monitoring.

Keywords: environmental monitoring, ammonia, nitrogen fertilizers

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Fluorescent lamps as a secondary source of rare earth elements: A method for the recovery of yttrium

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Rare earth elements (REEs) are essential for green technologies and high-tech technologies, driving an exponentially growing demand for them, which comes alongside a diminishing supply. [1–3] In fluorescent lamps the concentration of REEs is several times higher than that found in primary ores, with yttrium being the most abundant REE present, accounting for about 90% of the total REEs. Thus, fluorescent lamps waste emerge as a highly attractive secondary source for yttrium recycling addressing the potential supply risk. [1–4] In this sense, this work aims primarily at the extraction and recovery of yttrium from the powder obtained by diminishing used fluorescent lamps. Fluorescent lamp powder was previously obtained by comminution of spent fluorescent lamps and sieving to control particle size. A fraction with particle size <250 µm was used in this work. In order to determine the initial Y concentration by Flame Atomic Absorption Spectrometry (FAAS), the sample was digested in a microwave system. For this, 50 mg of sample were weighed in each flask and after adding 4 mL HNO_3, 1 mL HCl, 1 mL H_2O_2, and 1 mL HF, the system was submitted to the following program: 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 6 min at 400 W, and 6 min at 650 W. After cooling, 0.3 mg H_3BO_3 was added, and the mixture was submitted to a second program: 3 min at 200 W, 2 min at 0 W, 2 min at 400 W, and 2 min at 500 W. The quantification by F AAS was carried out using CsCl 0,04% as ionization buffer and the results indicated that the sample contained 17 ± 3 mg g^{-1} of Y (n = 5). For extraction process, the sample was submitted to acid-assisted ultrasound extraction. In a univariate, HNO_3 provided higher extraction yield than HCl and was therefore selected for further optimization. A central composite design was applied to evaluate mass (50-150 mg, 5 levels) and HNO_3 concentration (1-14 mol L^{-1}, 5 levels). Both linear and quadratic effects of mass and HNO_3 concentration were significant (α = 0.05). The response surface analysis indicated 100 mg of sample and 7 mol L^{-1} HNO_3 as optimal conditions. A Doehlert design was then employed to optimize extraction time (10-90 min, 5 levels) and temperature (25-80 °C, 3 levels). Only the linear effects of time and temperature were significant (α = 0.05). Response surface evaluation indicated 80 °C and 70 min as the optimal conditions. Under these optimized parameters, extraction yielded 18.1 ± 0.3 mg g^{-1} Y (n = 2), corresponding to 100% extraction efficiency. The precipitation process was carried out using oxalic acid, tested at stoichiometric proportion and with 10%, 30%, and 50% excess. The pH was monitored using a pH meter and adjusted to 2.00 using a NaOH solution. Afterward, the system was left to stand overnight for precipitate digestion. The resulting precipitate was filtered, dried and then calcined in a muffle furnace at 900 °C for 2 h. A portion of the resulting solid was dissolved in acid, and quantification of Y was carried out by ICP-MS. The best precipitation efficiency (98% of Y available) was obtained with 30% excess of $H_2C_2O_4$. Under this condition, the purity of the obtained powder was 7.7% of Y_2O_3. Among contaminants determined by ICP-MS, Eu was present at 0.5% of total mass of the final solid. Other contaminants included Ca (11.2% of total mass) and Na (8.9% of total mass), while Al, K, Fe, and Ba, each accounted for less than 1%. The solid will be further analysed by XRF for detailed characterization. In addition, strategies will be explored to improve the purity of the recovered material. The results demonstrated that Y can be effectively extracted and recovered from fluorescent lamp powder, with 100% extraction and precipitation yield of 98%. These results highlight the potential of this waste as a secondary source of yttrium.

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[CNPQ, TAC, UFSC]

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GREEN SAMPLE PREPARATION METHOD FOR FURTHER DETERMINATION OF Cd AND Pb IN PORK LARD BY F AAS

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The presence of heavy metals such as Cd and Pb, in animal-derived food products as pork lard, poses significant health risks due to their bioaccumulative behavior. Thus, there is a critical need for efficient, cost-effective, and environmentally sustainable analytical methods. This study proposes an alternative method for sample preparation of pork lard using dispersive liquid-liquid microextraction in reversed-phase (RP-DLLME) for subsequent determination of Cd and Pb by flame atomic absorption spectrometry (F AAS). In an eco-friendly way, in the preparation of the samples, a green solvent d-limonene was first added to the sample, aiming at maintaining the liquid phase during all steps of the RP-DLLME procedure. This approach allows the replacement of xylene, used in recent work involving RP-DLLME[1]. Then, a mixture of two solvents, a dispersant (n-propanol) and an extractant (diluted HNO_3), is added to the tube containing 5 g of pork lard sample diluted with d-limonene, already heated. Then the samples were shaken and centrifuged for further extraction of the aqueous phase containing the analytes. External calibration using aqueous reference solutions in the range of 0.2 to 2 mg L^{-1} was performed for F AAS determination. As a reference method, Cd and Pb determination were performed by ICP-MS an inductively coupled plasma mass spectrometer (iCAP-TQ, Thermo Scientific, Germany) was employed in single quadrupole mode (112Cd and 208 Pb were monitored). For the pork fat samples digestion, the microwave-assisted wet digestion with pressurized digestion cavity (MAWD-PDC) method was used. Digestions were performed with a microwave oven with a pressurized digestion cavity (7301, Anton Paar, Austria). The MAWD-PDC was carried out by using 250 mg of sample and 6 mL of concentrated nitric acid in 15 mL quartz vessels. Hence, the MAWD-PDC procedure was performed using 40 bar of initial pressure and the following heating program: i) 5 min up to 80 ºC; ii) 10 min at 80 ºC; iii) 20 min up to 120 ºC; iii) 10 min at 120 ºC; iv) 20 min up to 220 ºC; v) 15 min at 220 ºC; vi) Cooling to 50 ºC. After the procedure, the digests were diluted up to 25 mL with water. The LOQ for Cd and Pb after MAWD-PDC and ICP-MS were about 0.0004 and 0.005 mg kg^{-1}, respectively. For the proposed RP-DLLME method, a solvents mixture of n-propanol (dispersant, 700 µL) and 1.0 mol L^{-1} HNO_3 (extractant, 300 µL) was injected into the sample, preheated to 70 °C. After flasks were centrifuged (10 min at 4000 rpm), the oily phase was partially withdrawn and the aqueous phase was collected using a syringe, transferred to volumetric flask and volume was completed to 5.0 mL, for further elemental determination by F AAS.The limits of quantification for Cd and Pb were 0.018 and 0.035 mg kg^{-1}, respectively. For Cd and Pb, the recoveries were higher than 92%, and the precision (RSD) was less than 7%. The proposed RP-DLLME method was tested on four brands of commercial pork lard, which were analysed by a comparison method (MAWD-PDC and ICP-MS). The evaluation of green aspects of the proposed RP-DLLME method was performed using the AGREEprep® software to establish Green Chemistry metrics[2], with calculated scores of 0.65 for the proposed RP-DLLME method and 0.42 for the reference method. Due the RP-DLLME enables the of pre-concentration of the analytes, this procedure was suitable for the preparation of pork lard samples, allowing determination by F AAS with acceptable recovery values and low LOQ. The proposed RP-DLLME method present low reagent consumption, use of diluted acids, simplicity of operation, and reduced time consumption, according to Green Analytical Chemistry Principles.

