



# 7<sup>th</sup> BRAZILIAN MEETING ON CHEMICAL SPECIATION

Bento Gonçalves, Brazil  
November 26<sup>th</sup> to 27<sup>th</sup>, 2023

## BOOK OF ABSTRACTS and SCIENTIFIC PROGRAM





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## Organization



# Welcome to the 7<sup>th</sup> EspeQBrazil

The **7<sup>th</sup> Brazilian Meeting on Chemical Speciation (7<sup>th</sup> EspeQBrazil)** returns to Rio Grande do Sul state, in the charming city of Bento Gonçalves, where its third edition was also organized. In this current edition of EspeQBrazil, after the pandemic, there is much to celebrate, as robust scientific endeavors have once again proven to be the safest means to address many global challenges.

Since its first edition in 2008, inspired and chaired by Dr. Marco Zezzi Arruda (UNICAMP, Brazil), the **Brazilian Meeting on Chemical Speciation** has been an outstanding event for scientists, students, and scientific companies, aiming to discuss the state-of-the-art in chemical speciation, new applications, and the challenges in this field. The **7<sup>th</sup> EspeQBrazil** is set to host distinguished national and international speakers and participants who will significantly contribute to the dissemination and enrichment of knowledge in the chemical speciation field.

This year, the **7<sup>th</sup> EspeQBrazil** and the 16<sup>th</sup> Rio Symposium on Atomic Spectrometry (16<sup>th</sup> RSAS) will occur in the same venue, in subsequent days, considering many suggestions and the growth of speciation analysis in the atomic spectrometry field. We aim to bring together the scientific communities of both meetings to engage in a global dialogue on the latest advancements in Chemical Speciation and Atomic Spectrometry. We expect that the integration promotes further developments for both areas and fruitful cooperation and advancements can arise from **7<sup>th</sup> EspeQBrazil**.

The Organizing Committee is proud to welcome all the participants in the **7<sup>th</sup> EspeQBrazil**, in which an intense scientific program will be provided. The pleasant city of Bento Gonçalves also offers many tourist attractions as well as excellent hospitality and gastronomical infrastructure for the participants.

Welcome to the 7<sup>th</sup> Brazilian Meeting on Chemical Speciation.

**Márcia Foster Mesko**

**Chair of the 7<sup>th</sup> Brazilian Meeting on Chemical Speciation**

**Federal University of Pelotas (UFPeI) - Brazil**



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## Sponsors

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## Sponsors



## Support





# GENERAL INFORMATION

## EVENT VENUE

### **Dall'Onder Grande Hotel**

Rua Herny Hugo Dreher, 197

Zip code: 95703-200

Bento Gonçalves – RS, Brazil

+55 (54) 3455.3555

## GENERAL OFFICE AND REGISTRATION (Carménère Hall)

November 26<sup>th</sup>, 2023: 09:00 to 19:00 h

November 27<sup>th</sup>, 2023: 08:30 to 18:30 h

## EXHIBITION AREA (Carménère Hall)

November 26<sup>th</sup>, 2023: 09:00 to 22:00 h

November 27<sup>th</sup>, 2023: 08:30 to 18:30 h

## PARTICIPANT MATERIAL

It is guaranteed only for pre-registered participants. To get the EspeQBrazil kit (bag, Book of Abstracts, etc) you must present your personal document.

## CONGRESS BADGE

The use of the identification credential is mandatory to access the locations of the meeting. In case you lose your badge, go to the EspeQBrazil office to print a new pass upon payment of a R\$ 20.00 fee.

## ACCESS TO THE 7<sup>th</sup> EspeQBrazil

Access to the conference rooms will only be allowed with the presentation of the badge.



## **MEDIA DESK**

All speakers with presentations must go to the Media Desk (at Carménère Hall) to test the presentation material. This is very important so that your lecture can be presented without problems.

## **POSTER INFORMATION**

The 7<sup>th</sup> EspeQBrazil will have a poster session on November 27<sup>th</sup>. Posters must be fixed on their allocated space between 08:30 and 10:45 h, on November 27<sup>th</sup>. After the session, posters must be removed by the authors. Posters not removed by the authors will be removed by the Organizing Committee and will be available for pick up by the authors until 18:00 h of November 27<sup>th</sup>, at the EspeQBrazil office. After this period, the posters will be discarded.

## **ORAL PRESENTATIONS**

Participants with oral presentations or flash poster presentations must present themselves to the room monitor at least 30 minutes before the start of the session in which they will participate. Files used in the presentations must be saved previously at the Media Desk. Authors must use the slide template in 16:9 format (widescreen) that will be available on the event website.

## **CHANGES TO THE EVENT PROGRAM**

The organizing committee reserves the right to modify the scientific and social program of the event at any time, to solve technical or operational difficulties or for any reason considered essential for the development of the event's activities.

## **CERTIFICATES**

The certificates will be made available to the participants in digital form, on the event webpage, in the participant area (<https://rsas-espeq.com.br/participante/login>).

## **SIMULTANEOUS TRANSLATION**

There will be no simultaneous translation.



## **INTERNET**

The 7<sup>th</sup> EspeQBrazil will provide wireless internet to the participants of the event on the premises of the Dall'Onder Grande Hotel.

## **FOOD**

The restaurant of the Dall'Onder Grande Hotel will offer a buffet service for lunch and a *à la carte* service for dinner. In the surroundings of the hotel other restaurants and fast food are available for the participants of the event.

## **TOURIST INFORMATION**

The company Dall'Onder-Viagens e Turismo, the official agency of the 7<sup>th</sup> EspeQBrazil, will offer an exclusive service to the participants of the event, located in the lobby of the hotel.

## **EMERGENCY NUMBERS**

Ambulance/Medical service: 192

Military police: 190

Fire department: 193



# COMMITTEES

## ORGANIZING COMMITTEE

Márcia Foster Mesko, UFPel (Chairwoman)

Érico Marlon de Moraes Flores, UFSM

Fábio Andrei Duarte, UFSM

Paola de Azevedo Mello, UFSM

Rochele Sogari Picoloto, UFSM

Rodrigo Cordeiro Bolzan, UFSM

Sergio Roberto Mortari, UFN

## SUPPORT COMMITTEE

Darlina Mello Souza, UFSM

Ethel Antunes Wilhelm, UFPel

Filipe Soares Rondan, UFPel

## SCIENTIFIC COMMITTEE

Amauri Antonio Menegário, UNESP

Cláudia Carvalhinho Windmoller, UFMG

Érico Marlon de Moraes Flores, UFSM

Fábio Andrei Duarte, UFSM

Juliana Naozuka, UNIFESP

Josué Carinhonha Caldas dos Santos, UFAL

Kelly da Graças Fernandes Dantas, UFPA

Letícia Malta Costa, UFMG

Márcia Foster Mesko, UFPel

Marco Aurélio Zezzi Arruda, UNICAMP

Marco Tadeu Grassi, UFPR

Maria das Graças Andrade Korn, UFBA

Paola de Azevedo Mello, UFSM

Sergio Roberto Mortari, UFN

Valfredo Azevedo Lemos, UESB

Wladiana Oliveira Matos, UFC



## Tributes

***“In recognition for the outstanding contribution to the field of Chemical Speciation”***



**Joanna Szpunar**

French National  
Research Center  
France



**Jörg Feldmann**

University of Graz  
Austria



**Marco Aurélio  
Zezzi Arruda**

UNICAMP  
Brazil



**Maria das Graças  
Andrade Korn**

UFBA  
Brazil

## Opening Conference Speaker



**Ewa Bulska**

University of Warsaw  
Poland

## Closing Conference Speaker



**Jörg Feldmann**

University of Graz  
Austria

## Plenary Lecture Speaker



**Marco Aurélio  
Zezzi Arruda**

UNICAMP  
Brazil



## Invited Speakers

**Alicia Mollo**

Universidad de la República, Uruguay

**Amauri Antonio Menegário**

UNESP, Brazil

**Cláudia Carvalhinho Windmoller**

UFMG, Brazil

**Daniela Santos Anunciação**

UFAL, Brazil

**Fabiane Goldschmidt Antes**

Embrapa, Brazil

**Joanna Szpunar**

French National Research Center, France

**Jörg Bettmer**

University of Oviedo, Spain

**Josué Carinhanha Caldas Santos**

UFAL, Brazil

**Kelly da Graças Fernandes Dantas**

UFPA, Brazil

**Letícia Malta Costa**

UFMG, Brazil

**Marco Tadeu Grassi**

UFPR, Brazil

**Mirna Sigrist**

Universidad Nacional del Litoral, Argentina

**Rodrigo Moreto Galazzi**

UNICAMP, Brazil

**Wladiana Oliveira Matos**

UFC, Brazil

**Zoltan Mester**

National Research Council Canada, Canada



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# SCIENTIFIC PROGRAM



## Scientific Program - Schedule

### November 26<sup>th</sup>

TIME	MALBEC	PINOT CENTER	CARMÉNÈRE HALL
10:00 – 12:00 h		Short Courses 1 and 2	
14:00 – 15:45 h	Workshop		
17:30 – 19:10 h	Opening Ceremony		
19:30 – 23:00 h			Welcome Cocktail

### November 27<sup>th</sup>

TIME	MALBEC	CARMÉNÈRE HALL
09:00 – 10:30 h	Session 1	
10:30 – 11:00 h		Coffee-break
11:00 – 12:05 h	Session 2	
14:00 – 15:00 h	Session 3	
15:00 – 16:30 h		Poster Session
16:00 – 16:30 h		Coffee-break
16:30 – 18:10 h	Session 4	
18:00 – 18:40 h	Closing Conference	
18:45 – 19:30 h	Closing Ceremony	



## November 26<sup>th</sup> (Sunday)

9:00 - 17:00 h

### Registration

Carménère Hall

### Short Courses (10:00 - 12:00 h)

#### Short course 1: Chemical speciation in environmental studies: strategies, challenges and instrumental advances

**Room:** Pinot Center

**Speakers:** Cláudia Carvalhinho Windmoller (UFMG, Brazil) and Daniela Santos Anunciação (UFAL, Brazil)

#### Short course 2: Chemical speciation for nutritional and food analysis

**Room:** Pinot Center

**Speakers:** Kelly da Graças Fernandes Dantas (UFPA, Brazil) and Letícia Malta Costa (UFMG, Brazil)

### Workshop (14:00 - 15:45 h)

#### Workshop: Trends in chemical speciation analysis

**Room:** Malbec

**Coordinator:** Amauri Antonio Menegário (UNESP, Brazil)

14:00 - 14:05 h **Opening:** Amauri Antonio Menegário (UNESP, Brazil)

14:05 - 14:25 h **Trends in chemical speciation analysis: in-situ measurements using DGT**  
**Speaker:** Marco Tadeu Grassi (UFPR, Brazil)

14:25 - 14:45 h **Studies on chemical speciation in biological and environmental systems: the influence of experimental models**  
**Speaker:** Josué Carinhanha Caldas Santos (UFAL, Brazil)

14:45 - 15:05 h **Advances in arsenite determination by ion chromatography and electrochemical detection in water for human consumption**  
**Speaker:** Alicia Mollo (Universidad de la República, Uruguay)

15:05 - 15:25 h **Exploring beyond the four arsenic species commonly reported in rice**  
**Speaker:** Mirna Sigrist (Universidad Nacional del Litoral, Argentina)

15:25 - 15:45 h **Discussion**





## Opening Ceremony

Room: Malbec

17:30 - 18:00 h

### Opening and Welcome

Márcia Foster Mesko (UFPel, Brazil)

*Chair of the 7<sup>th</sup> EspeQBrazil*

### Tributes

Honored 1: Joanna Szpunar (French National Research Center, France)

Honored 2: Jörg Feldmann (University of Graz, Austria)

Honored 3: Marco Aurélio Zezzi Arruda (UNICAMP, Brazil)

Honored 4: Maria das Graças Andrade Korn (UFBA, Brazil)

18:00 - 18:30 h

### Cultural presentation

18:30 - 19:10 h

### Opening conference:

#### Speciation, where it came from and where it is going?

Ewa Bulska (University of Warsaw, Poland)

19:30 - 23:00 h

### Welcome cocktail

Carménère Hall

## November 27<sup>th</sup> (Monday)

### Session 1 (9:00 - 10:30 h)

Chair: Paola de Azevedo Mello (UFMS, Brazil)

Room: Malbec

9:00 - 9:40 h

### From fractionation to speciomics: to infinity and beyond

**Plenary lecturer:** Marco Aurélio Zezzi Arruda (UNICAMP, Brazil)

Sponsored by **Nova Analítica**

9:40 - 10:05 h

### Isotope probes in iron speciation analysis in plants and bacteria

**Invited speaker 1:** Joanna Szpunar (French National Research Center, France)

10:05 - 10:30 h

### A traditional tool for elemental speciation: HPLC-ICP-MS and its use for the characterisation of nanomaterials

**Invited speaker 2:** Jörg Bettmer (University of Oviedo, Spain)

10:30 - 11:00 h

### Coffee-break





Session 2 (11:00 - 12:05 h)	
<b>Chair:</b> Wladiana Oliveira Matos (UFC, Brazil)	
<b>Room:</b> Malbec	
11:00 - 11:10 h	<b>Oral presentation 1: Mass balance analysis of PFAS in communal waters</b> <u>Viktoria Müller</u> , Andrew Kindness, Jörg Feldmann The James Hutton Institute, United Kingdom/ University of Graz, Austria
11:10 - 11:20 h	<b>Oral presentation 2: DGT with ferrihydrite binding phase for analysis of labile species of Ge in freshwater and determination by ICP OES</b> <u>Mayara P. dos Santos</u> , Shelden M. de Paula, Rafael G. Dolatto, Éder J. dos Santos, Marco T. Grassi UFPR, Brazil
11:20 - 11:30 h	<b>Oral presentation 3: Chemical speciation of hexavalent chromium in organic fertilizer by LC-ICP-MS and spectrophotometry</b> <u>Ívero P. Sá</u> , Samara Gomes Banhos, Mykaelli Andrade Santos, Pascoal F. Nhamue, Ana Rita A. Nogueira UFSCar, Brazil
11:30 - 11:40 h	<b>Oral presentation 4: Specimomics analysis of transgenic soybean somatic embryogenesis using HILIC coupled simultaneously with TQ-ICP-MS and ESI-HRMS/MS</b> Lilian Seiko Kato, <u>Vinnícius Henrique da Silva</u> , Ana Beatriz Santos da Silva, Jorge Henrique Pedrobom, Diego Campaci de Andrade, Guilherme Crispim de Faria Cruz, Marco Aurélio Zezzi Arruda UNICAMP, Brazil
11:40 - 12:05 h	<b>Phosphorus speciation as tool to improve nutrients recovery from agricultural wastes</b> <b>Invited speaker 3:</b> Fabiane Goldschmidt Antes (Embrapa, Brazil)
12:05 - 14:00 h	<b>Lunch</b>
Session 3 (14:00 - 14:25 h)	
<b>Chair:</b> Marco Tadeu Grassi (UFPR, Brazil)	
<b>Room:</b> Malbec	
14:00 - 14:25 h	<b>Nanomaterials in non-chromatographic speciation analysis of arsenic</b> <b>Invited speaker 4:</b> Wladiana Oliveira Matos (UFC, Brazil)



**Flash poster presentation (14:30 - 15:00 h)**

**Coordinators:** Rochele Sogari Picoloto and Alessandra Schneider Henn (UFSM, Brazil)

**Room:** Malbec

14:30 - 15:00 h

**Flash poster presentation 1: Selenium species As urease inhibitors for the development of fertilizers with increased efficiency**

Aryanna Sany Pinto Nogueira Costa, Maria de Fátima Correia da Silva Neta, Josué Carinhanha Caldas Santos, Daniela Santos Anunciação  
UFAL, Brazil

**Flash poster presentation 2: Speciation and chemical fractionation of REE in water samples from the Paraíba do Sul River**

Raquel C. Gradwohl, Luiz Felipe P. P. Moreira, Melina B. T. Zanatta, Amauri A. Menegário  
UNESP, Brazil

**Flash poster presentation 3: Stability thiomersal in simulated vaccine samples: A speciation study made using cold vapour techniques**

Jarol R. Miranda-Andrades, Rodrigo A. Gonçalves, Joseane A. Mendes, Douglas F. Oliveira, José Marcus de Oliveira Godoy, Ricardo Q. Aucelio  
PUC-Rio, Brazil

**Flash poster presentation 4: Two-dimensional paper-based device for evaluating Ni and V porphyrins through laser ablation inductively coupled plasma mass spectrometry**

Eduarda Quadros Machado, Julián Eduardo Bállen Castiblanco, Leandro Wang Hantao, Marco Aurélio Zezzi Arruda  
UNICAMP, Brazil

**Flash poster presentation 5: Rhodamine-derived fluorescent probe for redox speciation of ionic iron in environmental samples**

Sângela Ferreira da Silva, Amanda Luise Alves Nascimento, Karrolyne Rocha da Costa, Ari Souza Guimarães, Josué Carinhanha Caldas Santos  
UFAL, Brazil

**Flash poster presentation 6: Influence of exposure to gold nanoparticles on proteins and iron metalloproteins distribution in bean sprouts**

Aline P. Oliveira, Juliana Naozuka, Cassiana S. Nomura  
USP, Brazil



<b>15:00 - 16:30 h</b>	<b>Poster session</b> Carménère Hall
<b>16:00 - 16:30 h</b>	<b>Coffee-break</b>
<p align="center"><b>Session 4 (16:30 - 17:45 h)</b></p> <p><b>Chair:</b> Josué Carinhanha Caldas dos Santos (UFAL, Brazil) <b>Room:</b> Malbec</p>	
16:30 - 16:55 h	<p><b>From tofu to black fly larvae: metal speciation in novel protein sources</b></p> <p><b>Invited speaker 5:</b> Zoltan Mester (National Research Council Canada, Canada)</p>
16:55 - 17:20 h	<p><b>Chemical speciation analysis by HPLC-ICP-MS: from environmental to foodstuff samples</b></p> <p><b>Invited speaker 6:</b> Rodrigo Moreto Galazzi (UNICAMP, Brazil) Sponsored by <b>Analytik Jena</b></p>
17:20 - 17:45 h	<p><b>Speciation and fractionation of rare earth elements in the environment: state of art and new challenges</b></p> <p><b>Invited speaker 7:</b> Amauri Antonio Menegário (UNESP, Brazil)</p>
<p align="center"><b>Closing Conference</b></p> <p><b>Chair:</b> Érico M. M. Flores (UFSM, Brazil) <b>Room:</b> Malbec</p>	
18:00 - 18:40 h	<p><b>Closing conference:</b></p> <p><b>Could whales suffer from decommissioning of oil and gas pipelines – a bedtime story?</b></p> <p>Jörg Feldmann (University of Graz, Austria)</p>
<p align="center"><b>Closing Ceremony</b></p> <p><b>Room:</b> Malbec</p>	
18:45 - 19:30 h	<p>Márcia Foster Mesko (UFPEL, Brazil) <i>Chair of the 7<sup>th</sup> EspeQBrazil</i></p> <p>Information and remarks of the 7<sup>th</sup> EspeQBrazil Poster Awards Closing</p>



# Sponsors Technical Lectures

<b>Diamond Sponsor technical lecture: Analytik Jena</b> <b>November 30<sup>th</sup>, 2023</b> <b>Room: Pinot Center - Room A</b>	
<b>15:30 - 15:55 h</b>	<b>High resolution inductively coupled plasma optical emission spectroscopy: technology and special applications.</b> <b>Speaker:</b> Júlio Cezar Paz de Mattos (Analytik Jena, Brazil)
<b>Gold Sponsor technical lecture: Perkin Elmer</b> <b>November 27<sup>th</sup>, 2023</b> <b>Room: Pinot Center - Room A</b>	
<b>12:15 - 12:40 h</b>	<b>Updates on new technologies present in Perkin Elmer systems that contribute to analyzes focused on chemical speciation.</b> <b>Speaker:</b> Marcelo Anselmo Oseas da Silva (Perkin Elmer, Brazil)
<b>Gold Sponsor technical lecture: Agilent Technologies</b> <b>November 27<sup>th</sup>, 2023</b> <b>Room: Pinot Center - Room A</b>	
<b>14:30 - 14:55 h</b>	<b>Hyphenated systems for elemental speciation: advances in HPLC and ICP-MS/MS.</b> <b>Speaker:</b> Bruno Menezes (Agilent Technologies, Brazil)
<b>Gold Sponsor technical lecture: Nova Analítica</b> <b>November 29<sup>th</sup>, 2023</b> <b>Room: Pinot Center - Room A</b>	
<b>12:15 - 12:40 h</b>	<b>Total workflow approach to sample preparation for ICP analysis.</b> <b>Speaker:</b> Mariana Ortega Garcia (Nova Analítica, Brazil)
<b>Gold Sponsor technical lecture: Thermo Fisher Scientific</b> <b>November 29<sup>th</sup>, 2023</b> <b>Room: Pinot Center - Room C</b>	
<b>15:00 - 15:25 h</b>	<b>Analytical technologies - boost your productivity.</b> <b>Speaker:</b> Felipe Rezende (Thermo Fisher, Brazil)
<b>Sponsor technical lecture: Vert</b> <b>November 29<sup>th</sup>, 2023</b> <b>Room: Pinot Center - Room C</b>	
<b>12:00 - 12:25 h</b>	<b>Simplify digester: a reliable alternative for sample preparation aiming at elemental analysis by ICP techniques.</b> <b>Speaker:</b> Gabriel Gustinelli Arantes de Carvalho (Vert, Brazil)



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# ABSTRACTS



# Opening conference

## SPECIATION, WHERE IT COME FROM AND WHERE IT IS GOING?

**Ewa Bulska**

University of Warsaw, Biological and Chemical Research Centre, Warsaw, Poland, 02-089  
e-mail: ebulska@chem.uw.edu.pl

Speciation is an extremely important concept not only for modern analytical chemistry, but also for environmental research, clinical and industrial analysis, and even for the protection of historic objects. When refereing the aspect of chemical analysis, it is primarily the ability to provide measurement results that can reliably answer brave questions. Speciation is, above all, learning about diversity, often occurring in very low concentrations and in samples with complex chemical composition. Hence, the most important task of an analyst is to understand chemical equilibria, thoroughly understand the question of speciation, and, in particular, prepare a tailor-made research scenario. The examples were selected to show that in speciation research it is important to obtain complementary results. Hence the use of various analytical methods simultaneously or sequentially. Examples of selenium speciation research, a classic of the species, will be used to illustrate the above considerations. Examples include examining the speciation of iron, magnesium and fluorine will be also used to illustrate the main futhure of speciation. Thus the diversity in chemical species, oxidation states, as well as isotopic specietion will be presented. To conclude, the aim of the presentation is to show speciation as a holistic property of the studied objects, which makes it necessary to use non-routine analytical procedures. The aim is to higlihted that speciation is a big challenge, and that's where its beauty lies.

- 1 Gawor A., Gajewski Z., Paczek L., Czarkowska-Paczek B., Konopka A., Wryk G., Bulska E., "Fluorine-Containing Drug Administration in Rats Results in Fluorination of Selected Proteins in Liver and Brain Tissue", International Journal of Molecular Sciences, 23(8) (2022);
- 2 Karasinski J., Tupys A., Halicz L., Bulska E., "A Novel Approach for the Determination of the Ge Isotope Ratio Using Liquid-Liquid Extraction and Hydride Generation by Multicollector Inductively Coupled Plasma Mass Spectrometry", Analytical Chemistry, 93(40) (2021) 13548-1355;
- 3 Karasinski J., Tupys A., Yang L., Mester Z., Halicz L., Bulska E., "Novel Approach for the Accurate Determination of Se Isotope Ratio by Multicollector ICP-MS", Analytical Chemistry, 92(24) (2020) 16097-16104;
- 4 Wróbel K., Karasiński J., Tupys A., Arroyo Negrete M.S., Halicz L., Wróbel K., Bulska E., "Magnesium-Isotope Fractionation in Chlorophyll-a Extracted from Two Plants with Different Pathways of Carbon Fixation (C3, C4)", Molecules, 25(7) (2020) 1644;
- 5 Gawor A., Ruszczyńska A., Czauderna M., Bulska E., "Determination of selenium species in muscle, heart and liver tissues of lambs using mass spectrometry methods", Animals, 10(5) (2020) 808;
- 6 Karasiński J., Nguyen-Marcinczyk C., Wojciechowski M., Bulska E., Halicz L., "Determination isotope fractionation of Cr (III) during oxidation by LC/Low-Resolution MC-ICPMS", Journal of Analytical Atomic Spectrometry, 35 (2020) 560-566.

**[The work was supported by the National Science Centre, Poland, under research project "Application of the ORM for precise determination of the isotope ratios of elements" grant, contract number UMO-2021/41/B/ST4/04231]**



# Closing Conference

## COULD WHALES SUFFER FROM DECOMMISSIONING OF OIL AND GAS PIPELINES – A BEDTIME STORY?

Nick Marczinczik<sup>a</sup>, Lhiam Paton<sup>a</sup>, Thomas Lindsay<sup>a,b</sup>, Thebny Thaise Moro<sup>a,c</sup>, Raquel Gonzalez de Vega<sup>a</sup>, David Clases<sup>a</sup>, Jörg Feldmann<sup>a,b\*</sup>

<sup>a</sup>University of Graz, TESLA-Analytical Chemistry, 8010 Graz, Austria

<sup>b</sup>University of Aberdeen, Chemistry, AB24 3UE Aberdeen, Scotland, UK

<sup>c</sup>Universidade Federal de Santa Catarina, Chemistry, Florianopolis, SC, Brazil

\*e-mail: joerg.feldmann@uni-graz.at

We are all aware of mercury in the marine environment. Mercury biomagnifies from sub-ppt to over 100 ppm in concentration in predatory fish. Speciation studies show that the majority is present as methylmercury at every trophic level – hence methylmercury accumulates while inorganic Hg does not. This lecture will show that whales show one of the highest levels of mercury and most of this not as methylmercury but in HgSe micro to nanoclusters (1,2,3). This may compromise the bioactive pool of selenium. We don't know if there is already too much mercury in the ocean, but do we want to risk adding significant amounts to it so that more whales are affected by mercury? Or so higher concentrations of MeHg reach fish commonly found in the human diet? The lecture will show how mercury accumulates in off-shore oil and gas pipelines and it will discuss what could happen if we leave them there? (4,5). The story unfolds when data are used generated by the following methods: CV-AFS, SS-ID-GC-ICPMS, TEM, XRF-mapping, AF4-MALS-ICPMS, sp-ICP-TOFMS, LA-ICPMS, AFM, RAMAN

1 Z. Gajdosechova et al. Sci. Rep. 10 (2016) 1-12.

2 M.A. Subirana, et al., Anal. Chem. 93 (2021), 12733-12739.

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# Plenary Lecture

## FROM FRACTIONATION TO SPECIOMICS: TO INFINITY AND BEYOND

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The determination of the total concentration in a sample, although important, does not reflect its complexity, once a diversity of species may be present. Then, fractionation studies and chemical speciation are welcome strategies to evaluate such species [1], and, more recently, all of these species can be better evaluated through the speciomimic strategies [2]. Then, this work permeates through fractionation, chemical speciation and speciomimics, and some examples are presented, such as the fractionation of proteins in serum sample or porphyrins in crude oil, the application of chemical speciation for As and Se species in rice, garlic, and Brazil nuts, and the speciomimic is exemplifying through a biotechnological material of soybean. Additionally, this work points out these strategies in an increasing of complexity in terms of analytes, ranging from target with standards available for characterizing the analysis to nontarget, using multi-modal analysis for the characterization of the species.

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





**7<sup>th</sup> BRAZILIAN MEETING ON  
CHEMICAL SPECIATION**

Bento Gonçalves, Brazil  
November 26<sup>th</sup> to 27<sup>th</sup>, 2023

# INVITED SPEAKERS



## ISOTOPE PROBES IN IRON SPECIATION ANALYSIS IN PLANTS AND BACTERIA

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Iron is an essential micronutrient for microorganisms, plants and higher organisms. However, despite its large abundance, its bioavailability in the environment is limited because of its presence in the form of scarcely soluble oxyhydroxides. The principal strategy of microorganisms and plants to acquire and transport iron is to synthesize diverse iron-chelating compounds called siderophores. The understanding of the uptake of iron from soil, its transport and metabolism is critically dependent on the fine knowledge of its speciation. This knowledge can be acquired by liquid chromatography coupled with elemental or molecular mass spectrometry. Although many iron-siderophore complexes have been identified in bacterial and eukaryotic cytosols, there are many that still remain to be discovered and characterized. Also, the quantitative determination of iron-siderophore complexes is a challenge due to chromatographic lability of the species and the co-existence of several complexes in the state of fragile equilibria that can be readily shifted by the modification of sample pH or by interaction with the chromatographic stationary phase. The lecture discusses the potential of enriched-iron isotopic probes for the detection and quantitative analysis of low molecular weight iron species. On one hand, plant fluids and bacterial cytosols contain considerable excess of free ligands able to form *in-situ* isotopically labeled iron species following the addition of isotopically enriched Fe<sup>3+</sup> to the sample. On the other hand, the added enriched isotopes can exchange iron already bound in coordination complexes. The custom created isotopic patterns facilitate data mining in large datasets obtained by high resolution electrospray MS allowing exploratory investigations and *de novo* identification of iron complexes. The isotopically-labelled iron species formed *in-situ* reflect the iron speciation in the sample. This enables the quantification of iron complexes by the comparison of the intensity of ICP MS and electrospray MS peaks corresponding to the molecules containing natural and isotopically-enriched iron, after their chromatographic separation. The method does not require a prior knowledge of the molecular structures of the iron species and hence eliminates the need for molecular standards. The same chemistry of isotopically labelled and non-labelled species allows the correction of the *on-column* phenomena, such as species degradation, formation of artefacts, or change in sensitivity because of the changing conditions during gradient elution. The applicability of the isotope iron probes will be demonstrated for the quantification of mixed-ligand multicore iron complexes with malate and citrate in coconut water used as a model endosperm liquid (1) and in the analysis of peat sampled in the French Pyrenean mountains (2) where 19 siderophores belonging to four different classes were identified and quantified.

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## A TRADITIONAL TOOL FOR ELEMENTAL SPECIATION: HPLC-ICP-MS AND ITS USE FOR THE CHARACTERISATION OF NANOMATERIALS

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Liquid chromatography in combination with inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) has been a powerful tool in elemental speciation since almost 30 years. The detection selectivity and sensitivity combined with various separation mechanisms available has enabled to explore, identify and quantify manifold metal-containing compounds in environmental, clinical, and nutritional samples. The nature of these species were predominantly redox systems, small organo(semi)metallic species, and complexes between metal ions and organic ligands. The usefulness of this hyphenated technique for the characterisation of nanomaterials was first demonstrated in a study in 2006<sup>1</sup>. It was shown that - besides the characterisation of gold nanoparticles of diameters smaller than 5 nm - it was possible to get information about the presence of low-molecular and ionic species. However, the most popular ICP-MS based technique for the analysis of nanoparticles is nowadays single particle ICP-MS (sp-ICP-MS), introduced by Degueldre and Favarger<sup>2</sup>. This technique has advanced significantly over the past years, but is still limited to the detection of very small particles (approx. < 10 nm). This presentation intends to highlight the potential of HPLC-ICP-MS as a complementary tool to sp-ICP-MS. Selected examples will be shown on the analysis of gold nanoparticles in different biological samples<sup>3</sup> and on the characterisation of biogenic selenium-containing nanostructures produced by yeast and mushrooms<sup>4,5</sup>.

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## PHOSPHORUS SPECIATION AS A TOOL TO IMPROVE NUTRIENTS RECOVERY FROM AGRICULTURAL WASTES

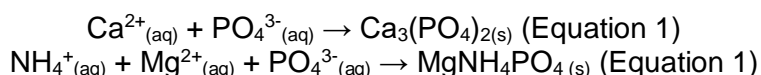
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Phosphorus is an extremely important macronutrient for the development and maintenance of terrestrial ecosystems and has gained increasing attention in the world scenario in the last few years. The uses of P encodes from fertilizers and products with higher added value as food additives and others. The growing demand for food, boosted by population growth, also increased the agricultural sector's pressure to produce more, to meet global needs. Consequently, the agricultural sector is the one that most consumes this resource, with up to 80–90% of the P flow sent to this sector because of crop production expansion. However, due to its finite nature, the availability of natural mineral resource is rapidly running out. Therefore, P recovery and recycling second-generation, that is, which comes from wastes becomes interesting for sustainable management.<sup>1</sup> On the same way, agricultural wastes, for example from protein production chains (broiler, swine and cows) are rich P sources and researches have been conducted in order to recover phosphorus from these wastes. Chemical processes based on precipitation of phosphates are the most employed as production of  $\text{MgNH}_4\text{PO}_4$  (struvite, equation 1) or  $\text{Ca}_3(\text{PO}_4)_2$  (equation 2).



The major drawback of technologies that recover phosphate from solution is that the P present in the particulate phase of solids or as organic species (phytates) cannot be recovered. Then, to improve its recovery efficiency, pre-treatments can be employed to extract or convert different P-species to  $\text{PO}_4^{3-}$ , or reactive P. Consequently, P speciation is important to evaluate these pre-treatments and determine the concentration of reactive P. In our studies, acid pre-treatment was applied to swine digestate, which is the liquid wastewater from anaerobic digestion of swine manure, to increase reactive P concentration. The economic viability of different conditions was evaluated to decide, together with process efficiency what is the optimal scenario considering real farm and wastewater treatment facilities for struvite production. Orthophosphate was measured by colorimetry using the ascorbic acid method.<sup>2</sup> Total P was measured by inductively coupled plasma optical emission spectrometry after acid digestion of samples. Results obtained showed that about 60% of total P was present in the particulate phase of solids. With this, to increase P recovery through struvite production, wastewater pretreatment should be employed. It was concluded that P speciation is an important strategy to make decisions to improve second-generation P production.

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[CNPq and FINEP]



## NANOMATERIALS IN NON-CHROMATOGRAPHIC SPECIATION ANALYSIS OF ARSENIC

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Arsenic toxicity depends on its chemical form. Therefore, Arsenic speciation analysis is usually required. In general, elemental speciation analysis is performed using High Performance Liquid Chromatography hyphenated with Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS). This type of analysis provides detailed information about the chemical species of the analyte(s) present in the sample. On the other hand, it has a high cost and it's not easy to operate, requiring high knowledge, experience, and training from the analyst. Since inorganic Arsenic species are more toxic than organic ones, the simple distinction between the organic and inorganic fraction of this element would be enough to stipulate food safety or environmental contamination by Arsenic, for example. Thus, non-chromatographic methods for Arsenic speciation analysis have been developed to reduce costs and time, besides making the speciation analysis simpler. In the past few years, several researches have explored nanomaterials, applying them in the most diverse fields. The scientific community's interest in nanomaterials is due to their unique characteristics, such as thermal, mechanical, and electronic properties; high surface/volume ratio; in addition to the possibility of their functionalization. The aim of this lecture is to present the application of nanomaterials as a strategy for Arsenic non-chromatographic speciation analysis.

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## FROM TOFU TO BLACK FLY LARVAE: METAL SPECIATION IN NOVEL PROTEIN SOURCES

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Alternative protein sources, such as plant-based proteins, cell-cultured meats and insect-based proteins, have gained increasing attention as a more sustainable, low carbon, low water consumption and ethical alternative to traditional industrial scale animal farming. Plant-based proteins, derived from sources such as soy, peas and wheat, have been consumed by humans and are generally considered safe. Properly cultivated these would have the smallest environmental footprint among all protein sources. Insect-based proteins, such as those derived from crickets, mealworms, and other insects, have gained attention as a potential alternative protein source. While insects have been consumed by humans in some cultures for centuries, there are still concerns about their safety, particularly with regard to potential allergenicity and contamination. In this lecture results on characterization of select metal species, along with digestibility, bio availability and bio accessibility of trace elements in these novel protein sources will be discussed.



## CHEMICAL SPECIATION ANALYSIS BY HPLC-ICP-MS: FROM ENVIRONMENTAL TO FOODSTUFF SAMPLES

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The physicochemical forms of most elements and their species result in different mobility, bioavailability, and toxicity, thus affecting environmental resources and living beings, including humans. Arsenic and mercury are considered the two most investigated elements in various matrices, such as the environment and foodstuffs, since both elements can be found in highly toxic forms depending on their chemical species<sup>1-4</sup>. Trivalent arsenic (As III) and pentavalent arsenic (AsV) are highly toxic, while monomethyl arsenic (MMA) and dimethyl arsenic (DMA) organic forms present significantly reduced toxicities<sup>1</sup>. On the other hand, organomercuric compounds, such as methylmercury (MeHg<sup>+</sup>), have higher toxicity than inorganic forms, and the organic species of mercury are widely recognized as neurotoxic<sup>3-4</sup>. In this context, reporting only the total element concentrations can often be misleading; therefore, HPLC-ICP-MS can provide valuable information to assess the benefits and/or risks of elements present in the sample<sup>2</sup>. For this purpose, distinct sample treatment procedures were considered to extract the elemental species from environmental and foodstuff samples, including an extraction method combined with microwave-assisted extraction (MAE) using a mild extraction solution. After sample treatment, total arsenic and mercury, as well as their respective chemical species, were determined by ICP-MS and HPLC-ICP-MS, respectively. The method validation was carried out by analyzing a range of Standard Reference Materials. According to the results, quantitative recoveries were achieved for the total element concentration, and for all monitored chemical forms, thus demonstrating the accuracy of the proposed methods for arsenic and mercury speciation in environmental and foodstuff samples. Furthermore, instrumental and method detection limits in the range of low ng/L and low µg/kg were found for arsenic and mercury species, respectively, making it feasible to determine each chemical form at low concentrations in environmental and foodstuff matrices, thereby providing information regarding possible environmental risks and food safety.

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[Analytik Jena GmbH]





## SPECIATION AND FRACTIONATION OF RARE EARTH ELEMENTS IN THE ENVIRONMENT: STATE OF ART AND NEW CHALLENGES

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Rare earth elements (REEs) encompass a group of elements, including lanthanides, scandium, and yttrium. Due to their unique properties, these elements play a crucial role in high-tech applications and processes. They are found in the environment at extremely low concentrations (in the range of nanograms per litre) and typically require sensitive determination through inductively coupled mass spectrometry (ICP-MS). REEs exhibit low solubility and limited mobility within the Earth's crust, rendering their abundance patterns invaluable for understanding geological and chemical processes and tracking anthropogenic activities. As emerging contaminants, there is a substantial knowledge gap regarding various aspects, including the speciation, distribution, and biogeochemical behaviour of these elements in the environment. These knowledge gaps underscore the need for further research and understanding of the behaviour and impact of REEs in our ecosystems. In this talk, studies related to the fractionation and speciation of REEs at least two decades will be presented, mainly to show how the evolution of knowledge related to new analytical approaches (mainly those based on the hyphenated technique) can change some statements about the solubility of the REEs proposed in the last century. For example, the classical approach (from the last century) based on filtration through a 0.45  $\mu\text{m}$  (or 0.22  $\mu\text{m}$ ) membrane doesn't represent the real solubility of REEs. Additionally, even though these data were useful to state part of the geochemistry of REEs (in this case, ultrafiltration - 5 to 30 kDa, also can be included), information about their situ lability wasn't considered, which can drive to potential mistakes (or not understanding) about REEs remobilisation in the water columns and/or sediments. In sequence, this presentation will show unpublished data based on recent analytical approaches to evaluate the fractionation and speciation of REEs: Diffusive gradients in thin films (DGT), ultrafiltration (10 and 30 KDkDa) (UF) and single particle ICP- MS (spICP-MS) techniques. Two study areas will be focused on: the Paraíba do Sul River (São José dos Campos, SP- Brazil) - river water, an industrial area potentially affected by anthropogenic discharge of REEs; the U mine in Caldas - soil and drainage water, an area containing high level of REEs. In the first area, data related to anomalies of La, Pr and Gd in DGT, dissolved and total fractions will be discussed, highlighting that the DGT technique can indicate the presence of the inert complex of Ga (Ga-DTPA or C<sub>14</sub>H<sub>24</sub>N<sub>3</sub>O<sub>10</sub>Gd), generally used in hospitals and potentially discharged in waters of the Paraíba do Sul River. In the U mine area, data related to the lability of different binding phases (carminic acid and Chelex-100) will be proven to be similar. Additionally, fractionation using sp-ICP-MS associated with filtration and UF approach (carried out in fractions of 0.45  $\mu\text{m}$ , 10 and 30 kDa) will be compared, showing different sizes of non-ionionic Ce. Finally, it will be shown that the rate of repositioning of REEs from solid phase to pore water in soils from mine pits is similar to or lower than those from waste piles (even for different pH).