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Evaluating filter media for air-quality studies: Particulate retention efficiency and sample preparation for metals determination by ICP-MS

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Air pollution is one of today's major environmental problems, particularly in metropolitan areas and their outskirts[1]. Poor air quality is associated with cardiovascular and neurological diseases and even cancer[2]. Further study of pollution constituents is needed to clarify their sources and effects. Given the diffuse nature of gases, sampling must improve, as preconcentration of atmospheric material is often required to reach current analytical detection limits. This study evaluated different materials as membranes for capturing atmospheric particulate matter to identify optimal conditions for collecting airborne particles and to facilitate subsequent sample preparation. Using a small-volume sampler under development at the Trace Analysis and Chemometrics Research Group (TAC), atmospheric particulate matter was collected simultaneously on cellulose acetate, fiberglass, and nylon filter membranes. Scanning electron microscopy (SEM) were used to characterize pore size and the types of particles retained on each filter. Comparative sampling campaigns assessed collection performance through particulate mass per unit air volume. Membrane compositions were also examined to identify potential interferences in the quantification of real samples. For this assessment, microwave-assisted acid digestion was carried out with 2.0 mL of HNO_3 (68%, w/w) and 0.5 mL of H_2O_2 (30%, w/w), using the following heating program: 250 W for 2 min, 0 W for 2 min, 250 W for 6 min, 400 W for 5 min, and 650 W for 10 min. Following digestion, the samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) to quantify 18 analytes. After evaluating the filters, a 2^k screening design, where k is the number of factors, was applied to the cellulose acetate filter to employ milder sample-preparation conditions that would allow lower dilution factors, thereby improving analyte detectability relative to the detection limits. SEM images revealed differences in pore size and morphology among the membranes, with smaller pores and greater retention capacity in cellulose acetate and nylon filters. This directly affected the retained mass, with these filters collecting 3 to 12 times more material than fiberglass per volume of air collected. Nylon was the most efficient for particle capture; however, it caused a marked flow-rate reduction and consequent equipment overheating, making its use infeasible under the tested conditions. Elemental characterization by ICP-MS revealed quantifiable levels of several analytes inherent to the filter matrices. However, analysis of variance (ANOVA) showed no significant difference between the contamination levels of cellulose acetate and fiberglass filters at the 95% confidence level. In comparative real-sample collections, both materials exhibited some quantifiable analytes and, again, no significant differences were observed between results obtained with the two filters ($\alpha = 0.05$). Sample preparation limited quantification due to the need for high dilution factors, which can mask the presence of some analytes. Given the organic nature of cellulose acetate, milder preparation conditions were proposed to facilitate particulate extraction. Therefore, a 2^3 experimental design was applied to investigate the effects of HNO_3 (10–50% w/w), H_2O_2 (0–30% w/w), and heating (20–60°C) on the digestion of a certified urban ash reference material (BCR-176) and of the cellulose acetate filter. Preliminary results did not reveal statistically significant effects for the factors investigated ($\alpha = 0.05$). Nonetheless, effect estimates suggest using lower heating and H_2O_2 levels and a higher HNO_3 concentration. Additional studies will probe wider temperature and concentration ranges to achieve significance and robustness. Even so, the preliminary findings indicate that milder digestions of particulate matter in cellulose acetate matrix are feasible. After fine optimization of sample preparation, the method will be applied to quantify potentially toxic elements in particulate matter from different environments, demonstrating its utility for air-quality studies.

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[TAC, UFSC, CNPq, LCME, Polimat]

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An Innovative Laser Ablation Laser Ionization (LALI) Mass Spectrometry Technique for Solid Materials Analysis

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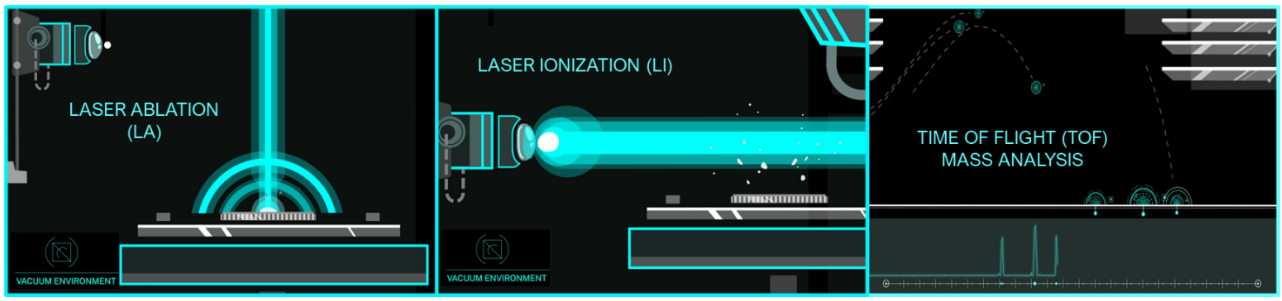
Mass spectrometry is a valuable technique for accurate, trace elemental analysis across a variety of applications. For solid materials, traditional high-performance mass spectrometry involves acid digestion to convert the sample into a liquid form. These sample preparation procedures can be complicated, time-consuming, and expensive. To access high performance with less sample preparation, some users combine Laser Ablation with Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Due to the complexity of each part of the combined LA-ICP-MS system and lack of continuity between different configurations, there are still numerous challenges associated with data collection and processing.

Addressing the challenges associated with traditional techniques for solid sample analysis, a new technique combines Laser Ablation Laser Ionization with Time of Flight Mass Spectrometry (LALI-TOF-MS). Compared to conventional techniques, LALI-TOF-MS has three key advantages: 1) reliable measurements of the full periodic table, from lithium to uranium, including important low-mass elements like carbon, nitrogen, and oxygen; 2) large-scale elemental mapping with micron-level resolution; and 3) high-resolution, high-sensitivity 3D characterization.

LALI uses two lasers to first ablate material directly from a solid sample's surface and then ionize neutral particles created by the ablation process. By targeting neutral particles, the ionization laser creates ions that are more representative of the sample's constituents than those created from plasma techniques. This also eliminates the use of argon gas and the resulting spectral interferences from argon. After ionization the TOF mass analyzer creates a full mass spectrum at each laser spot. This facilitates multi-element quantification and mapping. The entire analytical process is conducted under vacuum, allowing analysis of air- and moisture-sensitive materials. The vacuum environment also enables reliable quantification of low-mass atmospheric elements (e.g., C, N, and O) which are not easily quantified by traditional plasma techniques.

LALI-TOF-MS acquires millimeter-scale elemental maps with resolutions ranging from 5-150 microns, based on the user-adjusted ablation laser spot size. Repeating the ablation process for multiple layers results in 3D elemental characterization. Because the ablation laser's power is adjustable, the depth profiling capabilities are suitable for a variety of applications. For analysis of thin films or coatings, the power is adjusted to remove as little as 10s of nanometers per pass. To probe through multiple microns of material, the laser power is increased.

This presentation will describe the LALI-TOF-MS technology and present its capabilities across a variety of applications, including geoscience, metallurgy, and materials science.



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Green Analytical Approach for Nutritional Profiling of Unconventional Food Plants Using Deep Eutectic Solvent

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Unconventional food plants (UFPs) represent promising sources of essential nutrients and bioactive compounds, with particular relevance for food security and biodiversity conservation. However, their elemental composition remains poorly documented, and conventional sample preparation methods rely on acid mineralization, which is often time-consuming, hazardous, and environmentally unsustainable.

This study aimed to develop and validate a green analytical method for the determination of essential elements (Ca, Cu, Fe, K, Mg, Mn, Zn) in eight UFPs (almeirão, assa-peixe, caruru, dente-de-leão, ora-pro-nóbis, serralha, taioba, and trapoeraba-roxa) using a deep eutectic solvent (DES) composed of choline chloride, malic acid, and water in a 1:1:10 molar ratio. The DES was synthesized and characterized by FTIR. Extraction parameters were optimized through a central composite design (optimal condition: 60 °C, 30 min, 1.84 g DES), and elemental determination was performed by F AAS and ICP OES. Validation with three plant-based CRMs (NIST 1515 apple leaves, NIST 1547 peach leaves, and NIST 1570a spinach leaves) demonstrated high linearity (R^2 > 0.9882), good precision (RSD ≤ 13%), and acceptable accuracy (76–95% recovery). Compared with conventional acid digestion, the method provided similar recoveries with reduced reagent toxicity, waste, and energy consumption, as confirmed by AGREEprep assessment.