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# Short Course 1

## CHEMICAL SPECIATION IN ENVIRONMENTAL STUDIES: STRATEGIES, CHALLENGES AND INSTRUMENTAL ADVANCES

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The contamination of aquatic ecosystems by different species of highly toxic trace elements has been explored in environmental studies due to the risks arising from accumulation along the trophic chain<sup>1</sup>. The course will summarize the latest methods and techniques developed focusing on strategies, challenges and instrumental advances applied to speciation in environmental analysis and its importance to evaluate the toxicity and mobility of contaminants. The elements Hg and As will be highlighted from the perspective of sample treatment strategies for separation and quantification. Humic substances exhibit heterogeneity of ion binding due to the chemical heterogeneity of their functional groups. Their ion-binding is further modified by electrostatic effects, which influence the strength of binding according to solution chemistry and the molecular charge. Interaction of humic substances and inorganic and organic arsenic species will be discussed on a basis of a modeling study<sup>2</sup>. Besides, aspects like sample treatment and instrumental analysis applied to redox and molecular speciation of As and Hg will be mentioned. The basic concepts on non-traditional stable isotope analysis will be presented. How the development of the multiple-collector inductively coupled plasma-mass spectrometry (MC-ICP/MS) enables this field of research, all progress in the sequence and potential studies to the future. How the use of the isotope fractionation can be used to establish isotope signatures and also to investigate the biogeochemistry processes of a metal in the environment. Because of the high toxicity of Hg it is one of the metals with a great number of scientific articles describing the diversity of employments of isotope studies to get very important information on its environmental cycle. Hg presents seven isotopes with different abundances. The variations in their isotope ratios uses to be greater than for other metal isotopes. It therefore presents more possibilities of mass dependent and mass independent fractionation compared to other elements. The key interactions of Hg in aquatic environment resulting in methylation and demethylation processes were studied<sup>3</sup>. The authors showed that the low and high molecular mass molecules released by the phytoplankton complex the Hg species and contribute to the abiotic reduction of the metal. The contributions of different anthropogenic sources of Hg (coal-fired power plant, Hg mining, zinc smelting and gold mining) in China was assessed<sup>4</sup> using Hg isotope analysis. The results allowed the taken of public interventions in a much more effective way. The use of Hg in small scale artisanal gold mining is one of the biggest environmental problems in the Amazon Region. The isotopic ratio analysis is a powerful technique that is already being used to study the biogeochemical cycle of the metal in this important ecosystem. Hg isotopic signatures<sup>5</sup> and the impact in tropical rivers<sup>6</sup> have been discussed using this stable isotopic analysis.

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[CNPq, FAPEAL, FAPEMIG, PPGQB-UFAL, and PPGQ-UFMG]



## Short Course 2

### CHEMICAL SPECIATION FOR NUTRITIONAL AND FOOD ANALYSIS: SHORT COURSE

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Foods are consumed raw, after cooking or in processed forms as nourishment and for enjoyment. The nutritional value can be quantified by spectrometric techniques able to estimate nutrients as total concentration. Furthermore, as important as the quantification of nutrients is to recognize if this specie is prone to be involved in reduction reactions in living organisms. It will be discussing sample pretreatments strategies developed to quantify species of some nutrients in different types of food, as such fruits, vegetables, beverages, and among others<sup>1</sup>. Additionally, principles of hyphenation of high sensitives techniques used to speciation analysis will be presented. Firstly, studies investigating the hydroponic cultivation of flaxseed and basil samples and the effects in the uptake of nutrients throughout the plant will be discussing. It will be highlighting interactions between As and Se on golden flaxseed (*Linum usitatissimum* L.) seedlings and the intoxication of the basil (*Ocimum basilicum* L.) with Cd. The focus will be devoted to the better understanding of the extension of Se in the mitigation of As translocation<sup>2</sup>. Related to the Cd it will be presented the effects of the nutrient's uptake<sup>3</sup> and distribution and accumulation of amino acids, sugars and peptides in basil samples as a defence mechanism to the Cd contamination<sup>4,5</sup>. The discussions will be extended to other foods consumed in the North region from Brazil. Nutrients were quantified after sample treatment strategies for speciation focusing on extracting fractions of high molecular weight and low molecular weight. Additionally, studies involving bioaccessibility tests by *in vitro* gastrointestinal procedures were able to evaluate the absorption of essential elements into the human body<sup>6-10</sup>.

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**[CNPq, CAPES, PPGQ-UFMG, PPGCTA-UFPA, PROPESP-UFPA, and PPGQ-UFPA]**



## Workshop: Trends in chemical speciation analysis

**Coordinator: Amauri Antonio Menegário  
(UNESP, Brazil)**



## TRENDS IN CHEMICAL SPECIATION ANALYSIS: IN-SITU MEASUREMENTS USING DGT

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Trace metal speciation in natural waters is a crucial factor to consider when evaluating potential environmental impacts. This aspect holds significant importance regarding factors such as bioavailability, transport, fate within aquatic ecosystems, as well as the establishment of water quality criteria.<sup>1</sup> Considerable attention has been directed toward the determination of metal species. In water, the predominant approach involves laboratory assessment after field sampling. Detection methods for individual metal species include spectrophotometry and atomic absorption. When dealing with multi-element species, electrochemical techniques are employed, encompassing methods like competitive-ligand exchange-cathodic stripping voltammetry,<sup>2</sup> as well as a combination of techniques, such as high-performance liquid chromatography coupled to inductively coupled plasma mass spectrometry.<sup>3</sup> More recently, an in-situ technique based on the Diffusive Gradients in Thin Films (DGT) for the measurement of labile metal species was proposed.<sup>4</sup> While DGT has demonstrated successful in-situ speciation detection for several elements, such as As, Sb, and Cr, there remain numerous challenges and paths for further research that require attention in the future, aspects that will be presented and discussed.

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## STUDIES ON CHEMICAL SPECIATION IN BIOLOGICAL AND ENVIRONMENTAL SYSTEMS: THE INFLUENCE OF EXPERIMENTAL MODELS

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Speciation analysis generally focuses on developing strategies associated with sample preparation or instrumental methodologies for quantifying different species. In addition, studies evaluating parameters related to availability or toxicity are recurrent. In this sense, the deleterious or beneficial effects, as well as the distribution of a given chemical species, can be influenced by the experimental model used. Thus, this lecture will present studies with As and Se species exploring different environmental models and Hg for various biological and environmental systems, applying molecular and elemental techniques to obtain quantitative information. The biological models evaluated were proteins/enzymes, cells, animals (rats, flies, zebrafish, and *Artemia salina*), and humans, while the environmental models were estuarine water, humic substances (organic matter), and soils. The interrelationship between the models at different levels of complexity is extremely important for establishing the chemical mechanisms that regulate the behavior and effect of each species. Finally, some perspectives on the state of the art in developing new technologies or unprecedented experimental models will be addressed in this presentation.

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



## ADVANCES IN ARSENITE DETERMINATION BY ION CHROMATOGRAPHY AND ELECTROCHEMICAL DETECTION IN WATER FOR HUMAN CONSUMPTION

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Universal access to safe drinking water is a human right, therefore, the analytical methodologies able to evaluate its quality is of utmost importance. Thus, any effort to attain simple, fast and robust methodologies, with limits of detection suitable for manifest high toxic contaminants at very low concentration is worthwhile. Nowadays, the determination of the total content of the element is not enough, being necessary also to determine the chemical species in which they are present, since in some cases the degree of danger depends on them. This work is part of a project on which our group is working, for the simultaneous determination of the major anionic components in drinking water and the trace level arsenic species. The first can be determined with conductimetric detection but the low concentration of the latter requires high sensibility in order to avoid sample preconcentration. For that purpose, analytical methodologies using ion chromatography with electrochemical detection have been developed. The determination of As(III) is performed by measuring the anodic current at a fixed potential (0.5 V). The detector is fitted with three electrodes using gold as working electrode. Its reconditioning after each measurement is essential in order to hold a reproducible response. Hence, constant (-1,5V) and pulsed (-1.5 V / 0.8 V) cleaning stages are being evaluated. In both cases very good results have been found for the determination of As(III) in water for human consumption by ion chromatography using amperometric detection, as very low limits of detection are attained.



## EXPLORING BEYOND THE FOUR ARSENIC SPECIES COMMONLY REPORTED IN RICE

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Rice is the most extensively researched cereal with regards to arsenic speciation due to its well-documented ability to accumulate significant amounts of arsenic (As), reaching concentrations of up to 1 mg/kg. The predominant arsenic species commonly found in rice grains are inorganic arsenic forms (i-As), dimethylarsinic acid (DMA), and, in much lower concentrations, monomethylarsonic acid (MMA). However, other arsenic-containing compounds can also be present. In this context, we will present findings from arsenic speciation analysis of rice samples grown and processed in Argentina, including polished, parboiled, and brown rice. This analysis was conducted using a method based on high-performance liquid chromatography and inductively coupled plasma mass spectrometry (HPLC-ICP-MS), with an acid extraction for sample preparation and anion-exchange chromatographic separation with oxalate as the eluent. In addition to the expected compounds (i-As, DMA, and MMA), unknown species were detected, with one of them being quantifiable in all the samples analyzed. This particular species was identified by combining HPLC-ICP-MS with molecular mass spectrometry using electrospray ionization (HPLC-ESI-MS/MS) in positive mode, and it was matched with species recently reported<sup>1</sup>. Finally, the arsenical speciation in rice produced in Argentina will also be briefly discussed in comparison to that from other regions across the world.

1 Raab A, Kubachka K, Strohmaier M, Preihs M, Feldmann J. Environ. Chem. (2022) EN2206



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# **CHEMICAL SPECIATION ANALYSIS/FRACTIONATION FOR NUTRITION AND FOOD SCIENCE**





## 001- ORGANOFLUORINE SPECIATION IN SEAFOOD: CHALLENGES TO OPTIMIZE THE SAMPLE PREPARATION METHOD

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The organofluorine compounds known as per- and polyfluorinated substances (PFAS) have increasing interest among researchers due to their unique characteristics. These compounds do not occur naturally, and they possess high stability, along with substantial chemical and thermal resistance. Moreover, certain PFAS are toxic and difficult for the human metabolism to eliminate.<sup>1</sup> These factors emphasize the significant importance of identifying the presence and concentration of PFAS in various products, particularly in food. Seafood stands as one of the major sources of PFAS in the human diet<sup>2</sup> and is widely consumed across the globe. Therefore, it holds great relevance to assess the presence and concentration of PFAS in seafood, using reliable analytical methods to obtain accurate results. Despite the well-established determination technique employed for PFAS determination (high-performance liquid chromatography coupled with tandem mass spectrometry using electrospray ionization, HPLC-ESI-MS/MS), the sample preparation step remains challenging due to the unique properties exhibited by each sample matrix. In the context of this study, the sample preparation was optimized using design of experiments for mixtures to determine the most suitable extraction solution for the subsequent determination of PFAS in seafood. Shrimp muscle was the chosen sample for optimization, and various mixtures were evaluated, involving different proportions of methanol (MeOH, UHPLC grade), acetonitrile (ACN, UHPLC grade), and ammonium hydroxide (250 mmol L<sup>-1</sup> NH<sub>4</sub>OH). In total, six solutions were assessed in duplicate. The observed responses pertained to the recoveries of 11 carboxylic and sulfonic acids PFAS, ranging from C<sub>4</sub> to C<sub>11</sub>. The GNU/Octave software (version 6.1.0) was employed for calculating the mathematical quadratic model and for statistical analysis. It was observed that the combination of the alkaline solution with organic solvents proved essential for extracting the analytes. This observation was substantiated by the quadratic model, which revealed that the significant coefficients pertained to the interactions between NH<sub>4</sub>OH x MeOH and NH<sub>4</sub>OH x ACN. The majority of evaluated compounds exhibited better responses (recoveries approaching 100%) to combinations of ACN and 250 mmol L<sup>-1</sup> NH<sub>4</sub>OH solution. Considering the extreme points within this experimental region, the recoveries achieved for eight of the eleven analytes ranged from 84% to 105%. The remaining three compounds exhibited recoveries ranging from 70% to 110% using a 250 mmol L<sup>-1</sup> NH<sub>4</sub>OH: ACN (1:9 v/v) extraction solution and from 61% to 121% using this mixture in a 3:7 v/v proportion. Consequently, the optimal condition for extracting analytes from seafood was determined to be within these experimental ranges, specifically using a 250 mmol L<sup>-1</sup> NH<sub>4</sub>OH: ACN (1:5 v/v) ratio. Employing this optimized condition, six seafood species (mussels, shrimp, divided into head/shell and muscle, and four types of fish) underwent the extraction procedure and subsequent analysis using HPLC-ESI-MS/MS for PFAS determination. Among the evaluated samples, ten PFAS compounds were detected, ranging from C<sub>6</sub> to C<sub>11</sub> carboxylic or sulfonic acids. Six of these compounds exhibited concentration values below the limits of quantification (LOQs < 2.5 µg kg<sup>-1</sup>). For the other compounds (PFHxA, PFHpA, PFDA, PFPS, and PFOS), PFAS concentrations ranged from 1 to 20 µg kg<sup>-1</sup>. The shrimp sample contained the highest total PFAS content, and this difference was not statistically significant (Student's-t test, 95% confidence level) between using the entire shrimp or just the muscle portion. In a subsequent stage, the sum of all PFAS in each sample will be compared to the total fluorine content, obtained using an optimized method.

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[CNPq, CAPES, INCTBio, and Universität Graz]

## 002 - INFLUENCE OF CULINARY TREATMENT ON THE CHEMICAL FRACTIONATION AND DISTRIBUTION OF MINERALS IN CORN

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Corn is a widely consumed food, used pure or in food preparations. It can be found *in nature*, canned, or in sachet form, but the industrialized versions (sachet or canned) are the most consumed. However, sachet/canned product is divided into two parts, grains (corn) and an aqueous solution. It is important to determine the elemental composition of both fractions because some minerals can migrate to the aqueous solution. Furthermore, since corn is used in various forms (*fresh*, cooked, or frozen), there is a possibility of nutrient loss during cooking or storage. In this sense, the present study proposes the evaluation of the distribution of Ca, Fe, K, Mg, Na, P, S, and Zn in corn grains and aqueous solution through culinary preparations. In addition, the chemical fractionation study of these nutrients in the different mediums was also performed. The following conditions for the distribution study of Ca, Fe, K, Mg, Na, P, S, and Zn were evaluated: (i) fresh grain, (ii) aqueous solution, (iii) fresh grain plus aqueous solution cooked, and (iv) fresh grain plus aqueous solution frozen. Moreover, for the chemical fractionation of Ca, Fe, K, Mg, Na, P, S, and Zn in fresh grain, the following solutions were evaluated: (i) H<sub>2</sub>O, (ii) 1 mol L<sup>-1</sup> HNO<sub>3</sub>, and (iii) 1 mol L<sup>-1</sup> HCl. The determination of Ca, Fe, K, Mg, Na, P, S, and Zn in grains after both distribution and fractionation studies were performed by inductively coupled plasma optical emission spectrometry (ICP-OES) after microwave-assisted wet digestion (MAWD) using 250 mg of sample and 6 mL of concentrated HNO<sub>3</sub>. For this, a microwave oven (Ethos Easy, Milestone, Italy) equipped with 44 polypropylene vessels (100 mL) and maximum temperature, pressure, and power of 210 °C, 35 bar, and 1800 W, respectively, was used. For analyte determination, a spectrometer equipped with axial view (ICP-OES, Ciros CCD, Spectro Analytical Instruments, Germany) was used. Results for the influence of culinary treatment on Ca, Fe, K, Mg, Na, P, S, and Zn distribution were: without cooking, 70% of K was in an aqueous solution from the sachet while 20% of Ca, Fe, Mg, Na, P, S, and Zn was in this solution, consequently 30% of K and 80% of Ca, Fe, Mg, Na, P, S, and Zn were found in the fresh grain. Additionally, when corn grain plus aqueous solution was cooked (100 ± 5 °C), 30% of K and 70% of Ca, Fe, Mg, Na, P, S, and Zn remained in the corn grain. However, after freezing (only grain), similar to fresh grain, 30% of K, 80% of total Ca, Fe, Mg, Na, P, S, and Zn still remained in the corn grain. Moreover, results for the chemical fractionation of Ca, Fe, K, Mg, Na, P, S, and Zn using H<sub>2</sub>O, 1 mol L<sup>-1</sup> HNO<sub>3</sub>, and 1 mol L<sup>-1</sup> HCl determination by ICP-OES are shown in Table 1.

Table 1. Results for Ca, Fe, K, Mg, Na, P, S, and Zn by ICP-OES.

Solution	Analytes, $\mu\text{g g}^{-1}$							
	Ca	Fe	K	Mg	Na	P	S	Zn
H <sub>2</sub> O	58.0 $\pm$ 3.4	11.0 $\pm$ 1.3	5815 $\pm$ 260	720 $\pm$ 39	25.5 $\pm$ 1.9	2120 $\pm$ 11	9700 $\pm$ 565	12.5 $\pm$ 0.3
HNO <sub>3</sub> <sup>a</sup>	74.6 $\pm$ 0.5	13.1 $\pm$ 0.3	5844 $\pm$ 106	765 $\pm$ 9	26.4 $\pm$ 0.8	2270 $\pm$ 13	12730 $\pm$ 166	15.2 $\pm$ 0.5
HCl <sup>b</sup>	56.3 $\pm$ 0.9	56.5 $\pm$ 0.5	4169 $\pm$ 17	606 $\pm$ 15	26.2 $\pm$ 0.4	2003 $\pm$ 42	12722 $\pm$ 315	13.4 $\pm$ 0.3

<sup>a</sup>1 mol L<sup>-1</sup> HNO<sub>3</sub>; <sup>b</sup>1 mol L<sup>-1</sup> HCl (Results are expressed in µg g<sup>-1</sup>, as mean and standard deviation, n=3).

As shown in Table 1, by using water, a low solubility of S was observed in comparison to the other evaluated solutions. In addition, when diluted HNO<sub>3</sub> was employed, a higher solubility of Ca, P, and Zn than other solutions evaluated was obtained. On the other hand, when diluted HCl was used, results for Fe were higher than by using H<sub>2</sub>O or diluted HNO<sub>3</sub>, but lower values than by using H<sub>2</sub>O or diluted HNO<sub>3</sub> were obtained for K, Mg, and P. Finally, by using H<sub>2</sub>O, diluted HNO<sub>3</sub> or HCl, the Na solubility was similar in all evaluated solutions. Then, information regarding the chemical fractionation of nutrients, such as Ca, Fe, K, Mg, Na, P, S, and Zn is essential to know the solubility of the analytes in different mediums. Moreover, it is important to know the analyte distributions because depending on the culinary treatment, some analytes can migrate from corn grains to the aqueous solution (mainly K).

<sup>1</sup> Castro JK, Vieira LP, Batista SD, Braz. J. Anal. Chem. 10 (2023) 1-12.

<sup>2</sup> Lajunen LHJ, Spectrochemical Analysis by Atomic Absorption and Emission, The Royal Society of Chemistry, 1991.



## 003 - BIOACCESSIBILITY OF METALS IN FOOD SUPPLEMENTS BY OPTICAL EMISSION SPECTROMETRY AFTER *IN VITRO* PROTOCOLS: SUITABILITY AND CHALLENGES

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Food supplements may contain combinations of vitamins, minerals, amino acids and herbal/botanical raw materials. Thus, essential and non-essential elements, intentionally added or not, can be present in these products. The determination of their bioaccessibility rather than the total elemental composition is crucial, once the bioaccessibility may affect the nutritional utilization and the toxicity of these compounds.<sup>1</sup> Different methods can be used to assess the elements bioaccessibility. The Bioaccessibility Research Group of Europe (BARGE) developed a unified bioaccessibility method (UBM) in order to produce a validated and standardized protocol. Another similar method was established in consensus by the international network INFOGEST of the COST action (European Cooperation in Science and Technology). It should be noted that these methods present some differences in terms of time of extraction, reagents concentration, enzymes, pH, etc.<sup>2</sup> In this work, the bioaccessibility of essential (Co, Cu, Fe, Mg, Mn, Mo, Ni, V, and Zn) and non-essential (Al, As, Ba, Be, Bi, Cd, Cr, La, Pb, and Sr) elements was evaluated using the UBM BARGE and the COST INFOGEST protocols and the extracts were directly analyzed by inductively coupled plasma optical emission spectrometry (ICP OES), after dilution. Four food supplement samples were evaluated, covering vitamins and minerals, minerals, and botanical types. The total concentration of elements was determined by ICP OES after microwave-assisted wet digestion. The UBM BARGE procedure consists of a three-stage process, simulating the digestive processes of the mouth, stomach, and small intestine, where the first stage simulates the gastric phase (saliva + gastric fluid), and the second stage simulates the gastrointestinal phase (duodenal fluid + bile). On the other hand, the COST INFOGEST method comprises the gastric and the gastrointestinal phases in one stage (saliva + gastric fluid + intestinal fluid). All extractions were performed at 37°C. The total concentration of Ag, As, Be, Cd, Co, La, Ni, Pb, and V was lower than the limit of quantification (LQ). The bioaccessible fractions using the UBM BARGE method were low for some elements, such as Al, Ba, Cr, Fe, Sr and Zn (up to 34%), and high for others, such as Cu, Mg, Mn, and Mo (above 98% for some elements). Considering the COST INFOGEST method, higher bioaccessible fractions were found for Cr, Cu, Mo and Mn (above 77%) and the bioaccessible fractions for Al, Ba, Fe, Mg, V and Zn were up to 39%. In addition, the amount of extracted elements after the COST INFOGEST method was higher than those obtained using the UBM BARGE method. Due to the use of HCl in both bioaccessibility assessment protocols and its complexing capacity, the extraction of essential and non-essential elements in food supplements was assessed using only 1 mol L<sup>-1</sup> HCl, without the use of the other reagents, following the same pH solutions, time and temperature conditions. In this case, the extractions for Al, Cr, V, and Zn were up to 47% and higher extractions (above 88%) were observed for Ba, Cu, Fe, Mg, Mn, Mo, and Sr. Thus, it was possible to confirm that the leaching of some elements occurs during the application of both protocols (gastric and gastrointestinal fractions) with HCl solution and heating (37 °C, 1 mol L<sup>-1</sup> HCl, without any enzyme).