In terms of absolute concentrations, macroelements such as K, Ca, and Mg were generally present at higher levels (up to 1375 mg/100 for K in assa-peixe, 707 mg/100 for Ca in assa-peixe, and 737 mg/100 for Mg in caruru), while microelements like Cu, Mn, Fe, and Zn occurred in lower amounts (typically below 7 mg/100). These values are consistent with literature data[1] for UFPs, reinforcing the reliability of the DES-based extraction method.

Nutritional assessment revealed that UFPs can provide significant contributions to Dietary Reference Intakes (DRI)[2], particularly for Mn, Mg, and Ca, with marked interspecific differences. Almeirão provided moderate amounts of Ca (17–21%) and Mn (25–38%), while assa-peixe stood out for its high Ca contribution (71–88%), complemented by Mn (48–73%) and Cu (33–68%). Caruru showed an exceptional Mg supply (180–566%), exceeding 100% of the DRI, along with relevant Mn, Cu, and Fe. Dente-de-leão presented modest values, mainly for Mn (11–17%) and Cu (13–27%). Ora-pro-nóbis exhibited high Mn (78–93%) and Mg (34–82%), while serralha contributed consistently to Ca (24–30%), Mn (37–45%), and Cu (34–70%). In contrast, taioba showed lower percentages, with Mg (10–25%) and Mn (24–29%) as the most relevant elements. Finally, trapoeraba-roxa confirmed its nutritional potential with particularly high Mn (97–183%) and Ca (53–66%). Overall, Zn and Fe contributions were modest across species, rarely surpassing 20% of daily requirements, with iron being especially limited for women due to their higher physiological needs. These results emphasize that, while not balanced in all nutrients, UFPs can significantly improve intake of specific elements such as Mn, Mg, and Ca, contributing to nutritional adequacy and diet diversification.

In conclusion, the proposed DES-based method offers a greener alternative to conventional digestion for multi-element analysis of plant foods, aligning with the principles of Green Analytical Chemistry and the United Nations Sustainable Development Goals (SDGs 2, 9, 12, 15). Beyond its analytical innovation, this approach supports the valorization of native and naturalized plants, contributing to sustainable food systems and family farming.

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FLUOROMETRIC METHOD FOR NITRITE DETERMINATION IN WATER SAMPLES BY PAPER-BASED ANALYTICAL DEVICE

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An innovative and sustainable method was developed, based on the fluorimetric reaction with 2,3-diaminonaphthalene (DAN) for the determination of nitrite in different water samples, using a Paper-based Analytical Device (PAD) as the reaction and analytical platform. The reaction between 2,3-diaminonaphthalene and nitrite occurs in an acidic medium, where nitrite is converted into nitrous acid and reacts with DAN to form 1-[H]-naphthotriazole. This product exhibits higher fluorescence intensity and greater stability in a basic medium, with a characteristic emission peak at 405 nm[1]. Nitrite determination assays were performed on hydrophobic cellulose substrates, the PADs were developed using Whatman™ 1PS hydrophobic filter paper, employed as the reaction zone and sample support. The PADs were manually assembled, cut according to the dimensions and shape of the sampler designed for solid sample analysis in the spectrofluorometer, with a width of 6 mm, length of 13 mm, and rounded edges. Reaction was based on the addition of 10 µL of sample or nitrite standard solution, 1 µL of 0.30 mol L^{-1} EDTA, and 2 µL of DAN, under the protection of light. After the reaction, 2 µL of 0.50 mol L^{-1} sodium hydroxide was added, followed by immediate spectrofluorimetric analysis. Preliminary studies were conducted to optimize reaction temperature (4, 10, 22, 30, and 40 °C), DAN concentration (5, 10, 30, 40, 50, 70, 85, and 100 mg L^{-1}), and reaction time (2, 5, 10, 15, 20, 30, and 40 minutes). The optimized conditions were: reaction temperature 10 ºC, DAN 50 mg L^{-1}, reaction time 10 minutes. Interference tests were also conducted using K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, F^-, NO_3^-, HCO_3^-, SO_4^{2-}, and SO_3^{2-}, and nitrite recoveries ranged from 86 to 114%, indicating high tolerance to common matrix concomitants typically present in water samples. The values obtained for the limit of detection were 0.35 µg L^{-1}, the limit of quantification was 1.17 µg L^{-1}, comparison of these results that the LOD and LOQ values obtained in the proposed procedure are lower than those reported in the literature, indicating good sensitivity of the method. A linear calibration range to 150 µg L^{-1}, and R^2>0.99. The precision, based on the relative standard deviation (RSD%), was 3.5% (N=7). Accuracy was confirmed by recovery studies on real samples, ranging from 83 to 115%. Water samples were analysed and only three showed quantifiable concentrations of 6,1 to 29,3 µg L−1, values below the maximum allowed by legislation (Table 1). The methodology developed was evaluated based on the ten principles of Green Sample Preparation (GSP), using the green analytical metric known as AGREEprep[2], achieved a score of 0.77, above average. The developed method is simple, fast, selective, with good sensitivity, no effluent generation, and very low consumption of reagents (5 µL), especially when compared to reference methods for nitrite determination.

Table 1. Measured values and recoveries obtained using the proposed methodology for the analysis of various water samples (N=3)

Sample	Added concentration (µg L^{-1})	Measured concentration (µg L^{-1}) ± s (N=3)	Recovery (%) ± s (N=3)
Mineral water	0	<LOQ	-
	10	10.0 ± 0.3	100 ± 3
	50	53.4 ± 2.4	107 ± 5
Tap water	0	<LOQ	-
	10	9.2 ± 2.2	92 ± 22
	50	52.3 ± 1.6	105 ± 3
Public drinking fountain	0	<LOQ	-
	10	10.1 ± 0.5	101 ± 5
	50	47.1 ± 2.5	94 ± 5
Wall-mounted public drinking fountain	0	<LOQ	-
	10	9.4 ± 0.6	94 ± 6
	50	41.5 ± 0.1	83 ± 1
Natural spring water fountain	0	6.1 ± 0.4	-
	10	16.8 ± 0.5	107 ± 5
	50	49.1 ± 0.5	86 ± 1
River water	0	14.0 ± 1.2	-
	10	22.6 ± 0.8	86 ± 8
	50	57.9 ± 0.9	86 ± 2
Reservoir water	0	29.3 ± 0.7	-
	10	39.0 ± 0.1	97 ± 1
	50	87.0 ± 0.9	115 ± 2

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SYNTHESIS OF NOVEL MAGNETIC NANOMATERIALS FOR EXTRACTION OF TRACE ELEMENTS IN EDIBLE OIL AND ANALYSIS BY ICP-OES