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2 Brodkord, A., et al (2019) INFOGEST static in vitro simulation of gastrointestinal food digestion. *Nature Protocols*, 14 (4). p 991-1014. ISSN 1754-2189.

[CNPq, CAPES, CAS and C&EN news and UFSM]

## 004 - CHLORINE AND SULFUR DETERMINATION IN CHICKPEA BY ION CHROMATOGRAPHY WITH CONDUCTIMETRIC DETECTION

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Chickpea (*Cicer arietinum* L.) has been widely consumed due to the search for proteins of vegetable origin with high nutritional value, becoming an excellent alternative or complement to the diet. Hydration is a relevant process for nutrient absorption and better digestibility, but mineral losses may occur at this stage.<sup>1</sup> Ion chromatography with conductimetric detection (IC-CD) works for mineral determination, such as halogens and sulfur, in their anionic forms. However, a prior step in sample preparation is necessary to convert the sample into an adequate solution compatible with the determination technique and containing the species of interest fully available for determination.<sup>2</sup> Microwave-induced combustion (MIC) eliminates organic matter from the matrix, does not require the use of concentrated acids, and minimizes losses of elements by volatilization. In addition, the final solution is compatible with several techniques, including IC-CD.<sup>3</sup> Therefore, this study aimed to determine chlorine and sulfur in soaked and not-soaked chickpea samples from conventional and organic cultivation, using MIC in sample preparation for subsequent determination by IC-CD. Samples were purchased from Pelotas/Rs Brazil local market. The samples were compared regarding their cultivation (conventional x organic), hydration process (with and without soaking), and cooking method. They were decomposed by MIC and the concentration of chlorine and sulfur was determined by IC-CD.

Table 1. Chlorine and sulfur concentrations in chickpeas, soaked and not-soaked samples, , determined by IC-CD after MIC decomposition.

Cooking method	Sample	Concentration (mg kg <sup>-1</sup> )	
		Chlorine	Sulfur
Without cooking	Conventional SE	1191 ± 56 <sup>aA</sup>	1832 ± 81 <sup>aA</sup>
	Conventional CE	554 ± 44 <sup>bA</sup>	1628 ± 16 <sup>bA</sup>
	Organic SE	1268 ± 81 <sup>aA</sup>	1487 ± 92 <sup>aB</sup>
	Organic CE	606 ± 70 <sup>bA</sup>	1308 ± 6 <sup>bB</sup>
Pressure cooker	Conventional SE	679 ± 4 <sup>aA</sup>	1654 ± 74 <sup>aA</sup>
	Conventional CE	234 ± 14 <sup>bA</sup>	1591 ± 55 <sup>aA</sup>
	Organic SE	491 ± 37 <sup>aB</sup>	1280 ± 5 <sup>aB</sup>
	Organic CE	121 ± 8 <sup>bB</sup>	1270 ± 75 <sup>aB</sup>

\*A lowercase letter in the same column means a comparison between soaked (CE) and not-soaked (SE) samples; a Capital letter in the same column means a comparison between the same cultivar (conventional and organic).

Using the proposed method was possible to obtain limits of detection of 23,33 mg kg<sup>-1</sup> for Cl and 135,83 mg kg<sup>-1</sup> for S, and the relative standard deviation was between 0.6 and 6.2% for both analytes. Sulfur concentrations were higher than Cl concentrations for all evaluated samples. A notable variation in chlorine and sulfur concentrations was observed (Cl: 120-1268 mg kg<sup>-1</sup>; S: 753-1832 mg kg<sup>-1</sup>). Samples without soaking showed a concentration two times higher compared to those with soaking, for Cl, without using any cooking process. The soaked treatments, for Cl and S, had the lowest levels, which may be related to the soaking process, where the loss of minerals to the medium may occur. Concentrations in conventional samples were higher than in organic samples, for S; the reason for this possibly is the use of fertilizers during conventional cultivation.

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[CNPq, FAPERGS and CAPES]





## 005 - EVALUATION OF FLUORINE DISTRIBUTION IN BLACK TEA LEAVES, INFUSIONS, AND RESIDUE: EXPLORING ELEMENTAL FRACTIONATION

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Tea is one of the most consumed beverages in the world. Chinese legends report its consumption since 2700 BC due to its healing properties.<sup>1</sup> However, the excessive consumption of tea can cause harm to health, due to the presence of some toxic potential compounds, such as, for example, halogenated compounds. Among the halogens, special attention has been given to fluorine. In general, the presence of this chemical element in plants may be related to soil absorption and anthropogenic activities, such as the use of pesticides or agrochemicals. In addition, fluorine can be naturally present in plants and remain during the growth until consumption of the final product.<sup>2</sup> Excessive fluorine consumption can inhibit some enzymes involved in metabolic reactions, which may lead to deleterious effects on human health, such as dental and skeletal fluorosis, liver and kidney damage, and neurodevelopmental anomalies.<sup>3</sup> The determination of fluorine is necessary for the quality control of tea consumption. Thus, the present work aims to develop reliable analytical methods allowing the quantification of total fluorine in tea and infusions. For this, the microwave-induced combustion (MIC) method was optimized, evaluating parameters such as sample mass and absorbing solution for analyte retention. Sample masses from 100 to 700 mg were evaluated in the form of tablets, prepared in a hydraulic press (60 kN). Ultrapure water and NH<sub>4</sub>OH solutions (50 to 200 mmol L<sup>-1</sup>) were evaluated as absorbing solutions, with NH<sub>4</sub>OH 150 mmol L<sup>-1</sup> being the most appropriate solution for the absorption of fluorine. Fluorine determination was performed by ion chromatography (IC) and by ion-selective electrode (ISE) potentiometry. Black tea leaves sample, previously ground, was used for the optimization of the method. For this, the plant was submitted to a standard infusion process (1 g of sample in 100 mL of water – 95 ± 5 °C – for 5 min), and samples were collected at different stages: before and after infusion, as well as the residue remaining after the infusion process. The total concentration of fluorine in the different fractions mentioned was determined by IC and ISE after sample preparation by MIC. Additionally, the infusions were also analysed directly by the two techniques, and the obtained results were in agreement (97%) for both techniques. All the solutions were always filtered and diluted before analysis. Fluorine concentration in the solid black tea sample, before infusion, was 263 ± 20 mg kg<sup>-1</sup> and 245 ± 39 mg kg<sup>-1</sup>, analysing by IC and ISE, respectively. The total concentration of fluorine in the infusion was 287 ± 32 mg kg<sup>-1</sup>, and in the residue was below the limits of detection (15 mg kg<sup>-1</sup>, for both determination techniques) indicating that all fluorine present in leaves of black tea was in fluoride form, which was totally leached during the infusion process. Based on the results obtained, it was possible to trace the distribution of fluorine in black tea leaves before and after the infusion process. The method will be applied to different types of tea leaves to evaluate the fluorine fractionation.

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[CAPES, CNPq, INCTBioanalítica, FAPERGS, and UFPel]

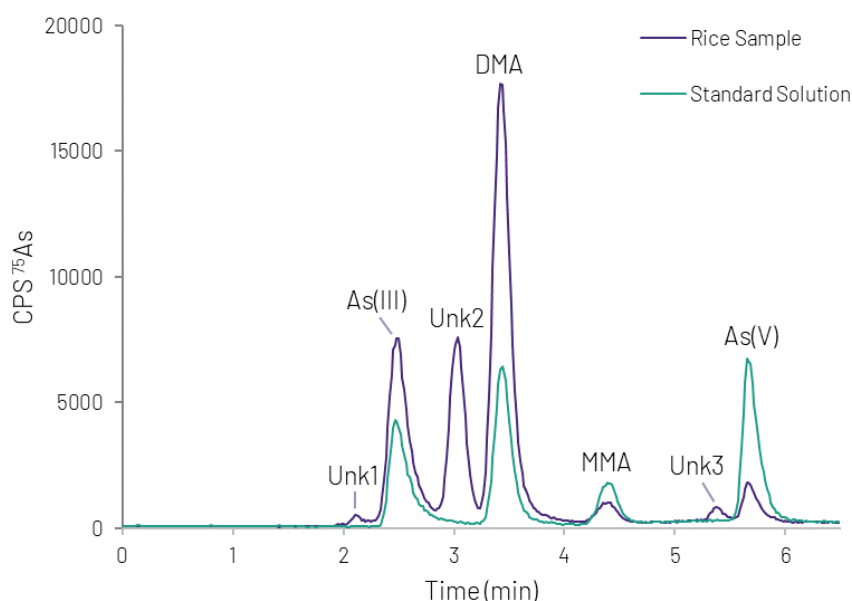
## 006 - ARSENIC SPECIATION IN RICE AND WHEAT FLOUR

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In this work, we present a validated method for the quantification of individual As species in rice and wheat flour samples, along with the results obtained from the analysis of market samples. The method is based on high-performance liquid chromatography and inductively coupled plasma mass spectrometry (HPLC-ICP-MS), using an acid extraction for sample preparation and anion-exchange chromatographic separation with oxalate as the eluent, a total run time of 6.5 minutes and excellent reproducibility in retention times. Quantification limits of 4.47, 0.69, 1.60, and 4.34  $\mu\text{g/kg}$  were achieved for arsenite, dimethylarsinate, monomethylarsonate, and arsenate, respectively. The method was applied to commercial samples of different types of rice (polished, parboiled, and brown) and some wheat flours. Wheat flour samples predominantly showed the presence of inorganic species, while all As species were found in rice samples. Wheat flour samples had substantially lower concentrations compared to rice samples. In rice samples, up to three unknown species were also detected. These were quantified using Compound Independent Calibration, and concentrations of up to 63.5  $\mu\text{g/kg}$  were found for one of them, referred to as Unk2. Unk2 was quantifiable in nearly all samples. On the other hand, in a wheat flour sample claiming to be from “agroecological” production, a concentration of 7.2  $\mu\text{g/kg}$  of DMA was found, which was significantly higher than in other flours. This sample also had a high concentration of As(III) among the flour samples (54  $\mu\text{g/kg}$ ). Among rice samples, polished rice had lower concentrations of all species, especially As(V). Parboiled rice showed a speciation pattern similar to brown rice. None of the samples exceeded the limits established for inorganic arsenic by the European Union and MERCOSUR. Several correlations were observed among different species and with the total As content.



## 007 - GRAPHENE QUANTUM DOTS-TiO<sub>2</sub> NANOPARTICLE ASSISTED PHOTOCATALYTIC MERCURY SPECIATION IN FISH SAMPLES BY CV-AAS

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Mercury (Hg) is one of the most dangerous environmental pollutants due to its toxicity and ability to accumulate in human body and environmental compartments<sup>1</sup>. Hg exists mainly in the forms of elemental mercury (Hg<sup>0</sup>), inorganic mercury (Hg<sup>+</sup>, Hg<sup>2+</sup>) and organic mercury (e.g. MeHg, EtHg, PhHg). MeHg is the most toxic species among all mercurial ones as it is neurotoxic and readily by humans and animals of the food chain<sup>2</sup>. This work presents an analytical method for the speciation and determination of mercury in fish tissue samples by cold vapor atomic absorption spectrometry (CV-AAS). Determinations were made after application of an extraction process, followed by photodegradation assisted by hybrid nanoparticles composed by graphene quantum dots and titanium dioxide nanoparticles (GQDs-TiO<sub>2</sub>)<sup>3</sup>. Due to different kinetics in photocatalytic reactions of the mercury species in the presence of GQDs-TiO<sub>2</sub>, speciation was achieved without chromatographic separation and with CV-AAS detection. The extraction process of the mercury species in fish samples was carried out following the protocol reported in the literature<sup>2</sup>. Briefly, amounts (0.50 ± 0.3 g) of fish tissue and 5 mL of HCl (5 mol L<sup>-1</sup>) were mixed in a 15 mL centrifuge tube. After ultrasonic agitation (10 min), the suspension was centrifuged at 4,000 rpm (10 min) and the supernatant was transferred to a 50 mL polypropylene centrifuge tube. For photocatalytic degradation studies and subsequent quantification by CV-AAS, 200 µL (of a 3 mg mL<sup>-1</sup>) of GQDs-TiO<sub>2</sub> dispersion and appropriate volumes of sample extracts were used. Then, they were transferred to a quartz tube (15 mL) containing 5 mL of water, inside the UV photoreactor, connected to a dedicated mercury CV-AAS system with a multi-pass detection cell. The best conditions of the method were obtained with 5 mL of solution, containing 100 µL of GQDs-TiO<sub>2</sub> dispersion (3 mg mL<sup>-1</sup>), H<sub>2</sub>O<sub>2</sub> (2% v/v), formic acid (1% m/v) with pH adjusted to 3. Under these conditions, generation of Hg<sup>0</sup> from mercurial species after 9 min (from Hg<sup>2+</sup>) and 13 min (from MeHg) occurred upon UV exposure. The generated Hg<sup>0</sup> was transferred, through controlled air flow, to the CV-AAS system. Under optimized conditions, detection limits for Hg<sup>2+</sup> and MeHg were 9 ng L<sup>-1</sup> and 16 ng L<sup>-1</sup> respectively. The method was validated by mercury speciation in the Certified Reference Material of DORM-2 as well as in 10 fish samples. The results of the analysis of the real samples indicated the presence of MeHg in fish samples at concentrations that varied between 56.3 ± 5.2 ng g<sup>-1</sup> and 22.7 ± 3.6 ng g<sup>-1</sup>. The results obtained were statistically comparable to those obtained by the method based on chemical derivatization and gas chromatography coupled to cold-vapor atomic fluorescence spectrometry (GC-CV-AFS).

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[FAPERJ, CNPq, CAPES]

## 008 - DISTRIBUTION OF Al, Ba, Bi, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sn, Sr, AND Zn IN WET PET FOOD

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A diet based on wet pet food is recommended mainly because this kind of food is more palatable and digestible than dried pet foods. Furthermore, it contains high protein, fat, vitamins, and minerals, which help improve the quality of the animal diet. However, wet food is comprised of a solid and a liquid/oily part. It is important to know the nutritional composition of both solid and liquid parts because some pets consume only the liquid part, missing out on essential nutrients. Then, information regarding the distribution of nutrients in the solid or liquid/oily portions of the wet food pet is important.<sup>1,2</sup> In this way, the present study investigates the distribution of Al, Ba, Bi, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sn, Sr, and Zn in the solid and liquid/oily portions of wet pet food from different flavors (chicken, fish, and meat). For this, the determination of Al, Ba, Bi, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sn, Sr, and Zn was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES) using an axial view optical spectrometer (Ciros CCD, Spectro Analytical Instruments, Germany). Before determination, a sample pre-treatment was required to separate the solid from the liquid/oily portion. After, the solid was dried in an oven at 105 °C for 1 h and then milled using a knife mill. The liquid portion was placed directly into a polypropylene tube and homogenized for 2 min, before weighing. Then, the solid and liquid portions were decomposed by microwave-assisted wet digestion (MAWD) using a single reaction chamber (SRC) system method. A microwave oven (SRC-UltraWave<sup>TM</sup>, Milestone, Italy) equipped with 5 quartz vessels (40 mL) and with maxima operational power, pressure, and temperature of 1500 W, 199 bar, and 300 °C, respectively was used. About 0.5 g of sample (solid and liquid/oil portions) was directly weighed inside the quartz vessels and 6 mL of concentrated HNO<sub>3</sub> were added. After, the quartz vessels were closed and positioned on the rotor, and it was inserted in the single reaction chamber, which was previously filled with 130 mL of ultrapure water, and 5 mL of concentrated HNO<sub>3</sub>. A starting argon pressure of 40 bar was applied before microwave heating. The microwave irradiation program used was as follows: *i*) ramp of 10 min at 130 °C; remaining for 10 min; *ii*) ramp of 5 min at 150 °C; remaining for 5 min; *iii*) ramp of 10 min at 250 °C; remaining for 30 min and *iv*) cooling. After cooling and pressure release, digests were collected and diluted with ultrapure water up to 25 mL for further Al, Ba, Bi, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Sn, Sr, and Zn determination by ICP-OES. The obtained results showed that Ba, Bi, Cu, Mn, and Sn were found only in the solid portion. On the other hand, even at low concentrations, Al, Ca, K, S, Sr, and Zn were found in the liquid portion (around 15% of the total concentration). In addition, concentrations ranging from 10 to 30% of total K, Na, Mg, and P migrated to the liquid portion. Therefore, pets that ingest only the liquid portion of these foods are susceptible to consuming small amounts of nutrients, which are soluble in the stabilizing solution.

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[FAPERGS, CAPES, CNPq, and UFSM]





## 009 - INFLUENCE OF EXPOSURE TO GOLD NANOPARTICLES ON PROTEINS AND IRON METALLOPROTEINS DISTRIBUTION IN BEAN SPROUTS

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The worldwide synthesis and applications of nanoparticles (NPs) across multiple domains to serve biological and industrial functions intensify their emission into the surroundings. The silver (AgNPs) and gold (AuNPs) nanoparticles found in the growth medium are potentially absorbed by plant roots and translocated to edible parts.<sup>1</sup> The NPs in plants can induce changes in the chemical composition, mainly essential elements and proteins, and, consequently, to alter the nutritional value of edible plants.<sup>2</sup> So, NPs influence on agricultural products should be studied, aiming to evaluate their effects on environmental and public health. This work aims to assess the effect of common bean (*Phaseolus vulgaris* L.) sprouts exposure to AuNPs on Fe translocation, protein distribution (albumins, globulins, prolamins, and glutelins) as well as Fe-proteins in plant tissue. In this study, common bean (*Phaseolus vulgaris* L.) sprouts were grown in aqueous medium containing Au<sup>3+</sup> or AuNPs. The sprouting was carried out for 8 days and 12-hour photoperiod. The roots from each seed (n=7) were kept submerged in 7 mL of deionized water containing different Au concentrations (0; 0.5; and 10.0 mg L<sup>-1</sup> at pH = 5.5 - 6.5) from AuNPs (60 nm) or HAuCl<sub>4</sub>. The total Au and Fe determination was done by inductively coupled plasma optical emission spectroscopy (ICP OES) after microwave-assisted acid digestion. Protein quantification was done by Bradford's method<sup>3</sup> and Fe-proteins by graphite furnace atomic absorption spectrometry (GF AAS) after fractionation of protein groups (albumins, globulins, prolamins and glutelins) by sequential protein extraction. It was found that in plants exposed to Au<sup>3+</sup> or AuNPs there was no translocation of Au (< LOQ: 11.5 µg g<sup>-1</sup>). However, in 10 mg L<sup>-1</sup> AuNPs-exposed plants the total Fe concentration in the stems significantly decreased compared to the control group (38±3%). No significant differences were observed, using 10 mg L<sup>-1</sup> Au<sup>3+</sup>-exposed. As far as protein distribution is concerned, plant exposure to Au<sup>3+</sup> increased albumin concentration compared to the control group, ranging from 43.3±0.2 to 56.2±0.2%. In contrast, growth medium supplemented with 10 mg L<sup>-1</sup> AuNPs decreased the globulins content in relation to the control group. No significant differences were verified in plants supplemented with the same concentration of Au<sup>3+</sup> (1.63±0.32 mg g<sup>-1</sup>). It should also be highlighted that there were no changes in prolamins concentration in the plants cultivated under all growing conditions. Considering Fe associated to proteins, Fe-prolamins content was below the LOD (82.5 ng g<sup>-1</sup>) for all plants. As verified in the protein distribution studies, Fe-proteins concentration in glutelin extract was not altered in AuNPs and Au<sup>3+</sup>-exposed plants. However, there were reductions of up to 66% in Fe-globulins concentration for plants grown in medium supplemented with both Au<sup>3+</sup> and AuNPs. In conclusion, although there is no translocation of Au in the plant, there were changes in solubility, composition and/or synthesis mainly of globulins as well as a decrease in the total Fe concentration and Fe-globulins. It raises issues on nutritional value of AuNPs-exposed edible plants.