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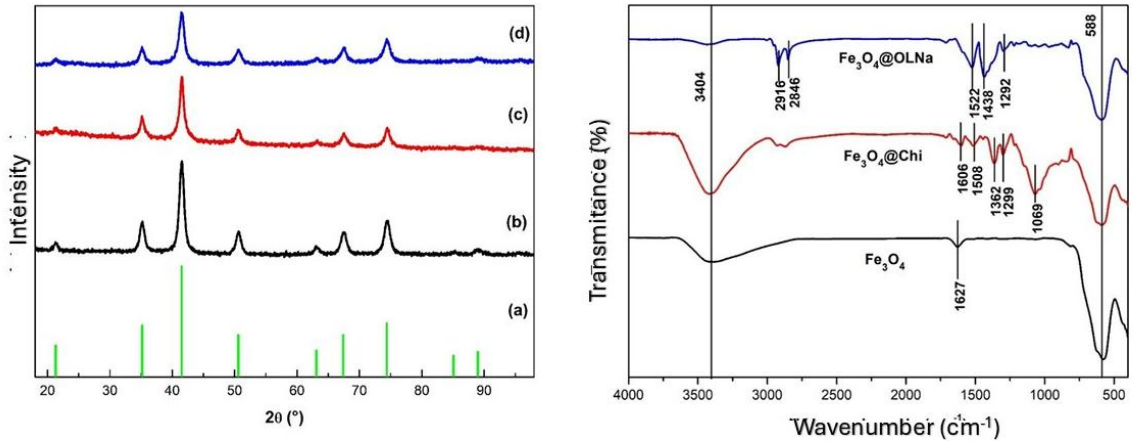
Edible oils may contain several inorganic elements related to their production. Due to their high carbon content, the decomposition and analysis of trace elements in this type of sample is not a trivial task, often requiring the use of small masses or solvent extractions. Therefore, analytical methods for analyzing trace elements in oil are of interest in analytical chemistry. In this present study, functionalized magnetic nanoparticles were developed with the aim of promoting the extraction of metals present in oil using Magnetic Solid Phase Extraction (MSPE) technique. Fe_3O_4 nanoparticles were synthesized via co-preciptation assisted by sonochemistry and functionalized by chitosan (Fe_3O_4@Chi) and sodium oleate (Fe_3O_4@OL) in order to improve their selectivity, nanoparticle stability and interactions with the oil matrix. The magnetic nanoparticles were characterized by X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR) (Figure 1), which confirmed, respectively, the nanostructure of the synthesized materials, with crystallite sizes ranging from 10.36 nm to 11.23 nm, and successful functionalization evidenced by the appearance of characteristic bands between 2916 cm^{-1} and 1069 cm^{-1} for each functionalizing agent, as well as mass loss due to thermal instability with the increasing temperature. In a preliminary MSPE test, 20 mg of nanomaterial was dispersed in 20 mL of oil, after this, the mixture was shaken for 15 min and separately using a neodymium magnet. For desorption, 3 mL of HNO_3 10% v v^{-1} was added in nanoparticle and mixed for 3 min. The solution was carried for ICP-OES analysis. The Fe_3O_4@OL have the best recoveries and a reduction in the concentration of leached iron was also observed when compared with other materials. The method showed satisfactory efficiency in calcium recovery, with rates ranging from 57% to 116%, Cu, Fe, Mn, and Zn have recovery between 30 and 85%. The results indicate that the functionalization was successful and that the proposed approach in this study has potential, although method optimization is necessary to achieve higher recoveries rates, as well, choose the optical conditions.

Figure 1: XRD and FTIR for Fe_3O_4, Fe_3O_4@Chi, and Fe_3O_4@OLNa.



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[CNPq, CAPES, NUTEC, FUNCAP]

RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY
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DIRECT SOLID SAMPLING BY PLASMA-MEDIATED VAPOR GENERATION

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Plasma-mediated vapor generation (PMVG) represents a recent approach for sample introduction, demonstrating excellent performance in atomic spectrometric techniques aimed to detecting trace elements. Typically generated using a dielectric barrier discharge (DBD) reactor, the plasma produces reactive species that convert the analyte into the gaseous phase. This method avoids the use of chemical reagents and has proven to be highly efficient across various applications[1].
Despite its application to a wide variety of analytes and sample matrices, PMVG still remains predominantly limited to liquid samples. Direct PMVG from solid samples has not yet been reported. Solid samples are typically treated by digestion or extraction prior the digests/extracts introduction into the PMVG reactor as a liquid. However, these sample preparation methods are often time-consuming and require multiple reagents. To overcome this limitation, the present work investigates the possibility of direct introduction of solid samples by PMVG for mercury determination using atomic absorption spectrometry (AAS). All method parameters were optimized prior to analysis.
A lab-made 3D-printed PMVG reactor was constructed in a DBD configuration. For sample introduction, approximately 20 mg of raw shark tissue (used for optimization) was placed on a small piece of fiberglass paper (10 x 10 mm), which was then inserted into the reactor. Argon was used as a discharge and carrier gas at 50 mL min^{-1}. The electrodes were connected to a lab-made high-voltage sinusoidal power supply, delivering 3 kV. The reactor's gas output was connected to a cold dryer (-2 °C) for water vapor condensation, followed by an amalgamator tube filled with gold-coated alumina to preconcentrate Hg released during the PMVG step. The amalgamator was electrically heated to 700 °C to release the trapped Hg, and its gas output was connected to a T-shaped quartz absorption cell (unheated), positioned in the optical path of an AAS instrument.
The calibration curve was linear across the entire concentration range tested (10 to 1000 µg L^{-1} of $MeHg^+$, 20 µL), with a coefficient of determination of 0.9996. Peak height of the transient signal was used as the measurement criterion rather than peak area due to the lower relative standard deviation (< 10%). The limit of detection was 3 µg kg^{-1} (50 pg Hg absolute). The use of the amalgamator results in significant improvement of the limit of detection, since all the Hg gradually volatilized from the solid sample during the PMVG step (180 s) was rapidly released from the amalgamator, resulting in a narrow peak (full width at half maximum of 4 s). A comparison between standard solutions containing 100 µg L^{-1} of Hg^{2+} or $MeHg^+$ showed no significant difference in the signal intensities. This demonstrates the capability of the reactor to convert both species into free Hg atoms. The total Hg in shark and salmon tissue samples, determined by PMVG-AAS, was 728 ± 48.3 µg kg^{-1} and 12.3 ± 1.91 µg kg^{-1}, respectively. These results were in agreement with those obtained by a conventional method using a single-purpose mercury analyzer instrument, which were 670 ± 137 µg kg^{-1} and 13.0 ± 1.74 µg kg^{-1}, respectively, for shark and salmon. Additionally, approximately 10 mg of certified reference materials (CRM) were analyzed by the proposed PMVG method, yielding and agreement of 95% for the CRM DORM-4 (fish protein), and 108% for the CRM DOLT-4 (dogfish liver).
Although the results are still preliminary, the proposed method demonstrates a proof of concept of direct application of a PMVG reactor to solid samples. The developed system was able to volatilize Hg from fish tissues and release it in the form of cold Hg vapor without the need for additional reagents, and using a low power plasma reactor. In summary, this work presents the first successful use of PMVG directly to an untreated solid sample.

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DEVELOPMENT AND APPLICATION OF SUSTAINABLE VAPOR GENERATION METHODS FOR TRACE ELEMENT ANALYSIS BY SPECTROMETRIC TECHNIQUES

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Trace element analysis in environmental samples is commonly performed using spectrometric techniques that rely on efficient sample introduction systems. Methods for introducing samples by vapor generation have emerged as highly valuable alternatives for improving the detection limits of these techniques[1]. Therefore, this study aimed to develop and apply sustainable vapor generation methods as alternatives to conventional introduction methods, reducing or eliminating the use of expensive, unstable, and toxic-waste-generating reagents. A photochemical vapor generation (PVG) methodology coupled with ICP OES was proposed for Cr determination. The PVG system was built using a 19 W flow through lamp as UV reactor. The experimental conditions of PVG system were studied using a continuous flow mode and 50 µg L^{-1} Cr^{3+} standard solution in 30% (v v^{-1}) formic acid medium. The generated volatile Cr species were directed by a carrier gas, N_2, to a gas-liquid separator and introduced into the ICP OES. The highest efficiency in the generation of volatile species was obtained using a 19 W flow through UV reactor, irradiation time of 60 s and a carrier gas flow rate of 40 mL min^{-1}. A thermochemical vapor generation (TVG) system was built in our lab[2], using an infrared lamp and formic acid medium, coupled to the atomic absorption spectrometer (AAS) to determine total Hg in water and sediment samples from estuaries in Northeastern Brazil. Hg concentrations in sediments ranged from 24.9 to 28.5 µg kg^{-1} at Parnaíba Delta (less impacted) and 89.7 ± 7.1 µg kg^{-1} at Cocó River (more impacted), while the values in water samples were 2.2 ± 0.4 µg L^{-1} and 10.1 ± 1.2 µg L^{-1}, respectively. All levels remained below the limits of CONAMA Resolution No. 452/2012, indicating a low ecotoxicological risk. The ecological grade assessment (AGREE)[3] indicated that both systems (PVG-ICP OES and TVG-AAS) are sustainable, highlighting their potential for efficient environmental monitoring of trace metals.

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[CAPES, CNPQ]

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A simple single standard internal standardized slope ratio calibration for direct mineral analysis by laser-induced breakdown spectroscopy

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The mineral sector is essential worldwide, supporting various production chains. In 2024, U.S. non-fuel mineral production was valued at $106 billion, slightly higher than in 2023. Metal production rose to $33.5 billion, while industrial mineral production remained at $72.1 billion. This sector generates thousands of jobs globally[1]. To ensure the quality of minerals, rapid and accurate analytical methods are essential. Laser-induced breakdown spectroscopy (LIBS) is a promising technique for direct, rapid multi-element analysis, but it usually suffers from intense matrix effects[2]. This study proposes a internal standardized slope ratio calibration approach (IS-SRC) combined with sodium borate fusion or lithium borate fusion for the determination of Li, Al, Ti, Si, Fe, Ca, Mn and K in several mineral samples by LIBS. Sodium and boron or lithium and boron were used as internal standards to mitigate matrix effects and improve the method's accuracy. The IS-SRC method, shown in Figure 1, was validated by determining Al, Fe, Li and Si in spodumene; Al, Fe, Si and Ti in bauxite; Al, Ca, Si and Mn in manganese ore; Al, Ca and Si in portland cement; and Al, Fe and K in soil. The spodumene (from different locations in the state of Minas Gerais, Brazil) results were compared with values obtained for the same samples (Spodumene 1, used as standard, and Spodumene 2, used as sample) by ICP OES. For other mineral matrices, reference materials were used as standards and samples. The method provided relative errors between -25% and 15% and relative standard deviations (RSD) ranging from 0.1% to 2.2%. The limits of detection for all analytes were in the 0.0002% - 0.1% range.

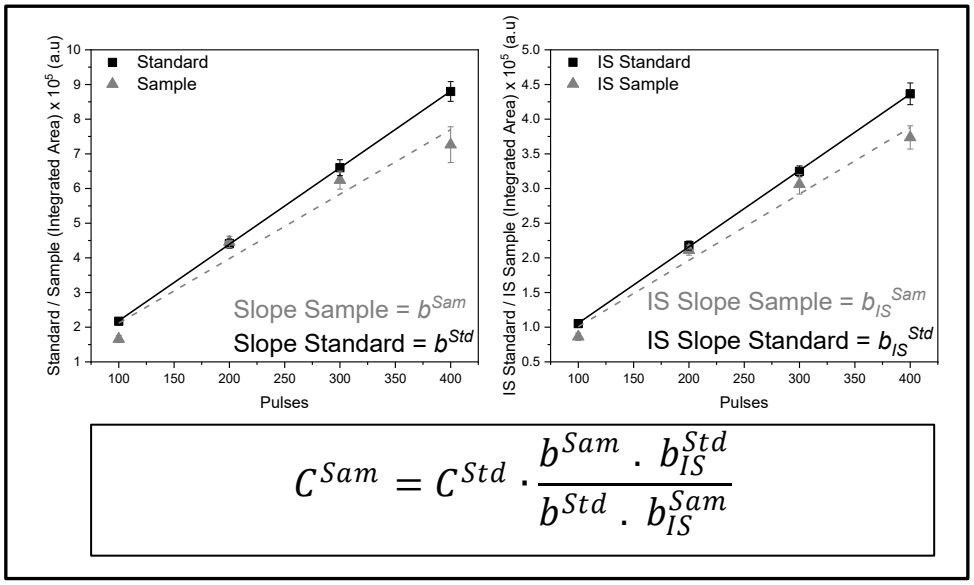

Fig. 1. Plots and equation for the IS-SRC method

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RSAS 2025 17th Rio Symposium ON ATOMIC SPECTROMETRY
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Elemental Determinations in *Leucaena leucocephala* by Spectroscopic Techniques

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Leucaena leucocephala, a leguminous tree-shrub plant, is widely regarded as invasive plant in tropical and subtropical regions, poses a threat to native biodiversity and complicates the management of natural ecosystems. Its rapid growth, high biomass production and protein content make it suitable for applications in agriculture and/or renewable energy. The removal and replacement of *Leucaena* trees may be a probable management approach to specie control. *Leucaena* and its derivates is useful for application in agriculture and/or energy production[1], and elemental characterization is crucial to determine their energy potential and suitability of biomass for different processes. Leucaena twigs, leaves and pods were collected at Fazenda Jequitibá (Pirassununga, São Paulo State), mixed, crushed in a chipper JF 2D chopper, then in a Willey type knife mill. A mass of 100 g of crushed *Leucaena* was torrefied in a muffle furnace (low O_2 atmosphere) at 260°C for 1 h. Dried and powered samples of *Leucaena* and biochar were digested in a closed vessel conductively-heated digestion system (CHDS) using diluted nitric acid[2]. Aluminum, C, Cu, Fe, K, Mg, Mn, P, S, and Zn were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Found concentration (mg kg^{-1}) were in the following ranges: 23 - 435 (Al), 5 – 12 (Cu), 113 – 429 (Fe), 7265 – 35391 (K), 863 – 3274 (Mg), 29 – 382 (Mn), 597 – 3219 (P) and 18 – 67 (Zn). Relative standard deviations (n=10) were within 1-15% interval. The digestion efficiency was evaluated based on residual carbon content (934 - 1906 mg L^{-1}), which were considered acceptable for ICP determinations.

In addition to the inorganic characterization, aimed at exploring the applications of *Leucaena* biochar, its potential as a vehicle for controlled nutrient release was also evaluated. Nitrogen, phosphorus and potassium (N-P-K)-enriched biochar containing 10% (m/m) N-nitrate, P-phosphate, K-KCl was pressed (5 ton) into pellets (500 mg each). Pellets were then immersed in 20-mL deionized water and the release of nutrients to solvent was evaluated for up to ten hours at one-hour intervals. The concentration of total N, P and K was carried out by molecular (NO, PO) and atomic (K) spectrometric determinations[3] using the AnalytikJena contrAA300 high-resolution continuous source flame spectrometer. The results showed that N-nitrate was completely released within 5 h; P-phosphate and K-KCl were only partially released (70% of the expected content) even after 7 and 8 hours, respectively. These findings suggest the potential use of *Leucaena* biochar as a controlled-release fertilizer and soil conditioner, demonstrating its relevance for agricultural applications.

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Real-time FRET analysis of zinc, albumin, and fatty acid-mediated modulation of insulin oligomerization

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Zinc ions (Zn^{2+}) are essential for insulin stability and bioavailability. Within pancreatic β-cells, insulin is stored as Zn^{2+} stabilised hexamers that require dissociation into monomers to become biologically active after secretion[1]. This dynamic assembly disassembly process is tightly regulated by zinc-buffering proteins, primarily Human Serum Albumin (HSA), which promotes the release of Zn^{2+} from insulin complexes in plasma[2]. However, under pathological conditions such as Type 2 Diabetes Mellitus (T2DM), elevated concentrations of non-esterified fatty acids (NEFAs) notably long-chain fatty acids like Palmitate compete with Zn^{2+} for binding sites on HSA, inducing conformational changes that reduce its zinc-binding affinity[3]. In this study, we developed a real-time FRET-based assay to investigate how HSA modulates Zn^{2+} mediated insulin complex dynamics, encompassing both the formation and dissociation of Zn^{2+} stabilised insulin hexamers, and how this balance is influenced by the presence of NEFAs. Our system quantitatively monitors the kinetics of these processes under near physiological conditions. We demonstrate that, in the presence of HSA alone, insulin dissociation proceeds efficiently, consistent with albumin's role as a Zn^{2+} binding protein. However, the addition of palmitate, which binds to HSA, markedly impairs dissociation of insulin multimers. This impaired decomplexation reduces the availability of active insulin in circulation. These findings support the hypothesis that NEFA-induced inhibition of insulin dissociation may contribute to insulin resistance, offering a mechanistic explanation for metabolic dysfunction observed in T2DM. Moreover, this work underscores the regulatory role of zinc in insulin dynamics and demonstrates the value of fluorescence-based analytical techniques for real-time measurement of biologically relevant metal-induced protein oligomerisation. From a therapeutic standpoint, this mechanism may help explain the delayed onset and variable action profiles of Insulin observed in individuals with elevated non-esterified fatty acids (NEFAs), such as those with Type 2 Diabetes Mellitus (T2DM) and Obesity. As most clinical insulin formulations rely on Zinc stabilised hexamers, reduced Human Serum Albumin (HSA) Zn^{2+} buffering could delay the release of active monomeric insulin.