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[FAPESP: 2022/02167-9 and 2021/14125-6]



## 010 - EVALUATION OF ARSENIC SPECIES IN DIFFERENT CANNED TUNA FISH (*Thunnus*) SAMPLES

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Arsenic is a ubiquitous and potentially toxic element. The inorganic species [As (III) and As (V)] are of greater concern than the partially methylated species [monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), among others]. Arsenobetaine (AsB) is the species that constitutes the greatest portion of arsenic in marine organisms and is considered inert and non-toxic.<sup>1</sup> The objective of this study was to determine the concentration of the species AsB, DMA, MMA, As (III) and As (V) in canned tuna fish samples. Arsenic speciation analysis was conducted on in oil and in brine canned solid tuna samples using ionic chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS). The total arsenic determination was performed using ICP-MS. The extraction was done using 0.2000 g of freeze-dried sample with 3 mL of 10 mmol L<sup>-1</sup> of NH<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub> at pH 10.5, in three successive steps. Initially, the samples were homogenized, after they were sonicated at 52 kHz for 15 minutes, centrifuged and the supernatant was separated. This procedure was repeated two more times and the extract was diluted to a final volume of 10 mL with a solution of 10 mmol L<sup>-1</sup> of NH<sub>4</sub>(CO<sub>3</sub>)<sub>2</sub> and filtered with a 0.45 µm syringe. The separation was carried out with an anion exchange column and detection was done with ICP-MS, monitoring the mass charge ratio (m/z) 75. For total arsenic determination, the samples were prepared using microwave-assisted acid digestion. The limits of quantitation for the five arsenic species were 0.59 mg kg<sup>-1</sup> (AsB); 0.10 mg kg<sup>-1</sup> (DMA); 0.12 mg kg<sup>-1</sup> (As (III)); 0.07 mg kg<sup>-1</sup> (MMA) and 0.10 mg kg<sup>-1</sup> (As (V)). The method showed no significant matrix effect (p<0,05). The precision and accuracy of the method were evaluated using certified reference material BCR-627 (tuna fish muscle tissue) (n=5) with certified values of 52 ± 3 µmol kg<sup>-1</sup> AsB and 2.0 ± 0.3 µmol kg<sup>-1</sup> DMA. The obtained experimental values (48.8 ± 1.2 µmol kg<sup>-1</sup> AsB and 1.91 ± 0.16 µmol kg<sup>-1</sup> DMA) were in agreement with the certified values and showed adequate precision within the analytical replicates. In the solid in oil samples the total arsenic content was between 2.65 and 5.81 mg kg<sup>-1</sup> and AsB accounted for 77-85% of the total arsenic content. In the solid in brine samples the total arsenic content was between 2.74-5.70 mg kg<sup>-1</sup> and AsB accounted for 48-76% of the total arsenic content. The other species were below method detection limits, indicating a difference in extraction efficiency between the two conserves, since the means of these percentages were different (p<0.05). The appearance of an unknown peak could indicate degradation of arsenobetaine however, more studies must be done to confirm this affirmation.

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[FAPES, CAPES, CNPq, Tommasi Ambiental, LabPetro/UFES, and PPGQUI/CCE/UFES]

## 011 - *IN-VITRO* BIOACCESSIBILITY STUDY OF CHLORINE, BROMINE, AND IODINE IN DIETARY SUPPLEMENTS

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Nowadays, there is an increase in dietary supplement consumption, and this product can contain relatively high concentrations of Cl, Br, and I. Chlorine is normally present as a counter-ion of several elements, whereas iodine is commonly added as a supplier. On the other hand, bromine can be considered a contaminant. Chlorine and iodine, considered essential elements for humans, play an important role in living cells and in the synthesis of thyroid hormones, respectively. On the other hand, the essential nature of bromine is still uncertain, but some studies report it can act as an antiepileptic agent. In addition, these elements can cause problems when absorbed at high or low levels, e.g., affecting blood pressure (Cl), decreasing iodine absorption (excess of Br absorption), and hypo- or hyperthyroidism (deficiency or excess of I absorption, respectively).<sup>1</sup> Although the information about the total content of these elements in foodstuffs is important, the knowledge about their bioaccessibility is crucial to understand their effects on human organism. *In-vitro* methods have been explored for the determination of the bioaccessibility of elements, however, studies for halogens are scarce.<sup>1</sup> Thus, the aim of this work was to determine the bioaccessible fraction of Cl, Br, and I from dietary supplements. For this, four samples of dietary supplements of different classes (vitamins and minerals, minerals, and botanicals) were used. Total concentration of Cl, Br, and I was determined by inductively coupled plasma mass spectrometry (ICP-MS) after microwave-induced combustion (MIC). The *in vitro* simulation consisted of a three-stage process, simulating the digestive processes of the mouth, stomach, and small intestine.<sup>2</sup> All extractions were performed at 37 °C. Extracts were collected in two separate phases during the digestion: the first was collected after the action of saliva and gastric fluid (denominated gastric phase), and the second was collected after the addition of duodenal fluid and bile (denominated gastrointestinal phase). The bioaccessible fraction of Cl, Br, and I in both phases was determined by ICP-MS. The results obtained are shown in Table 1. Bioaccessible fraction of Cl in both phases was lower than the limit of quantification (LOQ, 154 and 409 mg kg<sup>-1</sup> for the gastric and gastrointestinal phases, respectively) in all samples. Total concentration of Cl in all samples ranged from 0.233 to 3.45 mg g<sup>-1</sup>.

**Table 1.** Total concentration and bioaccessible fractions (between parenthesis, %) of Br and I in dietary supplements (results in µg g<sup>-1</sup>, mean ± standard deviation).

Sample	Bromine			Iodine		
	GP <sup>a</sup>	GIP <sup>b</sup>	TC <sup>c</sup>	GP <sup>a</sup>	GIP <sup>b</sup>	TC <sup>c</sup>
VM-1	< 15.1	< 57.5	1.57 ± 0.08	< 0.123	< 0.875	0.318 ± 0.015
VM-3	< 15.1	< 57.5	0.554 ± 0.023	52.2 ± 3.0 (50)	47.2 ± 0.7 (45)	104 ± 9
MN-2	< 15.1	< 57.5	7.84 ± 0.50	40.2 ± 6.1 (125)	20.1 ± 1.0 (62)	32.2 ± 2.7
BT-3	40.1 ± 3.3 (68)	< 57.5	59.3 ± 1.5	0.137 ± 0.005 (46)	< 0.875	0.296 ± 0.002

<sup>a</sup>Gastric phase (n=5); <sup>b</sup>Gastrointestinal phase (n=5); <sup>c</sup>Total concentration (n=3).

As can be seen, except for BT-3 sample in the gastric phase, the bioaccessible fraction for Br was lower than LOQ for all samples in both phases. On the other hand, the bioaccessible fraction for I could be measured in both phases for the samples VM-3 and MN-2. It was observed that the bioaccessible fraction was lower in the gastrointestinal phase. In general, the results obtained showed that the bioaccessible fraction was lower than the total content of the element, demonstrating the importance to evaluate the bioaccessibility.

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



**7<sup>th</sup> BRAZILIAN MEETING ON  
CHEMICAL SPECIATION**

Bento Gonçalves, Brazil  
November 26<sup>th</sup> to 27<sup>th</sup>, 2023

# **CHEMICAL SPECIATION ANALYSIS/FRACTIONATION FOR THE LIFE SCIENCES**

## 012 - UPLC-qToF-MS AND *IN SILICO* MODELLING TO ASSESS BUPROPION TRANSFORMATION PRODUCTS DURING OZONATION

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An increase in the occurrence of antidepressant compounds in natural waters has been observed over the past few years. The major environmental concern regarding these compounds in rivers and lakes is their potential impact on the neural systems of organisms inhabiting these habitats. Bupropion (BUP) is one of the most prescribed antidepressant compounds, presenting harmful effects even at low concentrations (in the range of  $\mu\text{g L}^{-1}$  to  $\text{ng L}^{-1}$ ). Among several technologies for the degradation of pharmaceutical compounds, ozonation has been employed in wastewater treatment as a powerful oxidation agent. Ozone acts as a strong electrophile, exhibiting high selectivity toward electron-rich functional groups in organic molecules. However, the reaction between ozone and pharmaceutical compounds can lead to the formation of transformation products which may have higher toxicity than the original compound. Therefore, the identification and quantification of transformation products during ozonation hold significant importance. The formation of transformation products during ozonation can be predicted using density functional theory (DFT) calculations to estimate the chemical reactivity of molecules in oxidation processes. Parameters like Hirshfeld population analysis, Fukui functions, and the energies of HOMO/LUMO orbitals provide useful information to elucidate transformation products formation<sup>1</sup>. Separation techniques such as ultra-performance liquid chromatography coupled with high-resolution time-of-flight mass spectrometry (UPLC-qToF-MS) have arisen as a sensitive and robust analytical technique for the identification and quantification of transformation products. In this sense, this study aimed to apply UPLC-qToF-MS and DFT calculations to predict and identify BUP transformation products during the ozonation process. Degradation experiments were carried out in a glass-jacketed reactor with a useful volume of 0.5 L. Model wastewater consisted of a 1 mg L<sup>-1</sup> BUP solution in ultrapure water. Ozone was produced using a commercial ozone generator (Ozonebras, Brazil) fed with dried air at a flow rate of 3 L min<sup>-1</sup>. Transformation products were separated using a UPLC System (Acquity<sup>TM</sup> UPLC, Waters, USA), in a C<sub>18</sub> column (Acquity UPLC<sup>®</sup> BEH C<sub>18</sub>, 1.7  $\mu\text{m}$ , 2.1  $\times$  50 mm, Waters, USA). The mobile phase consisted of (A) ultrapure water and (B) methanol, both acidified with formic acid (0.1%) on a gradient elution described previously<sup>2</sup>. The chromatographic system was connected to a qToF-MS spectrometer with an ESI ionization source (Lockspray<sup>TM</sup>, Waters, USA), operated in a positive mode with capillary voltage of 4.0 kV, sampling cone voltage of 10 V, and extraction cone voltage of 6.0 V, with a source temperature of 150 °C. Nitrogen was used as desolvation and cone gas with a flow rate of 500 L h<sup>-1</sup> and 10 L h<sup>-1</sup>, respectively, at a temperature of 400 °C. DFT calculations were carried out using Orca 5.0.4 and Multiwfn 3.8 software. Hirshfeld charge analysis, Fukui functions, and HOMO/LUMO energies were calculated at B3LYP/def2-SVP functional. For the BUP molecule, the energies of HOMO and LUMO orbitals were found -6.01 eV and -1.82 eV, respectively. For the ozone molecule, the energies of HOMO and LUMO orbitals were found -9.05 eV and -4.92 eV, respectively. On the electrophilic attack reaction, the LUMO orbital of ozone will receive the electrons present on the HOMO orbital of BUP. According to the reactivity prediction with Fukui functions, the major reaction sites on BUP molecule toward ozone attack are the N from the amine group and aromatic ring. Hydroxylation of the aromatic ring and dehalogenation and further hydroxylation are also possible pathways for ozone reactions, according to DFT calculations. Preliminary results from UPLC-qToF-MS have shown the major formation of bupropion N-oxide ( $[\text{M}+\text{H}]^+ = 256.1104$ ) followed by the product of substitution of Cl atom on the aromatic ring to OH group ( $[\text{M}+\text{H}]^+ = 222.1494$ ). The formation of those transformation products agrees with the predictions of DFT calculations and previous reports<sup>2</sup>. Further experiments will be carried out to optimize ESI conditions and verify the ionization of other possible Transformation products.

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[CNPq, FAPERGS, and CAPES]



## 013 - AGING AND OXALIPLATIN-INDUCED PERIPHERAL NEUROPATHY: FIRST EVIDENCE OF PLATINUM ACCUMULATION IN THE MICE BRAIN

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The aging of the population, especially among individuals aged 60 or over, has shown a notable increase. Aging has been identified as a fundamental risk factor for diseases such as cancer<sup>1</sup>. In this context, the use of chemotherapy drugs, such as oxaliplatin (OXA), in cancer treatment has progressively risen within the elderly population. Alongside this, it is known that neurotoxicity stands out as a primary adverse effect of OXA use, primarily characterized by peripheral neuropathy<sup>2</sup>. Despite the efficient defense mechanisms of the central nervous system, our research group recently demonstrated the accumulation of platinum in the spinal cord of mice following exposure to OXA<sup>3</sup>. Hence, our study aimed to enhance understanding of the toxicity associated with this chemotherapy. Specifically, we investigated whether the aging process is a risk factor for OXA-induced neuropathic pain and platinum accumulation in the central nervous system. To evaluate these effects, we employed a model of peripheral neuropathy induced by OXA in Swiss mice<sup>3</sup>, assessing platinum concentrations and their impact on mechanical<sup>4</sup> and thermal sensitivity<sup>5</sup>. Both young and old adult Swiss mice received intraperitoneal injections of OXA (10 mg kg<sup>-1</sup>) or vehicle (5% glucose solution, 10 ml kg<sup>-1</sup>) on days 0 and 2 of the experimental protocol. From day 5 to day 13 of the protocol, the mice underwent evaluations of mechanical and thermal sensitivities. On day 14, the animals were euthanized, and samples of spinal cord and brain tissue were collected. During the sample preparation phase, the brain (~300 mg) and spinal cord (~100 mg) were digested using concentrated nitric acid (HNO<sub>3</sub>) heated at 110°C for 24 hours. For determining platinum derived from OXA in the spinal cord and brain, we employed high-purity reagents and advanced inductively coupled plasma instrumentation - tandem mass spectrometry (ICP-MS/MS)<sup>6</sup>. The results, expressed in nanograms per gram (ng g<sup>-1</sup>), elucidate the platinum concentration in these tissues, with a detection limit of 0.1 ng g<sup>-1</sup>. Statistical analyses (One-Way ANOVA, Tukey's test, 95% confidence level) were conducted to compare groups. Our findings revealed that OXA treatment exacerbated the pain and identified platinum deposition in the spinal cord and, for the first time, in the brain of mice exposed to OXA. In conclusion, the connection between aging and OXA treatment heightens pain sensitivity, primarily through oxidative damage induced in the central nervous system due to platinum accumulation.

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**[UFPEI, CNPq, FAPERGS, CAPES, and L'ORÉAL-UNESCO-ABC "Para Mulheres na Ciência"]**

## 014 - INFLUENCE OF AGE ON OXALIPLATIN-INDUCED ANXIOUS BEHAVIOR AND COGNITIVE IMPAIRMENT: ROLE OF BIOELEMENTS

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Oxaliplatin (OXA) is a chemotherapeutic agent widely used in cancer treatment, and growing evidence demonstrates that OXA is associated with neurotoxicity that leads to emotional and cognitive impairments.<sup>1,2</sup> In this sense, appropriate levels of bioelements in the central nervous system (CNS) are crucial for the maintenance of physiological conditions, and bioelements imbalance can result in neurodegeneration.<sup>3</sup> Furthermore, aging is a complex process characterized by a decline in physiological function.<sup>4</sup> In this context, the aim of the present study was to investigate the influence of aging on OXA-induced neurotoxicity, specifically focusing on its effects on bioelements concentrations within the brain and its implications for emotional and cognitive domains. The tests were carried out using adult (2 months) and old (20 months) male Swiss mice. The OXA (10 mg kg<sup>-1</sup>, intraperitoneally (ip)) or 5% glucose solution (10 mL kg<sup>-1</sup>, ip) was administrated in mice on days 0 and 2 of the experimental protocol. Cognitive and anxiety-like behavior assessments followed established methods.<sup>5,6</sup> Only high-purity reagents were used to determine bioelements. For sample digestion, pro-analysis purity level 14.4 mol L<sup>-1</sup> HNO<sub>3</sub> (ChemLab, Belgium) further purified by sub-boiling distillation and ultra-pure 9.8 mol L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub> (Sigma Aldrich, Belgium) were used. Appropriate dilutions of 1 g L<sup>-1</sup> single element standard solutions (Instrument solutions, The Netherlands) were used for method development, optimization, and calibration purposes. Ultra-trace element determination was carried out using an Agilent 8800 ICP-MS/MS instrument (ICP-QQQ, Agilent Technologies, Japan). A certified reference material NIST CRM 8414 (Bovine Muscle Powder) was also analyzed for quality assurance and quality control (QA/QC) of the analytical method. The concentrations of calcium, cobalt, copper, iron, magnesium, manganese, potassium, phosphorus, selenium, sodium, sulfur, and zinc were measured in the brain of mice. Our results demonstrated that OXA exposure caused anxious behavior in young and old mice. Interestingly, anxious behavior in the older mice was exacerbated by OXA exposure. The OXA also induced cognitive impairment in young mice; nevertheless, aging-induced cognitive damage was not aggravated by OXA treatment. Evaluating bioelements concentrations in the brain revealed lower manganese concentrations in young mice exposed to OXA and potassium, and phosphorus, reductions in old mice exposed to OXA. Cobalt and copper concentrations in old OXA-treated mice were higher than in young OXA-treated mice. No difference in the other bioelements concentration was observed. These findings reveal for the first time bioelements imbalance in the CNS due to OXA treatment. The observed changes in bioelements concentrations may significantly contribute to OXA-induced anxiety behavior and cognitive impairment, particularly in the context of aging.

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[UFPel, CAPES/PrInt/UFPel (041/2017), CNPq (429859/2018-0, 312747/2020-9), FAPERGS (PqG 21/2551-0001943-3), and L'ORÉAL-UNESCO-ABC for Women in Science]

## 015 - SPECIOMICS ANALYSIS OF TRANSGENIC SOYBEAN SOMATIC EMBRYOGENESIS USING HILIC COUPLED SIMULTANEOUSLY WITH TQ-ICP-MS AND ESI-HRMS/MS

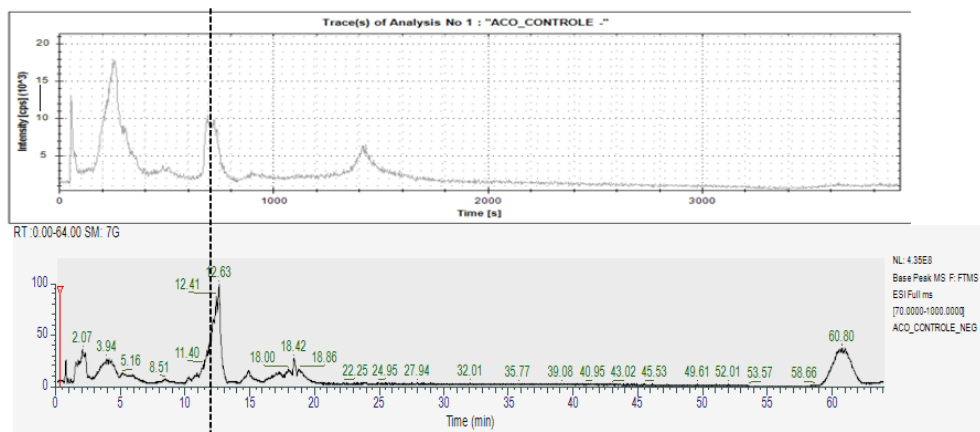
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According to Arruda *et al.* (2022) [1], Specimomics can be defined as studying the chemical species present in a given sample using omics approaches. In this context, metalloproteins are proteins that contain metal complexes; metallometabolites can generally be formed due to their complexing capacity with the inter and intracellular metals [1-2]. These metal occurrences are essential in maintaining plant cells' structure and enzymatic activity. Consequently, it is crucial to determine the nature of the species found in metal to understand their fate and role in species better. To this end, ICP-MS and ESI-MS can be implemented in a unique LC system for simultaneous structural identification of metals bound to organic complexes [1-3]. This way, a simultaneous coupling between HILIC-HPLC-TQ-ICP-MS/ESI-HR-MS was carried out to identify metallic species in the soybean somatic embryogenesis (callus) added with Au NPs and Ag NPs. Separation was performed using a HILIC column (Accucore 150 Amide-Hilic 250 x 2.1 mm, 2.6  $\mu$ m) and a gradient of (A) - acetonitrile and (B) ammonium formate five mmol, pH 5.5, according to the methodology described by Flis *et al.* (2016) [2]. The flow was set at 0.75 mL/min, and the sample injection volume was 50  $\mu$ L. After the column, the eluent was divided using a split-type valve, with 30% of the flow for the TQ-ICP-MS (iCAP TQ Thermo Scientific) and 70% for the ESI-HR-MS (Q Exactive Thermo Scientific). The TQ-ICP-MS was added to 20% oxygen introduced at the torch and a microconcentric nebulizer. The signal has been optimized to give maximum response to intensities of Ca, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, S, Zn, Au, and Ag. Figure 1 shows the chromatograms obtained in HILIC-HPLC-TQ-ICP-MS (top part, Cu chromatogram) and HILIC-HPLC-ESI-HR-MS chromatogram (bottom part, m/z chromatogram of organic compounds, negative mode) of the control soybean's callus. One line was drawn at a retention time (RT) of 12 min, showing the possibility of having Cu linked to organic compounds in this RT. Besides others, identifying the specie  $C_{27}H_{31}N_3O_6Cu$  in samples of control soybean callus in the RT of 12 min was possible. The data are processed to identify the (metalo)metabolites/proteins in the control soybean callus and added with NPs.