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[**FAPESP, CNPq, INCTBio and BBSRC**]

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Selective Lithium Recovery from Spent LIBs via Ultrasound-Assisted Formic Acid Leaching

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Lithium-ion batteries (LIBs) were introduced in the 1990s in response to the global demand for better energy storage technology. Today, they are widely used in mobile phones, computers, cameras, and electric vehicles[1]. However, their improper disposal raises environmental concerns, and the lack of efficient recycling routes limits the recovery of valuable metals[2]. In this study, formic acid was investigated as a selective leachant in the ultrasonic-assisted leaching of lithium from the black mass of spent LIB cathodes. Screening experiments (100 mg black mass; 10 mL HCOOH at 10, 25, or 50% v/v) were performed in an ultrasonic bath (42 kHz, 50 °C, 30 min). As shown in Figure 1a, the 10% v/v solution maximized Li solubilization, while higher concentrations (25–50%) significantly reduced recovery. This counterintuitive trend is attributed to chemical passivation, caused by surface reconstruction and metal–formate precipitation that block reactive sites, as well as to diminished cavitation efficiency in concentrated media, which limits bubble collapse and mass transfer. After optimizing the acid concentration, ultrasound time was investigated by applying 15, 30, 60, 90, 120, and 150 min of irradiation at 10% v/v HCOOH (42 kHz, 50 °C) (Figure 1b). Lithium recovery increased progressively with irradiation time, reflecting ultrasound-driven thinning of the diffusion boundary layer and disruption of solid–liquid interfaces, which enhance mass transfer and accelerate Li deintercalation under mild acidic conditions while preserving selectivity over transition metals. Recovery reached a maximum at 90 min, beyond which no significant improvement was observed (120–150 min). This plateau indicates that most of the readily accessible Li had already been solubilized, and additional irradiation provided little benefit as the system approached leaching equilibrium. Post-leach, the liquor was centrifuged, adjusted to pH 10.5–11.0 with 5 M NaOH, and Li_2CO_3 was precipitated using saturated Na_2CO_3/ethanol, then redissolved in 1% v/v HNO_3 for analysis. Lithium recovery was quantified by ICP-OES (Avio 200, PerkinElmer). The results highlight formic acid as a promising, greener alternative for selective lithium leaching from spent LIBs, especially when coupled with ultrasonic irradiation to maximize recovery efficiency. In particular, the optimized condition (10% v/v HCOOH, 42 kHz, 50 °C, 90 min) achieved efficient Li extraction while minimizing the use of aggressive reagents, offering a sustainable route for future recycling strategies.

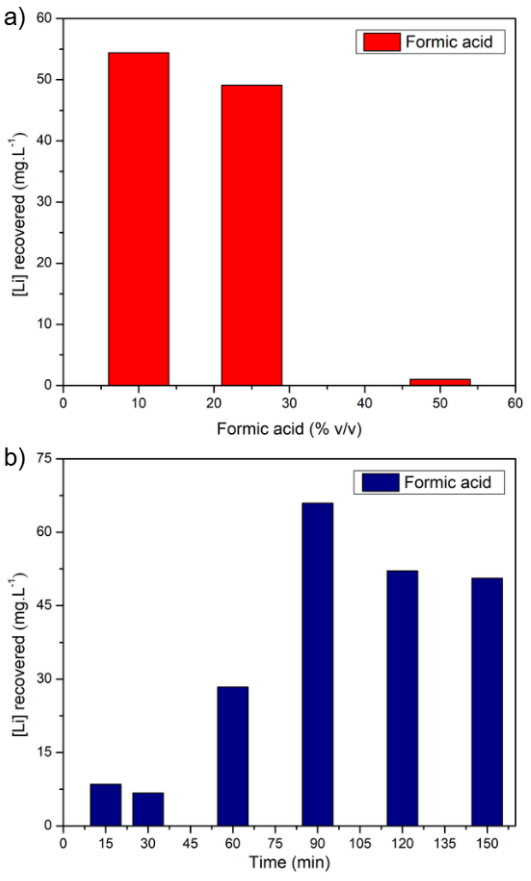

Figure 1. a) Total recovery of Li using different molar fractions of formic acid. b) Total recovery of Li at different ultrasound times using 10% formic acid.

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[CNPq, CAPES, FAPESP, USP]

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Ultrasonic-assisted leaching of Li and Co from black mass using deep eutectic solvent

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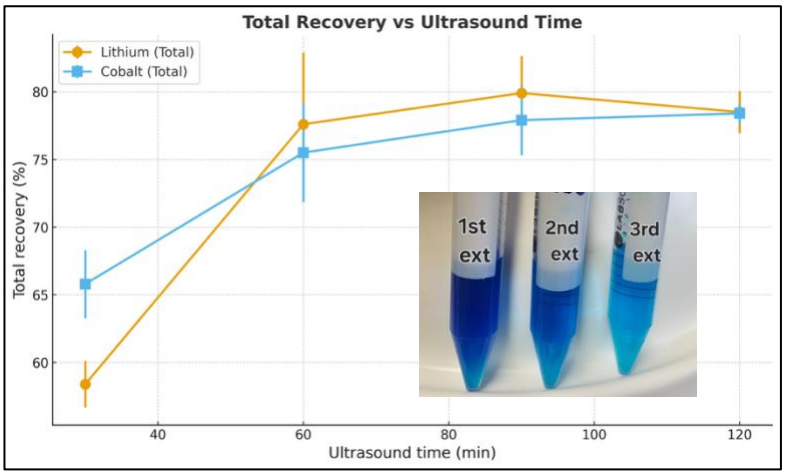
The recovery of critical metals from spent lithium-ion batteries is a key strategy for sustainable resource management and the circular economy. Conventional hydrometallurgical processes typically rely on strong mineral acids and elevated temperatures, which, although effective, generate hazardous waste and demand high energy inputs. As a greener alternative, deep eutectic solvents (DES) combine low toxicity, non-volatility, simple synthesis, and tunable physicochemical properties, making them promising media for selective metal recovery[1-2]. Here, we report for the first time the use of ultrasound (US) to assist the leaching of Li and Co from $LiCoO_2$ black mass employing a deep eutectic solvent based on choline chloride and formic acid (ChCl:HCOOH, 1:2 molar ratio). The DES was synthesized at 90 °C for 3 h under stirring (300 rpm) and was characterized in terms of its molecular structure and formation by ^{1}H-NMR and FT-IR, as well as by its viscosity and density. For each experiment, ~0.100 g of $LiCoO_2$ was treated with 5 g of DES-FA in an ultrasonic bath (35 kHz, 60 °C) for different irradiation times (30–120 min), followed by three sequential extractions. All measurements were performed by ICP OES. Lithium solubilization reached ~80% at 90 min, while cobalt extraction was stabilizing at ~79% after 120 min. The enhanced performance under US is attributed to sonochemical effects that promote cavitation and microjets, leading to the disruption of particle agglomerates, the thinning of diffusion layers, and the generation of highly reactive local environments. These processes accelerate deintercalation and mass transfer within the solid–liquid interface. Combined with the mild acidity of DES-FA, which enables simultaneous leaching of both metals while favoring faster kinetics for Li, ultrasound provided a synergistic effect that enhanced the overall process and preserved the distinct extraction profiles of Li and Co. The extraction behavior of the two metals can be explained by their different speciation in the DES-FA medium. Cobalt is likely reduced from Co(III) to Co(II) by formic acid and stabilized through the formation of chloro-complexes such as $[CoCl_4]^{2-}$ with chloride anions from ChCl, favoring its solubilization. In contrast, lithium does not form stable complexes with chloride under these conditions. It is primarily extracted as a solvated cation, stabilized by the extensive hydrogen-bond network of the DES. This difference accounts for the faster leaching kinetics observed for Li compared to Co. Selective recovery was achieved by pH-controlled precipitation, with cobalt oxalate at pH 4-5 and lithium carbonate at pH 10. The Eco-Scale score of 85 confirmed the greenness of the method. This pioneering approach highlights the potential of coupling DES chemistry with ultrasound. Together, they represent a sustainable and efficient route for recovering critical metals from battery waste.