**Figure 1.** Chromatograms were obtained simultaneously in HILIC-HPLC-TQ-ICP-MS (upper part, Cu chromatogram) and HILIC-HPLC-ESI-HR-MS (lower part, m/z chromatogram of organic compounds) of soybean callus sample with Ag NP. Line was drawn at a retention time (RT) of 12 minutes.

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[FAPESP, UNICAMP, GEPAM]



## 016 - ROLE OF 7-CHLORO-4-(PHENYLSELANYL) QUINOLINE IN PLATINUM DISTRIBUTION IN OXALIPLATIN-EXPOSED AGED RATS

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Aging is a multifaceted process marked by declining physiological function. Roughly, 20% of the world's population will be over 60 by 2050<sup>1</sup>, and this phenomenon may be accompanied by higher incidences of chronic age-related diseases, more notably cancer<sup>1</sup>. Chemotherapy-induced peripheral neuropathy is a major cause of ongoing pain in cancer survivors. Oxaliplatin (OXA) exposure leads to peripheral neuropathic disorders in 85-95% of cases<sup>2</sup>. Our research group recently made significant advancements in understanding the adverse effects of OXA and its treatment, particularly the pharmacological impact of 7-chloro-4-(phenylselanyl) quinoline (4-PSQ)<sup>3,4,5,6,7</sup>. Given our continued interest, this study aimed to assess the impact of 4-PSQ on aged Wistar rats exposed to OXA. Specifically, we investigated whether the aging process and platinum (Pt) accumulation pose a risk for OXA-induced neuropathic pain. Male Wistar rats received OXA (2 mg kg<sup>-1</sup>) or vehicle (5% glucose solution, 10 ml kg<sup>-1</sup>) by intraperitoneal route, from day 1 up to day 5. Subsequently, 4-PSQ (5 mg kg<sup>-1</sup>) or vehicle (canola oil, 10 ml kg<sup>-1</sup>) treatment was administered from days 5 to 14 of the experimental protocol by intragastric route. Mechanical hyperalgesia was measured post the final 4-PSQ administration, and, posteriorly, the animals were euthanized. Sample tissues, including the sciatic nerve, spinal cord, cerebellum, cerebral cortex, and hippocampus, were collected and digested using HCl: HNO<sub>3</sub> 3:1 v/v in a water bath at approximately 95°C for 72 hours. The digests were subsequently stored for further analysis. The Pt content was determined by inductively coupled plasma mass spectrometry (ICP-MS), using the isotope 194. The method's limit of quantification, considering all evaluated tissues, was only 0.33 µg kg<sup>-1</sup>, which enabled the Pt determination in all samples from the subjects submitted to OXA treatment<sup>3</sup>. Statistical analyses were performed (One-Way ANOVA, Tukey test, 95% confidence level) to compare the treatment groups. Our study revealed exacerbated pain sensitivity following OXA administration. This groundbreaking investigation establishes the positive correlation between Pt levels in the peripheral and central nervous system and between tissue Pt accumulation and pain sensitivity. It is worth mentioning that Pt concentration ranged from 11 to 109 µg kg<sup>-1</sup> considering all tissues and all subjects treated with OXA. These outcomes illustrate that heightened Pt concentrations in the analyzed tissues coincide with lowered paw withdrawal thresholds, signifying heightened pain sensitivity in the subjects. This discovery holds pivotal implications for the quest to identify new and effective treatment avenues for OXA-induced neuropathic pain. Additionally, our results provide compelling evidence that 4-PSQ treatment effectively mitigates Pt accumulation in the sciatic nerve and cerebral cortex of aged rats afflicted with peripheral neuropathy. This novel finding underscores the potential therapeutic value of 4-PSQ in ameliorating neuropathic pain and OXA-induced neurotoxicity.

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**[UFPeI, CAPES, CNPq, FAPERGS, and L'ORÉAL-UNESCO-ABC "For Women in Science"]**

## 017 - SIMULTANEOUS COUPLING HPLC-TQ-ICP-MS/ESI-HR-MS FOR ARSENIC SPECIATION IN MARINE TURTLE LIVER SAMPLE

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The total As concentration (tAs) reported in marine organisms can be high because is bioaccumulated and depending of As species is biomagnified by the trophic chain. For marine biological samples, species such as arsenobetaine (AsB), arsenolipids (AsLs), and arsenosugars (AsSug) have been reported, however, the biological activity are yet to be discovered [1]. High-Performance Liquid Chromatography coupled online with Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS) technique have been commonly used for speciation analysis, however, standards for all As species are not available.[2,3] Therefore, to As speciation without standards the High-Performance Liquid Chromatography coupled simultaneously with Inductively Coupled Plasma Mass Spectrometry and Electrospray Ionization High-Resolution Mass Spectrometry (HPLC-ICPMS/ESI-HR-MS) have been reported. [4] This work aims to use the simultaneous coupling of High-Performance Liquid Chromatography coupled simultaneously to TripleQuad Inductively Coupled Plasma Mass Spectrometry and Electrospray Ionization High-Resolution Mass Spectrometry (HPLC-TQ-ICP-MS/ESI-HR-MS) to identify As species in one liver sample of marine turtles (*Caretta caretta*) found dead during beach monitoring. The tAs was determined before the speciation analysis [5]. For the As speciation, 0.2g of sample and 5 ml of Methanol/Water (MeOH 9:1 H<sub>2</sub>O v/v), was shaken for 12 hours and the supernatant was collected (Fraction 0). Similarly, the same procedure was carried out using Hexane (Fraction 1) and Methanol/Dichloromethane (MeOH 1:2 DCM v/v) (Fraction 2). Then, the HPLC (Thermo Ultimate 3000) mobile phase flow rate was 0.75 ml/min, and 7µL of each fraction was injected into the HILIC column. The column eluent was 70% split to ESI-HR-MS (Thermo Q Exactive), and 30% to TQ-ICP-MS (Thermo iCAP TQ). [4,6] The ESI-HR-MS retention time and TQ-ICP-MS matched indicating that molecules were associated with As. In Fraction 0, As-lipid species (C<sub>23</sub>H<sub>38</sub>AsO, C<sub>13</sub>H<sub>27</sub>AsO<sub>3</sub>, C<sub>16</sub>H<sub>34</sub>AsO<sub>3</sub>), As-sugar (C<sub>7</sub>H<sub>15</sub>AsO<sub>5</sub>H, C<sub>10</sub>H<sub>21</sub>AsO<sub>6</sub>S, C<sub>4</sub>H<sub>9</sub>AsO<sub>3</sub>H, C<sub>10</sub>H<sub>21</sub>AsO<sub>6</sub>S, C<sub>10</sub>H<sub>19</sub>AsO<sub>8</sub>SO, C<sub>10</sub>H<sub>19</sub>AsO<sub>9</sub>SO), As-Methylated species (C<sub>3</sub>H<sub>9</sub>AsOH, C<sub>3</sub>H<sub>9</sub>AsSH, (CH<sub>3</sub>)<sub>3</sub>As, (CH<sub>3</sub>)<sub>3</sub>AsOH), As-Acid species (C<sub>4</sub>H<sub>9</sub>AsO<sub>3</sub>H, (CH<sub>3</sub>)<sub>2</sub>AsOH), As-Alcohol species ((CH<sub>3</sub>)<sub>3</sub>As(CH<sub>2</sub>)<sub>2</sub>COOH); Arsenobetaine ((CH<sub>3</sub>)<sub>3</sub>AsCH<sub>2</sub>COOH) and |Arsenocholine ((CH<sub>3</sub>)<sub>3</sub>AsCH<sub>2</sub>CH<sub>2</sub>OH) were identified. At Fraction 1, As-Hydrocarbon (C<sub>17</sub>H<sub>37</sub>AsO and C<sub>19</sub>H<sub>41</sub>AsO) and 1 As-glycerol (C<sub>11</sub>H<sub>24</sub>O<sub>6</sub>As) was found. The As species found at Fraction 2 were identical at Fractions 0 and 1.

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**7<sup>th</sup> BRAZILIAN MEETING ON  
CHEMICAL SPECIATION**

Bento Gonçalves, Brazil  
November 26<sup>th</sup> to 27<sup>th</sup>, 2023

# **TRACE ELEMENT SPECIATION ANALYSIS/FRACTIONATION FOR ENVIRONMENTAL AND GEOLOGICAL SCIENCES**



## 018 - A NOVEL REPORT ON ESSENTIAL AND TOXIC ELEMENTS BINDING TO METALLOPROTEINS IN THE BILE OF THE SPINY BUTTERFLY RAY (*Gymnura altavela*)

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Anthropogenic activities have been the main cause of contamination in aquatic environments, severely affecting the fauna and flora present in this habitat.<sup>1</sup> Among the animals that suffer greatly from the harmful effects caused by chemical contamination in this environment are elasmobranchs, a taxonomic group that includes rays and sharks. These animals, which have an important role in maintaining the aquatic ecosystem, are highly exposed to chemical contaminants due to their characteristics, such as slow maturation, low fecundity, among others.<sup>2</sup> One of the biochemical routes for metal detoxification in vertebrates involves binding to metallothionein (MT), which is a small-sized metalloprotein. This metalloprotein serves various metabolic functions, including defence against oxidative stress and the detoxification of both toxic and essential elements that may be present in excess in the organism.<sup>3</sup> While studies on the detoxification of these elements in fish tend to primarily focus on the liver,<sup>4</sup> bile, a fluid excreted by the liver after each feeding episode, has also been utilized as an indicator of recent exposure to pollutants in bony fish. Nevertheless, there is currently a lack of research concerning biliary assessments for elasmobranchs. In this context, this study presents a novel report on toxic and essential metal and metalloid binding to thermostable proteins present in the bile of the Spiny butterfly ray (*Gymnura altavela*), an endangered elasmobranch sampled off the coast of Rio de Janeiro, southeastern Brazil. Following a thermal extraction procedure<sup>5</sup>, 40 µg of total protein determined by the Lowry method modified by Peterson<sup>6</sup> were injected into a Superdex 75 Size Exclusion column (GE Healthcare®) coupled to a liquid chromatograph hyphenated to an ICP-MS (SEC-HPLC-ICP-MS). Proteins were monitored at 254 and 280 nm and the chromatograms were superimposed on the obtained spectra to assess metalloprotein retention times during 60 min runs using different-sized proteins for column calibration (Bovine Serum Albumin – 67 kDa, Ovalbumin – 45 kDa, Ribonuclease – 13.7 kDa, Reduced Glutathione – 0.3 kDa). Peaks for both essential (Cu, Mo and Zn) and toxic elements (As, Ni and Ti) bounded to biliary metallothionein, eluted between 20 and 25 min. Fe, Pb and Rb peaks were observed bound to other metalloproteins eluting before and after metallothionein. These results indicate a metal homeostasis and detoxification route employing biliary excretion in this species, although additional studies are required to further elucidate this biochemical route and potential associations to other metalloproteins in elasmobranchs.

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## 019 - A NEW CARBON-DOT MODIFIED WITH MSA/ETHYLENEDIAMINE AS A PROBE PLATFORM FOR iAs QUANTIFICATION BY SPECTROFLUORIMETRY

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The toxicity of arsenic (As) depends on its chemical form<sup>1</sup>. For example, inorganic arsenic species (iAs) are more toxic compared to organic arsenic species. Hence, As speciation analysis is commonly required rather than only As total content. In this project, Carbon Quantum Dots (CQDs)<sup>2</sup>, which present unique optical properties, were applied as selective probe platform for iAs breaking speciation analysis free from chromatographic separation. For this approach, new functionalized CQDs were developed. The hydrothermal synthesis of CQDs was carried out using citric acid (HCitr), mercaptosuccinic acid (MSA) and ethylenediamine (en). The process was optimized through a full factorial design in two levels with a central point using quantum yield (QY) as response. The optimal point was MSA/HCitr/en on a 2:1:1 ratio, at 200 °C, for 3 h. The CQDs were submitted to a purification process using 1 kDa dialysis membrane. The material obtained was stable at pH ranging from 4 to 8 and presented a fluorescence band around 450 nm with QY of 36%. pH values lower than 4 reduced the QY more than 8%. Atomic force microscopy (AFM) images showed a particle size of less than 10 nm. The analysis by vibrational spectroscopy in the infrared region with Fourier transform (FTIR) in KBr pellet showed characteristic binding bands: N-H (3400 cm<sup>-1</sup>), C=O (1650 cm<sup>-1</sup>), C-N (1390 cm<sup>-1</sup>) and C-H (2900 cm<sup>-1</sup>). In order to verify selectivity of the nanomaterial, 100 ppb solutions of different inorganic species (Ca(II), Mg(II), Fe(III), Zn(II), K<sup>+</sup>, Mn(II), Na<sup>+</sup>, Cr(III), Cl<sup>-</sup>, I<sup>-</sup>, Se(IV), Hg(II), NO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, As (III) and As (V)) in addition to the methylated As species (MMA and DMA) were used. The nanomaterial was selective to iAs species, even in the presence of MMA and DMA (Fig 1). The proposed method presented wide linear concentration range (1-40 µg L<sup>-1</sup>) for iAs (Figure 2). The results obtained so far reveal that the new CQDs have great potential as probe platform for iAs quantification by spectrofluorimetry presenting selectivity and sensitivity. The interaction mechanism between As-CQDs is currently being studied by our research group. It is intended to apply the proposed method for analyzing iAs in water and rice samples.

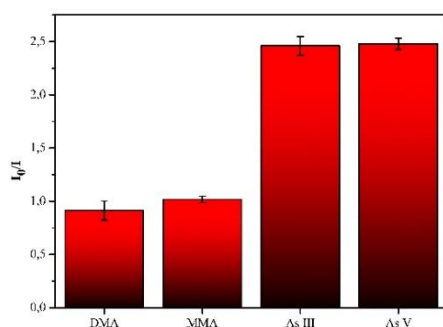


Figure 1: Ratio of quenching of As species

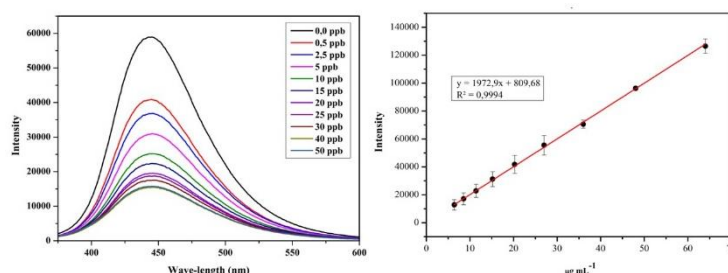


Figure 2: Fluorescence quenching after iAs added and linear range

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[CAPES, UECE, UFC, CNPq, and FUNCAP]



## 020 - SPECIATION AND CHEMICAL FRACTIONATION OF REE IN WATER SAMPLES FROM THE PARAÍBA DO SUL RIVER

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The use of different materials with specific properties to increase the functionality of a given product has raised the demand for many elements that are important components in the development of new technologies. These are defined as Technology Critical Elements (TCE) and include platinum group metals, rare earth elements (REE), and others such as Nb, Ta, Ge, and Te<sup>1</sup>. The inputs of these elements into the environment occur through mining discharges, industrial effluent disposals, and the use of agricultural waste containing these elements in their composition. The analysis labile content of an analyte emerges as a way to understand the behavior in the environment and to provide valid information about the quantity and possible contaminations that may occur. The DGT (Diffusive Gradients in Thin films) technique appears as an alternative to measure the free/labile species in an aquatic environment, which passively sample chemical species of interest<sup>2</sup>. This study aimed to evaluate the total, dissolved and labile concentrations of REEs in water samples from the Paraíba do Sul River. In addition, a speciation study was carried out using the CHEAQS software. The water samples were collected from seven different points along the Paraíba do Sul River during the dry season. The dissolved fraction was obtained by filtering, in the field, 50 mL of the samples with a cellulose acetate syringe filter, with porosity of 45µm and then acidifying it with HNO<sub>3</sub> 2% (v/v). The DGT devices were immersed in triplicate in the river for 24 hours. Chelex® resin was used as a binding layer, and polyacrylamide hydrogels were used as diffusive layers. In the laboratory, the devices were disassembled, and each Chelex-100 disk was inserted into centrifuge tubes for analyte elution with 2 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub>. The values of the DGT diffusion coefficient and the elution factor used for each REE were based on a previous study<sup>3</sup>. To evaluate the total content, the samples were digested in a microwave oven following the adapted protocol from EPA 3015A before determination by ICP-MS. The results showed that after normalization to Post-Archean Australian Shale (PAAS), both in total and dissolved fractions, the elements exhibited similar behaviors, as anticipated. However, at point 4A, an anomaly was observed in three elements (La, Pr and Gd). The anomaly occurrence of La is peculiar, especially at the analyzed site. Given its use in improving optical glasses and in oil catalysis, it was expected to find this element near industrial zones, not at a typical urban sewage point. For Pr, due to its similar industrial application with La, it's common to identify Pr where other lanthanides have anomalies. Gd was the third element to show an anomaly. Its main use is associated with intravenous contrasts for magnetic resonance in hospital settings. The presence of Gd in this location can be explained by the proximity of hospitals (both public and private) to the Paraíba do Sul River tributary. Although anomalies of La and Pr were detected in the total, dissolved and labile fractions, Gd were not present in the labile fraction. This suggests that Gd predominantly exist in the form of colloids < 45µm, but not in a free state. The speciation analysis conducted using the CHEAQS software revealed that in most of the samples, the presence of PO<sub>4</sub><sup>3-</sup> ions led to the predominant formation of solid precipitates. In a general way, the evaluated elements showed higher concentrations in places near industries. However, anomalies appeared at a location primarily marked by domestic sewage discharge. This indicates a possible interaction with treated effluents from neighboring industries to the tributary, intensifying the concentration of these elements at the examined site.

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[CAPES, FAPESP, and CNPq]

## 021 - MASS BALANCE ANALYSIS OF PFAS IN COMMUNAL WATERS

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Per- and polyfluoroalkyl substances (PFAS) are in the environmental chemistry spotlight due to their chemical and thermal stability. PFAS is monitored routinely with targeted liquid chromatography tandem mass spectrometry for different species, however this approach covers only a handful of PFAS. Sum parameters, like extractable organic fluorine content (EOF), bring a better understanding about the extent of PFAS pollution. EOF can be measured by thermally combusting the samples, then analysing the possible fluorine containing compounds either as  $F^-$  with ion chromatography, or indirectly as molecular ions using molecular absorption spectroscopy<sup>1,2</sup>. PFAS have been observed in a wide range of consumer and industrial products (e.g., cosmetics, water repellent clothes, food contacting materials, foodstuffs etc.), that often end up in the wastewater cleaning system. Wastewater treatment plants are known to not effectively clean up PFAS, with effluent having higher concentration of target PFAS than influent<sup>1-4</sup>. Even though this information has been reported by many research groups, only a few show the maximum potential PFAS concentration in wastewaters. Total oxidizable precursor assay is a sum parameter to estimate the potential amount of compounds that break down to different PFAS<sup>5</sup>. In this study, influent and effluent were collected and analysed for targeted PFAS and EOF content, then subjected to total oxidizable precursor assay to show the amount of degradable PFAS. The sum of 31 target PFAS species increased from  $0.022 - 0.046 \mu g L^{-1}$  in influent to  $0.14 - 0.21 \mu g L^{-1}$  in effluent and around  $0.01 \mu g g^{-1}$  in sludge, while EOF were found to be consistent ( $2.3 - 3.5 \mu g F L^{-1}$ ) in influent/effluent. Mass balance analysis showed an increase in the identified PFAS compounds in the effluent compared to the influent (from 0.9% - 1.3% to 3.6% - 6.1%), suggesting biotransformation of non-targeted PFAS precursor compounds. In conclusion, wastewater treatment plants transform some PFAS, and wastewater effluent is a source of PFAS contamination in surface water.

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## 022 - SPATIO-TEMPORAL VARIABILITY OF LABILE METALLIC SPECIES AT THE MOUTH OF THE DOCE RIVER, BRAZIL

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On November 5, 2015, the collapse of the Fundão dam released over 50 million m<sup>3</sup> of iron ore tailings into the Doce River basin in the state of Minas Gerais, Brazil. After 16 days this material reached the river estuary, the coastal environment, and marine ecosystems in the Atlantic Ocean, more than 600 km downstream. This event marked the largest of its kind all over the world<sup>1</sup>. With the aim of investigating whether the input of mining waste caused fluctuations in the concentrations of labile metallic species in the dissolved fraction of the water column, this study conducted a spatio-temporal evaluation of the labile concentrations of Ag, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, Sr, V, and Zn in the region of the Doce River mouth. The determination of labile concentrations was carried out using the diffusion gradient in-thin films technique (DGT) and inductively coupled plasma optical emission spectrometry (ICP OES). Aqueous samples (5 L) from the surface (0-15 cm) and bottom (50 cm below the water surface) were collected monthly in polyethylene flasks between November 2018 and September 2019 on the continental shelf in the Doce River mouth. At this location, six transects perpendicular to the coast were established, and eight collection stations were selected. Three stations were located along the central transect corresponding to the central estuary, two points in the southern region, and three points in the northern sector. These sampling stations were strategically chosen to encompass the dispersion plume and sediment accommodation transported by the river. The deployment of DGT devices was conducted in the laboratory, while field measurements of pH, oxidation-reduction potential, and salinity were taken for each station and respective depth. The elements As, Se, and Hg were determined using the chemical vapor generation technique and ICP OES. Quality assurance and control for the protocols were carried out through recovery tests in an ionic medium of NaCl at a concentration of 33 g L<sup>-1</sup>, as well as field control samples. The results indicate that the maximum labile concentration (µg L<sup>-1</sup>) of dissolved metallic species Fe, Al, and Zn predominated over the other elements during the study period. The labile concentrations of these three elements were compared between the rainy season (November 2018 to March 2019) and the dry one (April 2019 to September 2019). For the mouth sector, the concentrations of labile species were higher during the dry (or winter) season compared to the rainy period (Mann-Whitney,  $p < 0.05$ ). The highest levels (µg L<sup>-1</sup>) were observed in the central mouth sub-sector during the April 2019 campaign, ranging from 1.81 to 24.03 for Fe, 4.78 to 18.53 for Al, and 2.29 to 26.74 for Zn. Overall, the highest concentrations for this sub-sector occurred mainly in surface samples, suggesting the transport and re-release of labile species from the Doce River plume. The Fe concentrations recorded in this study reached levels even higher than those registered for the dissolved fraction, which was associated with the high levels of colloidal material resulting from mining waste<sup>2</sup>.

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**[The present study was carried out as part of the Aquatic Biodiversity Monitoring Program, Ambiental Area I, established by the Technical-Scientific Agreement, DOU number 30/2018, between FEST and Renova Foundation. This study was supported in part by the Instituto Nacional de Tecnologias Analíticas Avançadas, INCTAA.]**



## 023 - SELENIUM SPECIES AS UREASE INHIBITORS FOR THE DEVELOPMENT OF FERTILIZERS WITH INCREASED EFFICIENCY

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Urbanization given rise to a notable trend, that is reflected in the search for greater food production, especially vegetables and legumes. However, the amount currently produced is not enough to serve the world's population, thereby contributing to social inequality and food insecurity. Certain initiatives aligned with the Sustainable Development Goals (SDGs) and the Food and Agriculture Organization's (FAO) strategic framework<sup>1</sup>, aim to cultivate more efficient, inclusive and sustainable agri-food systems. These efforts aim to achieve improved production, nutrition, environmental quality and quality of life for all<sup>1</sup>. In an effort to increase agricultural production, minimizing nitrogen losses and investing in fertilizers are fundamental. Therefore, the aim of this study was to evaluate the effect of ionic species of inorganic Se [Se(IV) and Se(VI)], and Se<sup>0</sup> in the form of nanoparticles without (SeNPs) and with copper doping (SeCuNPs) as urease inhibitors to develop a fertilizer with increased efficiency. To evaluate the inhibition potential of the Se species, *in vitro* tests were carried out using Jack bean urease (*Canavalia ensiformis*) as a model<sup>2</sup>. The SeNPs and SeCuNPs were synthesized and characterized based on adapted literature<sup>3,4</sup>. Initially, a screening was carried out with different concentrations (0.01 to 5000 µg L<sup>-1</sup>) of SeNPs and SeCuNPs against urease to determine the IC<sub>50</sub>. These results were compared against classic urease inhibitors, namely NBPT and Hydroxyurea (HU). To evaluate the effect of organic matter on urease activity, humic substances (HSs) were used at a concentration of 100 mg L<sup>-1</sup>. Finally, four distinct soil samples with different physicochemical characteristics were used: S1 and S2 soils from Alagoas, S3 and S4 soils from São Paulo<sup>2</sup>. The goal was to evaluate the effect of NPs and NBPT on the inhibition of ureases present in these soils. SeNPs and SeCuNPs showed IC<sub>50</sub> of 5.88 ± 0.57 mg L<sup>-1</sup> and 0.83 ± 0.05 µg L<sup>-1</sup>, respectively. Comparing these values with those of the classic inhibitors HU (0.29 ± 0.06 mg L<sup>-1</sup>) and NBPT (0.16 ± 0.01 mg L<sup>-1</sup>), it can be inferred that Se NPs have promising potential. In the presence of HSs, the IC<sub>50</sub> values of SeNPs and SeCuNPs were 4.87 ± 0.13 mg L<sup>-1</sup> and 0.89 ± 0.01 mg L<sup>-1</sup>, respectively. Thus, it was observed that for SeNPs the IC<sub>50</sub> values varied by 20%, while for SeCuNPs there was a 900-fold increase in the IC<sub>50</sub>. In this sense, Se<sup>0</sup> is little affected by the presence of organic matter, while ionic Cu is strongly influenced. The ionic Se species were not as effective as the NPs in inhibiting ureases, since at 100 mg L<sup>-1</sup>, the maximum inhibition was 37% (Se(IV)) and 18% (Se(VI)). The copper species were effective in inhibiting urease, since at 1.0 µg L<sup>-1</sup>, Cu(II) inhibited 63%, while Cu(I) caused 92% inhibition, but they are highly blocked in the presence of HSs, due to the metal's complexation effect. These data show greater affinity between Se and Cu species with a lower oxidation state with urease, possibly due to interaction with the free Cys residue. Regarding to the tests on soil samples, SeNPs and SeCuNPs showed inhibitory effects comparable to NBPT. However, they did not differ from each other, indicating that the preponderant effect on inhibition comes from Se in nanometric form since the effect with ionic Cu was minimal due to the complexation process. The high inhibitory potential of SeNPs against soil ureases underscores that this nanomaterial is promising for developing fertilizers with increased efficiency in order to improve the fixation and use of N by plants.

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[PPGQB-IQB-UFAL, CAPES, FAPEAL, CNPq, and EspeQBrazil]

## 024 - CHEMICAL SPECIATION AND ASSESSMENT OF THE DISTRIBUTION OF RARE EARTH ELEMENTS IN SOIL SAMPLES FROM A CONTAMINATED AREA BY URANIUM MINING

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The group of seventeen chemical elements known as Rare Earth Elements (REE) includes fifteen lanthanoids (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), as well as Sc and Y. These elements are sparsely distributed within the Earth's crust and are typically found as trace elements in rock-forming minerals within the environment<sup>1</sup>. Owing to their unique physicochemical properties, their application has been increasingly emphasized in industrial practices and in various technological applications. Due to their intensified use in recent times, there has been an increasing release of REE into the environment<sup>2</sup>. Many REE are now recognized as emerging contaminants, and information on their background values and bioavailability remains limited<sup>3</sup>. Consequently, there is a crucial need to evaluate the behaviour of REE in the environment in order to assess the risks and possible ecotoxicity associated with these elements. The INB Caldas Mining-Industrial Complex (INB Caldas), situated in the state of Minas Gerais, was once a uranium mining site that is currently undergoing decommissioning. The industrial extraction activities took place between 1982 and 1995, primarily through open mining pit. Within these areas, structures like tailings dams, mine pits, and waste rock piles can serve as significant sources of contamination<sup>4</sup>. It is worth noting that uranium ores can contain REE as well as thorium, presenting several challenges in waste processing and management<sup>5</sup>. The *Diffusive Gradients in Thin films* (DGT) technique has gained recognition as a valuable tool for investigating various environmental processes, including assessment of elemental bioavailability and chemical speciation<sup>6</sup>. The objective of this study is performing the speciation analysis of REE in topsoil samples and thus seek to understand the distribution of these elements in this contaminated area. Samples were collected at a depth of 0-20 cm in an area outside the mine complex (reference point) and in the contaminated area near the mining pit. Total metal content in soils was determined by ICP-MS. The flux of REE in the soil samples was measured by DGT (24h deployment at controlled temperature (21°C) and constant water soil holding capacity). Pore water was extracted from soils sampled by using centrifugation and filtration through PTFE-filters with a pore size of 0.45 µm. The filtered solution was acidified and analysed by ICP-MS. The total concentrations of La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu measured in soils of mining pit area were 713.6 mg kg<sup>-1</sup>, 825.4 mg kg<sup>-1</sup>, 67.0 mg kg<sup>-1</sup>, 173.6 mg kg<sup>-1</sup>, 18.6 mg kg<sup>-1</sup>, 4.6 mg kg<sup>-1</sup>, 20.1 mg kg<sup>-1</sup>, 11.9 mg kg<sup>-1</sup>, 1.6 mg kg<sup>-1</sup>, 5.2 mg kg<sup>-1</sup>, 0.7 mg kg<sup>-1</sup>, 2.8 mg kg<sup>-1</sup>, 0.4 mg kg<sup>-1</sup>, respectively. The range of concentrations measured by DGT in the contaminated area varied from 0.6 µg kg<sup>-1</sup> for Lu to 2140.2 µg kg<sup>-1</sup> for La. The pore water content from sampled soils by DGT devices showed significantly higher values with concentrations varying from 6.6 µg kg<sup>-1</sup> for Lu and 23638.4 µg kg<sup>-1</sup> for La.

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[FAPESP, CAPES, CNPq, and INB]

## **025 - CHEMICAL SPECIATION OF HEXAVALENT CHROMIUM IN ORGANIC FERTILIZER BY LC-ICP-MS AND SPECTROPHOTOMETRY**

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Normative Instruction n. 7 of 04/12/2016 of the Ministry of Agriculture, Livestock and Food Supply (MAPA) defines the maximum values of contaminants allowed in organic fertilizers and soil conditioners, including chromium(VI), with a maximum allowed value of 2 mg kg<sup>-1</sup>[1]. The suggested method for this determination is the alkaline extraction by the USEPA 30602 method and the spectrophotometric determination by the 7196A method, with the reaction of Cr(VI) with 1,5-diphenylcarbazide[2]. However, in the case of organic fertilizers, which are quite heterogeneous, in many cases, the basic extraction has the inconvenience of also extracting humic acids present in the sample, resulting in a dark-colored extract, which makes spectrophotometric quantification impossible. Furthermore, humic acids reduce the chromium present in the solution. To overcome this drawback, an extraction method based on ISO 17075-2:2017 is proposed, consisting of extracting the analyte in the fertilizer sample in a pH 8 phosphate buffer. The detection can be done by spectrophotometry and also by Liquid Chromatography - Inductively Coupled Plasma Mass Spectrometry (LC-ICP-MS). In the spectrophotometric procedure, the pH of the extracted sample is adjusted to 2, the complexing agent 1,5-diphenylcarbazide is added, and the Cr(VI) concentration is determined at 540 nm. In the chromatographic method, the extract is diluted in a mobile phase composed of 25 mmol ammonium sulfate and 1 mmol sodium hydroxide, pH 8.0 and determined by LC-ICP-MS. Analytical parameters were calculated. For the spectrophotometric method, a detection limit of 0.12 mg kg<sup>-1</sup> and a quantification limit of 0.40 mg kg<sup>-1</sup> were obtained. For the chromatographic method, a detection limit of 0.016 mg kg<sup>-1</sup> and a quantification limit of 0.054 mg kg<sup>-1</sup> were obtained. Veracity was assessed by analyzing CRM 2701 Hexavalent Chromium in contaminated soil, and recoveries were 90-103% for both methods. These methods are suitable for the determination of Cr(VI) in organic fertilizers, meeting the requirements of IN 7 of MAPA. The proposed procedure employed extraction at pH 8 at room temperature and proved to be a simple, viable and sensitive way to determine this analyte.

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**[FINEP, Rede FertBrasil, and CNPq]**

## 026 - RHODAMINE-DERIVED FLUORESCENT PROBE FOR REDOX SPECIATION OF IONIC IRON IN ENVIRONMENTAL SAMPLES

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Metal ions play an important role in environmental systems, although these species can cause damage in high concentrations. Therefore, metal ions are regulated by different bodies in each country. Therefore, elements such as iron (Fe) must follow concentration limit standards in fresh, brackish, and effluent water, as excesses of this element can cause damage to the environment and, consequently, humans through water transmission. Therefore, developing simple, selective, and sensitive analytical methodologies that comply with legislation is always of scientific relevance. In this sense, fluorescent probes are excellent alternatives. However, there are significant design limitations for probes that show an off-on response for paramagnetic species such as iron.<sup>1</sup> The rhodamine-*N*-oxide (**S-RN**) probe was synthesized to obtain cell imaging with high iron content, as it proved to be sensitive and highly selective for Fe(II) metal ions in aqueous media. The **S-RN** probe was, therefore, used for the first time in this work to speciate ionic iron in environmental samples. The synthesis and spectroscopic characterization of **S-RN** followed protocols from the literature.<sup>1-2</sup> The principle of the method was based on the changes in photophysical properties (emission of radiation) before and after the interaction of S-RN with Fe(II) ( $\lambda_{\text{ex}} = 540 \text{ nm}$  /  $\lambda_{\text{em}} = 573 \text{ nm}$ ). **S-RN** is an organic compound; thus, the percentage of some organic solvents was evaluated in the reactional medium. The best profile was obtained preferably in aqueous medium, with tolerance to DMSO of up to 5% (v/v). The reactions were carried out at pH 7.0 using MES buffer solution (50 mM) to avoid pH modification of the sample medium. Since **S-RN** reacts selectively for Fe(II),<sup>3</sup> and the work aims to measure total iron ( $\text{Fe}_T$ ) from the conversion of Fe(III) to Fe(II), two reducing agents were evaluated for this purpose, hydroxylamine and ascorbic acid (5 - 40 mM). The best analytical performance was obtained with ascorbic acid at 20 mM. Under the optimized conditions, the method showed a linear range for Fe(II) of 28 - 420  $\mu\text{g L}^{-1}$  (0.5 - 7.50  $\mu\text{M}$ ), with a limit of detection (LOD) of 8  $\mu\text{g L}^{-1}$  (0.14  $\mu\text{M}$ ). The method proved to be selective for Fe(II) against the main species present in water (anions and cations), as well as having no matrix effect since it obtained quantitative recoveries (90 - 105%) in water samples. Finally, the method was applied to 03 water samples from the Mundaú-Manguaba Lagoon Estuarine Complex (CELMM, Maceió, Alagoas, Brazil), and the  $\text{Fe}_T$  concentration measured ranged from 0.89 to 1.77  $\text{mg L}^{-1}$  (in agreement with the reference method). The Fe(II) concentrations were lower than the LOD, indicating that these samples preferably contain only Fe(III). However, national legislation<sup>4</sup> establishes a maximum level of dissolved Fe in brackish water samples of 0.3  $\text{mg L}^{-1}$ . Thus, these samples have  $\text{Fe}_T$  values above the legal maximum, constituting an environmental problem. Finally, the method developed proved simple, easy to implement, selective, and allows iron speciation in water samples.

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[UFAL, IQB, PPGQB, CAPES, CNPq, and FAPEAL]



## 027 - FEASIBILITY STUDY FOR MERCURY REMEDIATION IN SOYBEAN PLANTS USING SiO<sub>2</sub>NPs: IONOMIC EVALUATION AND Hg SPECIATION

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Mercury (Hg) is recognized as a global pollutant, standing out for being present at various trophic levels. It is considered a bio accumulative trace element, with the food pathway being the primary route of contamination in humans<sup>[1]</sup>. The application of silica nanoparticles (SiO<sub>2</sub>NPs) as a mitigating agent on heavy metal contamination in plant crops, thereby reducing the abiotic stress induced by these contaminants, has shown promising results<sup>[2]</sup>. Therefore, the aim of this study was to investigate the potential of SiO<sub>2</sub>NPs to play an effective role against the absorption, accumulation, and toxicity of Hg in soybean plants, through chemical speciation and total determination of Hg. The protective role of SiO<sub>2</sub>NPs was assessed taking into account morphological characteristics of soybean plants and Hg total concentrations determined by ICP-MS, as well as Hg speciation studies (Hg (II), MeHg and EtHg) by HPLC-ICP-MS. The figure shows the chromatogram of the method used for the speciation of Hg in soybean plants.

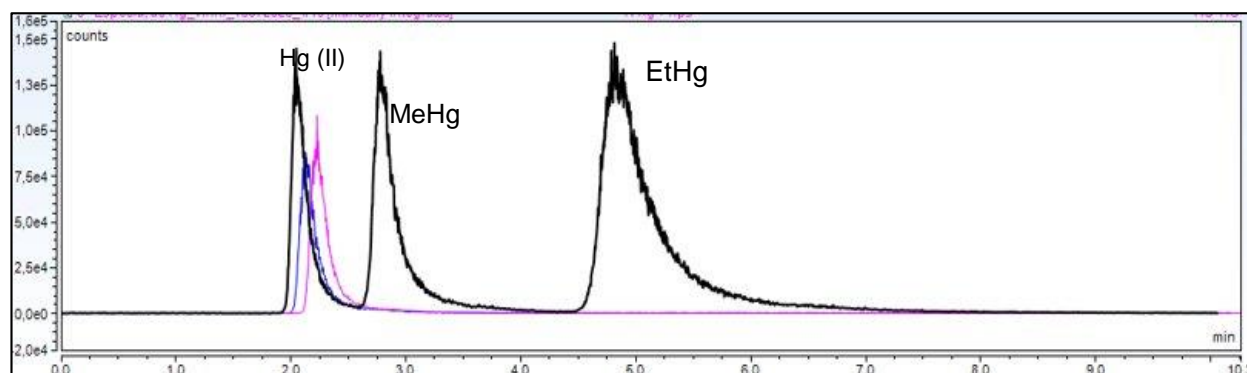


Figure 1- Chromatogram of the separation of Hg (II), MeHg, and EtHg by HPLC-ICP-MS

From the illustration above, an excellent chromatographic resolution for the investigated Hg species is observed, with an elution time of 5.0 min for the last analyte, enabling a satisfactory identification and quantification of the species under investigation. However, through this study of chemical speciation at different soybean plant compartments, only the specie Hg (II) was found among the investigated groups (Hg; SiO<sub>2</sub> Nps + Hg; and Na<sub>2</sub>SiO<sub>3</sub> + Hg), which indicates an absence of Hg methylation in the soil by the plant. However, there was a reduction in Hg absorption in the groups with the presence of Na<sub>2</sub>SiO<sub>3</sub> and NPs SiO<sub>2</sub>, respectively of 25% and 32% in the leaves, and 20% and 75% in the roots for the RR transgenic. For Intacta, the reduction was 23% and 28% in the leaves and 23% in the roots with both Na<sub>2</sub>SiO<sub>3</sub> and SiO<sub>2</sub> NPs. In fact, these results corroborate the potential of silica nanoparticles to mitigate environmental contamination by heavy metals in agricultural crops<sup>[3]</sup>. The chemical speciation study in soybean plants is a valuable analytical tool to help elucidate mechanisms related to the protective role of NPs SiO<sub>2</sub> against Hg toxicity in soybean plants.

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## 028 - SUSPECT SCREENING OF ORGANOARSENICALS IN PLANKTON

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Comprehensive assessments of complex organoarsenicals in environmental and biological samples remains challenging. Plankton, which compose the base of the foodweb in lake ecosystems, has potential to accumulate and biotransform inorganic arsenic into complex organic species<sup>1</sup>. Recent advancements in high-resolution mass spectrometry (HRMS) have made the unequivocal identification of several organic analytes in complex samples possible. Non-target and suspect screening of substances in environmental and biological samples are widely used for prioritisation purposes and can help elucidate biotransformation routes of compounds in living organisms, making it a relevant topic in analytical chemistry. In this work, we present a suspect screening workflow based in ultra-high performance liquid chromatography coupled to high-resolution mass spectrometry (UHPLC-HRMS) for the speciation analysis of organoarsenicals in plankton samples. The validated workflow was applied to phytoplankton and zooplankton collected from lakes of the Pantanal naturally contaminated with As. The certified reference material BCR-414 (Trace Elements in Plankton) was used during the validation step. Briefly, 0.5 g of sample was submitted to ultrasound-assisted extraction. Subsequently, the aqueous extracts were frozen for 12h at -20 °C to precipitate lipids and proteins. The samples were centrifuged (14,000×g; 30 min) and the precipitate was discarded. A further clean-up step consisted in the addition of 5 mL of hexane to the extract, and then it was vortex mixed for 30 s. The lipidic layer was discarded after centrifugation (14,000×g; 10 min). The resulting aqueous solution was filtered through a PVDF filter (0.22 µm) and analysed by UHPLC- HRMS. Chromatographic separations in hydrophilic interaction liquid chromatography (HILIC) mode were carried out by a Thermo Fisher Scientific Dionex UltiMate 3000 UHPLC system. The analytical column was a Titan<sup>TM</sup> Silica (10 cm × 2.1 mm; 1.9 µm). The chromatographic system was coupled to a Q-Exactive Quadrupole Orbitrap mass spectrometer equipped with heated electrospray ionisation (HESI) probe. Samples were analysed in both positive and negative ionisation modes (Full MS/ddMS<sup>2</sup> experiments). The obtained dataset was pre-processed with Thermo XCalibur (version 3.1.66.10) software and then processed with MZmine application (version 2.53)<sup>2</sup>. A suspect list comprised of 79 organoarsenicals was used as a reference library for exploratory analysis. The identification of the features was based on the following criteria: (i) matching experimental mass/charge ratio ( $m/z$ ) with the value present on the list with mass accuracy of <5 ppm, and (ii) matching at least 2 MS<sup>2</sup> fragments with the literature<sup>3</sup> under a retention time (RT) range for MS<sup>2</sup> scan pairing of 0.1 min and mass accuracy of <5 ppm per fragment. Total As analysis by hydride generation atomic fluorescence spectrometry (HG-AFS) after each extraction step attested that no losses of As occurred. The species dimethylarsinoylethanol (DMAE) (C<sub>4</sub>AsO<sub>2</sub>H<sub>11</sub>) is considered one of the intermediates in the production of arsenobetaine (AsB)<sup>4</sup> and was detected in both phyto- and zooplankton samples of the Pantanal. Corroborating the role of DMAE in the arsenosugars degradation, glycol-group dimethylated arsenosugar (C<sub>10</sub>H<sub>21</sub>AsO<sub>7</sub>) was detected in both phyto- and zooplankton of the Pantanal. Similarly, glycol-group dimethylated thio-arsenosugar (C<sub>10</sub>H<sub>21</sub>AsO<sub>6</sub>S) was also present, however, it was restricted to phytoplankton. To the best of the authors' knowledge, this is the first work to employ this approach to As species in aquatic organisms.