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[CNPq, BAM, CAPES, FAPESP]

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Ecological Risk Assessment of Tailings from the B1 Dam Failure (2019) at Córrego do Feijão Mine, Brumadinho, Brazil

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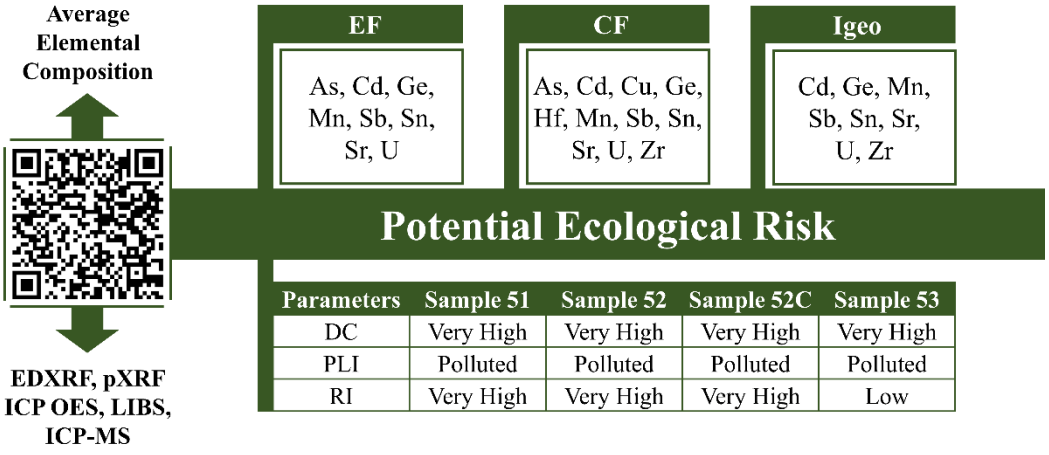
In 2019, the collapse of Dam B1 at the Córrego do Feijão mining complex released ~13 million m^3 of tailings into the environment. This event is regarded as one of the most devastating disasters in the history of the global mining industry in terms of human casualties, environmental degradation, and socio-economic repercussions on an unprecedented scale. The tailings, characterized by a complex and heterogeneous elemental composition, remain in the affected areas and continue to pose ecological risks due to their bioaccumulative properties and potential for environmental harm over short-, medium-, and long-term timescales. This study assessed the potential ecological risk[1] of four tailing samples (namely 51, 52, 52C, and 53), using Al and Sc concentrations in local soils as the background for normalization,[2] to characterize geochemical behavior through the calculation of the enrichment factor (EF), contamination factor (CF), degree of contamination (DC), geoaccumulation index (Igeo), pollution load index (PLI), ecological risk factor (ERI), and ecological risk index (RI). Elemental concentrations were previously determined using a multimethod analytical approach involving EDXRF, pXRF, ICP-MS, ICP OES, and LIBS, and are presented via a QR Code in Figure 1. The EF, CF, and Igeo indices revealed severe contamination by Cd, Ge, Sb, and Sn. In general, As, Cd, Cu, Ge, Mn, Sn, Sr, and Zr showed enrichment levels ranging from “substantial” to “extremely high”, while Al, Ca, and Cr remained close to natural background levels. Despite its abundance, Fe exhibited only a “moderate” EF due to the naturally high iron content in regional soils. The Igeo values indicated “high” to “very high” geoaccumulation for Cd, Ge, Mn, Sb, Sn, Sr, U, and Zr. Integrated indices (DC, PLI, and RI) confirmed a severe environmental impact across all samples. The PLI values, all exceeding the threshold value of 1, suggest cumulative pollution, especially in samples from the original tailings dam. RI values varied: three samples were classified as having “very high” risk (RI > 600), while one sample exhibited “low” risk (RI = 62), due to absence of Cd, which has a high toxicity factor (30) in the RI calculation. This variation highlights the index’s sensitivity to specific contaminants, even at low concentrations, and its limitation in excluding elements such as Sb and Tl from risk calculations. Moreover, despite ongoing remediation and compensation efforts, the long-term impacts associated with the tailings’ elemental composition are likely to persist, posing continued risks to ecosystems and human health.



Parameters	Sample 51	Sample 52	Sample 52C	Sample 53
DC	Very High	Very High	Very High	Very High
PLI	Polluted	Polluted	Polluted	Polluted
RI	Very High	Very High	Very High	Low

Figure 1. Integrated Assessment of Potential Ecological Risk Based on Elemental Composition and Contamination Indices

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DES-assisted leaching of metals from LED e-waste optimized by a Box–Behnken design

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The rapid growth of the electronics industry, driven by technological innovation, has led to an accelerated generation of electronic waste (e-waste). Among these residues, light-emitting diode (LED) lamps stand out as hazardous waste due to their high content of potentially toxic metals, which can cause severe environmental and human health impacts if improperly discarded. E-waste also has value as a secondary material source that could reduce raw material use. Geopolitical concerns add urgency, since many raw materials in e-waste are classified as critical by the European Commission (2023) due to high supply risks[1]. Therefore, developing sustainable strategies for the selective recovery of metals is essential. In this work, we investigated the leaching of metals from LED lamp waste using deep eutectic solvents (DES), which are promising alternatives to conventional leaching media due to their low cost, simple preparation, biodegradability, and tunable physicochemical properties. There are still a few studies on e-waste using DES[2-3]. Two DES were synthesized: choline chloride:lactic acid (DES-LA, 1:1, mol/mol) and choline chloride:urea (DES-U, 1:2, mol/mol), both obtained by heating at 60 °C until a homogeneous liquid was formed, followed by characterization by TGA, DSC, and FTIR. A Box–Behnken design was applied to optimize extraction conditions, and ICP OES was used to determine metal contents in the leachates after dilution.

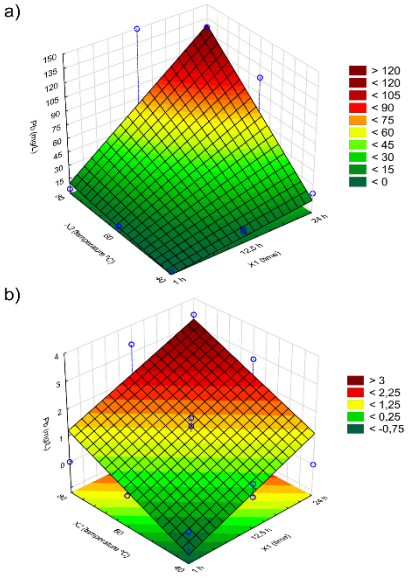

Figure 1. a) Fitted Surface for Choline Chloride/Lactic Acid DES; Variable: Pb (mg/L); 3 3-level factors , 1 Block, 15 Runs; MS Pure Error=45,03 b) Fitted Surface for Choline Chloride/Urea DES; Variable: Pb (mg/L); 3 3-level factors , 1 Block, 15 Runs; MS Pure Error=0,26

Extraction tests were performed on 100 mg of the spent LED samples. In these tests, 2 mL of DES was added to each vial, and a Dubnoff Shaking Water Bath was used to control temperature and agitation speed. Time intervals ranged from 1 to 24 hours, agitation speeds ranged from 50 to 150 rpm, and temperatures ranged from 40 to 80°C. After extraction, the DES solutions were centrifuged and stored in Safe-Lock tubes. Before determining the extracted metal content, the samples were diluted with ultrapure water. Figure 1 shows the obtained results for the Box-Behnken design. The DES-LA (a) (R^2 = 0.94; lack-of-fit (p) = 0.14) achieved significantly higher Pb leaching compared to the DES-U system (b) (R^2 = 0.74; lack-of-fit (p) = 0.26), with temperature and time identified as the main influencing factors. Other elements such as Fe, Co, Cu, Ni, and Ti were also mobilized, with percentage recoveries calculated in comparison to the initial mass of each sample (%(m/m). Under optimized conditions, Pb recovery reached 0.001–0.263%, while Fe reached 0.018–0.477%, Co reached 0–0.00025%, Cu reached 0.001–0.022%, Ni reached 0.0008–0.002% and Ti reached 0–0.0009%. These results highlight the potential of DES, particularly DES-LA, as environmentally friendly solvents and promising media for the selective recovery of metals from LED e-waste.

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PHOTOCHEMICAL VAPOR GENERATION: FROM HIGHLY SENSITIVE METHOD DEVELOPMENT TO VOLATILE SPECIES IDENTIFICATION

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Photochemical vapor generation (PVG) is an emerging alternative sample introduction technique for analytical atomic spectrometry, combining advantages of efficient separation of analyte from matrix and significantly higher introduction efficiency than possible with conventional pneumatic nebulization of solutions. Volatile analyte species are synthesized during UV irradiation of an aqueous photochemical medium typically containing low-molar mass carboxylic acids, mainly formic or acetic acid. Its applicability has gradually been expanded to many transition metals, including several platinum group elements, which produce volatile metal carbonyls from formic acid-based media with very high generation efficiencies. Over the past five years, our group has made significant contributions to the development of new, highly sensitive PVG-based methods coupled with inductively coupled plasma mass spectrometry (ICP-MS), especially for elements such as Ru, Ir, Re, and Rh[1–4].

In order to thoroughly understand the PVG mechanism, it is crucial to identify the final volatile products. The majority of volatile species have been identified using gas chromatography mass spectrometry (GC-MS). However, despite the high PVG yields, this approach has not succeeded in identifying the photochemically generated volatile species of Ru, Os, and Ir from HCOOH-based media[1,2,5]. Based on the use of HCOOH, these were presumed to be less stable metal carbonyls with the general formula $M_x(CO)_yH_z$.

This presentation will provide an overview of our recent successful attempts to identify photochemically generated volatile Ru, Os, Re, Ir, and Rh (hydrido)carbonyls using two alternative mass spectrometry ionization techniques - direct analysis in real time coupled with high-resolution mass spectrometry (DART-HRMS)[6] and selective ion flow tube mass spectrometry (SIFT-MS). The pros and cons of both approaches will be compared and discussed.

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An effective and low-cost method for further halogens determination by ICP-MS and IC in pharmaceutical drugs after pyrohydrolysis

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In recent years, there has been a significant increase in prescriptions for drugs used to treat diseases like depression and hypertension. Those drugs often contain halogens (F, Cl, Br, and I) in the active pharmaceutical ingredient (API) structure or as impurities on the excipients. Therefore, halogens are considered indispensable elements for the pharmaceutical industry. Thus, monitoring the concentration of these elements in such samples is required to ensure drug efficacy and consumer health[1]. However, relatively few studies report on the determination of halogens in pharmaceutical samples. The determination of halogens (F, Cl, Br, and I) can be performed by spectrometric techniques, such as inductively coupled plasma mass spectrometry (ICP-MS), chromatographic techniques, such as ion chromatography (IC), or electrochemical techniques such as potentiometry by ion-selective electrode (ISE)[2]. However, the sample needs to be in solution form, requiring a sample decomposition step. Several sample preparation methods have been used for these samples, such as microwave-induced combustion (MIC), microwave-assisted alkaline extraction, and alkaline fusion, among others. Pyrohydrolysis is one of these methods and it has been applied for the decomposition of several matrices and further halogen determination[3]. However, no studies have reported the use of this method for the subsequent determination of F, Cl, Br, and I in pharmaceutical drugs. Therefore, this work proposes for the first time a pyrohydrolysis based method to prepare samples of commercial pharmaceuticals, used for treating hypertension and depression, for the subsequent determination of F, Cl, Br, and I. For this, four antihypertensive and three antidepressant pharmaceuticals were used, containing the following APIs: atenolol (ATEN), chlortalidone (CLO), clomipramine hydrochloride (CLOM), hydrochlorothiazide (HID), indapamide (IND), and nortriptyline hydrochloride (NOR). Inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the concentrations of Br and I. The concentrations of F and Cl were measured by ion chromatography (IC), with potentiometry by ion-selective electrode (ISE) serving as an additional method for F quantification. Several reaction parameters were evaluated, such as oven temperature, reaction time, sample mass, absorbing solution, carrier gas flow rate, and water flow rate. The optimal experimental parameters were a temperature of 1000 °C, a reaction time of 10 minutes, a 500 mg sample mass, a 100 mmol L^{-1} NH_4OH absorbing solution, an oxygen carrier gas flow rate of 200 mL min^{-1}, and a water flow rate of 1.0 mL min^{-1}, using an insertion speed of boat into the reactor of 0.03 cm s^{-1}. The results of the proposed method were compared with those obtained by the reference method using microwave-initiated combustion (MIC) and the the results did not differ significantly (t-test, with a confidence level of 95%) for all samples. The method accuracy was evaluated by standard addition recovery tests on three levels (50, 100, and 150%). The results obtained were in agreement with the reference values and analyte recoveries were greater than 90%. The limits of quantification of the pyrohydrolysis method in combination with the determination techniques were 6.1 µg g^{-1} for F, and 19 µg g^{-1} for Cl by IC, 0.04 µg g^{-1} for Br and 0.003 µg g^{-1} for I by ICP-MS, and 3.0 µg g^{-1} for F by ISE. Therefore, the proposed pyrohydrolysis method was suitable for the determination of halogens in drugs, with minimal reagent consumption and waste compared to conventional methods, and providing digests compatible with multiple analytical techniques (ICP-MS, IC, and ISE).

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Development of a method for the determination of microplastics in sediment, based on microwave-assisted acid digestion and machine learning identification

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Analytical methods for the determination of microplastics in sediments typically involve matrix drying, sieving, grinding, and flotation as part of the sample treatment. However, the real need for these steps and analytical validation studies are scarce[1].

This work proposes a method that avoids the drying, sieving, and flotation procedures by using a direct acid attack of HNO_3/HCl (3:1) on wet sediment samples, assisted by microwave digestion. For detection, induced fluorescence using a UV camera, with Nile Red (NR) as the fluorophore and a cell phone camera for image capture were used. Identification and quantification was performed by using artificial intelligence. The results showed that when the digestion temperature was raised to 120˚C, PET recovery decreased due to plastic particle fusion.

However, at 60˚C, microwave digestion resulted in a 97% recovery of PET particles, eliminating chitin interference and canceling cellulose fluorescence without the need for flotation. This method proved effective for monitoring plastic microparticles in sediments from the Loa River, Chile, revealing that the river is predominantly contaminated with PET microparticles, particularly upstream in the Taira area.

This method proved useful for monitoring plastic microparticles in the sediments of the Loa River in Chile, revealing that the river is primarily contaminated with PET microparticles upstream in the Taira area, likely linked to plastic bottle pollution from tourists[2].

The use of artificial intelligence for color recognition to identify different types of plastic polymers, as well as for the automatic counting of detected particles, holds great potential for expanding the scope of methods like the one presented in this study. Even if ChatGPT, have still challenges to be addressed, such as optimizing the RGB color ranges required for selective identification and solving the issue of accurately delineating the boundaries of each particle to perform an accurate counting, the use of YOLO machine learning algorithms shows that it is possible to automate the identification and counting of microplastics in sediments samples[3].

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