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## 029 - TWO-DIMENSIONAL PAPER-BASED DEVICE FOR EVALUATING Ni and V PORPHYRINS THROUGH LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Crude oils contain higher concentrations of Nickel (Ni) and Vanadium (V), primarily in the form of porphyrins. However, their presence during crude oil processing poses challenges, particularly in hydrocracking, as Ni and V can irreversibly bind to catalyst surfaces, rendering them inactive. The conventional approach to analyzing metalloporphyrins involves chromatography methods, often preceded by a fractionation step known as the SARA (Saturates, Aromatics, Resins, and Asphaltenes) method [1,2]. Then, based on the method using TLC as an alternative approach [1], we are proposing a novel approach combining SARA fractionation and porphyrin speciation using the two-dimensional paper-based analytical device (2D-PAD) on a single plate, and laser ablation ICP-MS for evaluating Ni and V. In the first dimension, the SARA fractionation is carried out, and in the second one, after rotating the plate 90°, the separation of the porphyrins is proceeded. The SARA fractionations were performed initially from separation of asphaltene and maltene fraction with 1 mL of heptane for asphaltene precipitation. The maltene fraction, after drying with a lower flow of N<sub>2</sub> is resuspended with toluene and added to cellulose plate for separation. For SARA fractionation the maltenes and three porphyrins (nickel (II) octaethylporphyrin, vanadyl phtalocyanine and vanadyl (V) tetraphenoxy phtalocyanine) were eluted with hexane until 1 cm, until 2 cm using hexane:dicloromethane (70:30 (v/v)) and until 3 cm with toluene:methanol (50:50 (v/v)) [2]. The second dimension is used for the porphyrin separation, and the elution was carried out up to 1 cm with hexane, 2 cm with toluene, 3 cm with dicloromethane, and 4 cm with methanol. After drying, the plates are then cut into pieces of 0.8 x 5 cm (w x h), and fixed into the ablation chamber. The ablation was performed using a 110 µm-spot size, 20 Hz frequency, 60% laser intensity, and 110 µm s<sup>-1</sup>scan speed. Plasma conditions as 1200 W-power, 1.2 and 1.6 mL min<sup>-1</sup>nebulizer and auxiliary gas, respectively, were used, and the isotopes <sup>51</sup>V and <sup>60</sup>Ni were monitored. From porphyrins standard ablation signals and sample similar behaviors were attained, and correlate with the porphyrins present in each fraction. In the application of a 2D-PAD, the ablation profile in the resin fraction showed the major intensity of <sup>51</sup>V and <sup>60</sup>Ni distributed between 2 and 3 cm, the same behavior showed for tetraphenoxy V and octaethyl Ni porphyrins in the same fraction, presented intermediated polarity, however, it is not conclusive for phthalocyanine V due to its distribution throughout the separation. In the aromatic fraction, <sup>51</sup>V presented signal intensity distributed in 4 cm, which does not correspond with any V porphyrin standard evaluated, although such species present more polar characteristics than the standards evaluated. For Ni evaluation in the same fraction, and at 2 cm, is observed the distribution of signal corresponding to octaethyl Ni. For saturated fraction, V showed a major intensity in 4 cm and in the 2 and 3 cm, Ni is present at highest intensity in the sample. However, none of the standards of porphyrins evaluated, for both Ni and V, show signals in the saturated fraction. Such results are, in fact, expected, due to the complexity of the chemical structure of porphyrins, which involves conjugated aromatic rings. In conclusion, the 2D-PAD and LA-ICP-MS offers a streamlined approach for fractionation and speciation of Ni and V porphyrins in crude oil samples, once it provides qualitative insights through ablation signals, enabling the confirmation that aromatic and resin fractions predominantly contain porphyrins. Additionally, it offers a simplified, rapid, and efficient porphyrin analysis in complex crude oil matrices.

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**[FAPESP, PETROBRÁS, CNPq (140809/2021-0), and CAPES (88887339559/2019-00)]**



## 030 - CHEMICAL FRACTIONATION OF Ba, Ca, Mg, AND Sr IN CRUDE OIL FROM PRE-SALT AND DETERMINATION BY ICP-OES

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The presence of alkaline-earth metals in crude oil can cause some problems, such as corrosion of the distillation towers in refineries, and salt deposits on pipes, valves, and pumps.<sup>1</sup> In general, Ba, Ca, Mg, and Sr are present in crude oil as salts of chloride, carbonate, and sulfate and are found mainly in the aqueous fraction from crude oil emulsion.<sup>2</sup> In addition, when the crude oil is subjected to high temperatures during distillation, the hydrolysis of these salts can occur, resulting in acid vapor generation (e.g., HCl). In this sense, information regarding the solubility of these elements in aqueous and organic fractions of crude oil emulsion is important. In this way, a study of chemical fractionation of Ba, Ca, Mg, and Sr in the aqueous and organic phases of crude oil was developed and the following conditions were evaluated: *i*) type of extraction solution (H<sub>2</sub>O or diluted HNO<sub>3</sub> or HCl); *ii*) use of microwave-assisted extraction (MAE); *iii*) use of ultrasound-assisted extraction (UAE); *iv*) use of reversed-phase dispersive liquid-liquid microextraction (RP-DLLME); and *v*) use of liquid-liquid extraction (LLE). For the total determination of Ba, Ca, Mg, and Sr in crude oil, samples were digested by microwave-assisted wet digestion (MAWD) using 0.5 and 6 mL of concentrated HNO<sub>3</sub>. All experiments for chemical fractionation were carried out by using 2 g of crude oil and 2 mL of extraction solution. All determinations of Ba, Ca, Mg, and Sr were performed by inductively coupled plasma optical emission spectrometry (ICP-OES) using a spectrometer equipped with axial view (Ciros CCD, Spectro Analytical Instruments, Germany). A microwave oven (Synthos 3000, Anton Paar, Austria) equipped with 8 quartz vessels (80 mL) and maximum temperature, pressure, and power of 280 °C, 80 bar, and 1400 W, respectively, was used for MAE and MAWD. For the UAE, an ultrasound water-bath (model P120 H, Elmasonic, Germany), with a capacity of 8 L, temperature control (up to 85 °C), power of 220 W, and frequency of 37 kHz, was used. For the RP-DLLME and LLE methods, a water-bath (model CE-160/22, Cienlab, Brazil), capacity, and temperature control of 9 L and 85 °C, respectively was used. As a result of this investigation, Ba, Ca, Mg, and Sr were all migrated (higher than 94%) to the solution when H<sub>2</sub>O or 3 mol L<sup>-1</sup> HNO<sub>3</sub> solution were used in the MAE method (240 °C). In addition, similar results were obtained by using 3 mol L<sup>-1</sup> of HNO<sub>3</sub> in the UAE method and all analytes were migrated (higher than 90%) from the organic fraction into the aqueous fraction, at 85 °C. On the other hand, only Ca, Mg, and Sr were solubilized (higher than 85%) into the solution, when 3 mol L<sup>-1</sup> of HNO<sub>3</sub> was used as an extraction solution in the RP-DLLME method and LLE method (at 80 °C). Moreover, even when a mixture of HNO<sub>3</sub> and HCl (3 mol L<sup>-1</sup>) solutions was employed for the extraction, only 30% of the total Ba concentration was solubilized into an aqueous fraction, and around 70% was found in the organic fraction (RP-DLLME and LLE methods). Thus, as a conclusion, H<sub>2</sub>O or 3 mol L<sup>-1</sup> HNO<sub>3</sub> were suitable for complete solubilization only of Ca, Mg, and Sr (RP-DLLME and LLE methods). However, for Ba, hard conditions were needed to ensure the complete analyte extraction from crude oil to the aqueous solution (MAE or UAE methods using H<sub>2</sub>O and 3 mol L<sup>-1</sup> HNO<sub>3</sub>, respectively). Therefore, considering that some analytes are more (such as Ca, Mg, and Sr) or less (mainly Ba) soluble in aqueous fraction, it was necessary to evaluate the type of extraction solution and procedure employed.

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[UFSM, CAPES, and CNPq]

## 031 - ELEMENTAL CHARACTERIZATION IN WATER-SOLUBLE AND INSOLUBLE FRACTIONS OF PM<sub>2.5</sub> FROM RIO DE JANEIRO, BRAZIL, BY MIP OES AND ICP-MS

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Atmospheric particulate matter (PM) is a priority pollutant to be monitored, according to the World Health Organization, due to its high environmental and health risks and mortality rates similar to smoking. This pollutant can be collected in atmospheric filters as a function of its maximum particle diameter, for which the fine fraction, up to 2.5  $\mu\text{m}$  (PM<sub>2.5</sub>), is a matter of concern, considering that it concentrates contaminants from industrial activities and forest fires. Regarding the potentially toxic elements such as As, Cd, Co, Cu, Ni, Pb, and Zn, studies showed that they can be partially mobilized when in contact with aqueous and biological fluids. In addition, emerging contaminants, such as rare earth elements (REE), can also be present. [1] This work presents a preliminary study on the soluble forms of elements in atmospheric filters (n=30) collected in moderate contamination sites in Rio de Janeiro state (RJ). A simplified sequential extraction was adapted from the work of Fernández Espinosa et al. [2] to separate the water-soluble and the insoluble fractions of the particulate matter. The filter was cut in a 3 cm band to obtain about 0.3 g of PM, added with 5 mL of ultrapure water, and the soluble fraction was separated after 5 h shaking in an ultrasonic bath. Then, concentrate HNO<sub>3</sub> (5 mL) was added to the insoluble fraction and heated for 120 min at 90 °C. The fractions were filtered, and Ca, K, Mg, and Na were determined by microwave induced plasma optical emission spectrometry (MIP OES) and trace elements by inductively coupled plasma mass spectrometry (ICP-MS). Accuracy assessment was evaluated with the standard reference material of elements in drinking water (EnvironMat) ESL-3 (low concentration), and the recoveries varied between 101 % (Co) and 109 % (Zn). The total dissolved solids (TDS) concentration in the soluble fraction was established with the Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> concentrations and varied from 14 mg L<sup>-1</sup> to 56 mg L<sup>-1</sup>, indicating a high salinity. The higher concentrations of Na and Mg were found in the soluble fraction (average 74 % and 67 %, respectively), whereas K was concentrated in the insoluble fraction (63 %). The potentially toxic elements and REE in the soluble fraction were determined by ICP-MS, employing external calibration with matrix-matched analytical solutions by simulating the TDS with NaCl. The Na/Ca concentrations ratio was used to evaluate the non-sea salts (NSS) contribution. The NSS concentration was positively associated (Pearson,  $p < 0.05$ ,  $r > 0.6$ ) with the PM mass and the trace elements Mn, La, Ce, and Pb concentrations and negatively with Ba, Sr, and Li concentrations. The contribution of industrial regions was significant for these elements.

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## 032 - DETERMINATION OF MERCURY IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES IN LAGUNA MUNDAÚ (MACEIÓ, AL - BRAZIL)

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The Mundaú Lagoon (Maceió - AL, Brazil) is part of the Mundaú- Manguaba lagoon estuarine complex (CELMM) and is considered to be an environment of socio-economic importance due to fishing for the local bivalve, the sururu (*Mytella charruana*)<sup>1</sup>. In this context, the inappropriate disposal of domestic and industrial waste increases the rate of environmental degradation in this ecosystem, including possible contamination by potentially toxic species, such as mercury.<sup>2</sup> This study aimed to determine Hg in environmental (water, sediment, and sururu) and biological (blood and urine from local fishermen) matrices. Six sampling campaigns were conducted for the environmental samples from July 2021 to February 2023, each analyzing 11 sampling points. Cold vapor atomic fluorescence spectrometry (CV AFS) was used to determine Hg concentrations in the different types of samples. When necessary, the samples were acid-digested in a closed system. It is worth noting that in the water samples, the concentrations of total mercury (Hg<sub>T</sub>), total dissolved mercury (Hg<sub>DS</sub>), as well as the inorganic (Hg<sub>ino</sub>) and organic (Hg<sub>org</sub>) fraction of this element in the dissolved fraction were determined. In contrast, only the total mercury concentrations were determined in the other samples. The results obtained by this study concerning the environmental samples showed variations in the Hg concentration profiles between the samples, where from sample 1 to 3, there was a decrease in the concentrations obtained for Hg<sub>T</sub> and Hg<sub>DS</sub> in the water samples, and for Hg<sub>T</sub> in the sediment and sururu samples. Thus, the concentration ranges (µg L<sup>-1</sup>) of Hg<sub>T</sub>, Hg<sub>DS</sub>, Hg<sub>ino</sub>, and Hg<sub>org</sub> in the water samples were, respectively: sampling 1 (< 0.01 - 15.71), sampling 2 (< 0.01 - 7.65), sampling 3 (< 0.01 - 3.58), sampling 4 (< 0.01 - 1.40), sampling 5 (< 0.01 - 0.36) and sampling 6 (< 0.01 - 0.89). In general, only water and sediment samples showed Hg<sub>T</sub> concentrations above the permitted level, with excesses of 2× (sediment) to 80× (water) the maximum legal value. Throughout the sampling period, 50% of the water samples had Hg<sub>T</sub> concentrations higher than those permitted by law. In the water samples, Hg<sub>org</sub> was the majority species. However, national legislation only recommends limit values for Hg<sub>T</sub> with values of 0.2 µg L<sup>-1</sup> (water)<sup>3</sup> and 0.3 µg g<sup>-1</sup> (sediment)<sup>4</sup>. About the bivalve samples of the species *Mytella charruana* (native species) and *Mytilopsis sallei* (invasive species), all the Hg<sub>T</sub> concentrations were below the legislated values<sup>5</sup>, with concentrations ranges equal to 0.01 - 0.35 and < 0.01 - 0.07 µg g<sup>-1</sup>, respectively, in dry mass. The initial results indicate that the average value of Hg<sub>T</sub> levels in the blood of the CELMM fishermen (*n* = 20) was 4.68 ± 1.39 µg L<sup>-1</sup>; in contrast, for the control group (*n* = 20), it was 2.06 ± 0.63 µg L<sup>-1</sup>, which means that 25% of the fishermen had values higher than those recommended by the EPA<sup>6</sup>. For the urine samples from these two groups, values of 0.447 ± 0.19 µg L<sup>-1</sup> (fishermen) and 0.147 ± 0.03 µg L<sup>-1</sup> (control group) were obtained, although the concentrations were below the limits of current legislation<sup>7</sup>. However, the level of Hg<sub>T</sub> was around 3× higher with the fishermen. Finally, the monitoring of Hg in different samples can help understand the dynamics of the ecosystem and assist in implementing public policies aimed at making beneficial decisions for society.

1 SANTOS et al. Journal of the Brazilian Chemical Society, 32, 1762-1772, 2021.

2 CALDAS et al. Brazilian Journal of Aquatic Science and Technology, 17, 13-18, 2013.

3 CONAMA, Resolução nº 357 de 17 de março de 2005.

4 CONAMA, Resolução nº 454 de 1 de novembro de 2012.

5 ANVISA, Regulamento técnico Mercosul sobre limites máximos de contaminantes inorgânicos em alimentos, Resolução RDC nº 42, de 29 de agosto de 2013.

6 Environmental Protection Agency. <sup>7</sup>World Health Organization.

[UFAL, IQB, PPGQB, CAPES, CNPq, and FAPEAL]



## 033 - DGT WITH FERRIHYDRITE BINDING PHASE FOR ANALYSIS OF LABILE SPECIES OF Ge IN FRESHWATER AND DETERMINATION BY ICP OES

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The imbalance between the high demand for natural raw materials, especially chemical elements, and their low abundance in nature has concerned some governmental agencies throughout the world since 2008, hence, the United States National Research Council and the European Union periodically evaluate the criticalness of raw materials worldwide<sup>1</sup>. Chemical elements that previously had no or low relevant applicability became of essential importance in technology sectors. Due to their exploration and use, the fast industrial replacement, and the lack of adequate electronic rejects processing procedures, the remobilization of such elements in nature has been observed, and subsequent alterations in their natural cycle<sup>1</sup>. In the face of environmental impact and commercial relevance, Platinum Group Elements (PGE: Pt, Pd, Ir, Rh, Ru e Os) and Rare Earth Elements (REE: Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu), as well as Ga, Ge, In, Te, Nb, Ta and Tl, are currently classified as Technology-critical Elements (TCE)<sup>2</sup>. Germanium (Ge) gains attention within this group due to the information scarcity in the literature as to its freshwater behavior. Hence, the present study aims to use Diffusive Gradients in Thin-films (DGT) devices with alternative ligand phase to determine labile species of Ge by ICP OES. Based on the available literature's description of the presence of mainly neutral and anionic Ge species ( $\text{Ge(OH)}_4$ ,  $\text{GeO(OH)}_3^-$ ,  $\text{GeO(OH)}_2^{2-}$ ) in natural freshwater, the different ligand phases evaluated in the present study consisted of montmorillonite K-10 (MMT K-10),  $\text{TiO}_2$  and ferrihydrite. These were immobilized agarose hydrogels, with the exception of ferrihydrite, which was precipitated directly on the hydrogel disk by its immersion in  $\text{Fe}^{3+}$  salt solution for 2 hours followed by quick immersion in NaOH solution for 35 s, resulting in its precipitation in the hydrogel's surface. The results obtained for sorption essays showed that the ferrihydrite ligand phase sorbs 86% of Ge available concentration in aqueous solution, compared to 24% and 17% obtained for  $\text{TiO}_2$  and MMT K-10 ligand phases, respectively, hence ferrihydrite ligand phase being selected to compose the DGT device. The Ferrihydrite ligand phase DGT device, specific for anionic species, was not influenced by pH and ionic strength variations, displaying a linear sorption behavior according to DGT device immersion time. The Ge apparent diffusion coefficient determined experimentally was  $9.7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at 25 °C, and the obtained detection limit was  $0.025 \pm 0.008 \text{ nmol L}^{-1}$ . The instrumental method for Ge determination by ICP OES was validated, displaying selectivity, accuracy, and precision (recovery of 97-115% and RSD of 0.47-8.49%), as well as linearity in the concentration range evaluated ( $2\text{-}250 \text{ } \mu\text{g L}^{-1}$ ). The figures of merit of the instrumental method were established with a limit of detection of  $0.7 \pm 0.5 \text{ } \mu\text{g L}^{-1}$  (12.7% RSD) and a limit of quantification of  $2.1 \pm 0.2 \text{ } \mu\text{g L}^{-1}$  (10.8% RSD). The ferrihydrite ligand phase DGT device was successfully applied in lab-made microcosms for freshwater Ge distribution investigation.

1 Kouhail Y, Ishai D, Berkowitz B, Environ. Chem. 17 (2020) 118–132.

2 Cobelo-García A, Fillela M, Croot P, Frazzoli C, Laing GD, Ospina-Alvarez N, Rauch S, Schafer J, Zimmermann S, Environ Sci Pollut Res. 22 (2015) 15188-15194.

**[CAPES, CNPq, INCTAA, and FUNDAÇÃO ESPIRÍTO-SANTANSE DE TECNOLOGIA, (FEST)]**



## 034 - OPTIMIZATION OF AN EXTRACTION PROCEDURE OF GLUTATHIONE AND ITS DERIVATIVES FROM PLANTS FOR PS-MS ANALYSIS

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Glutathione (GSH), a tripeptide formed by glutamic acid, cysteine, and glycine [(γ-Glu-Cys)Gly], is fundamental in abiotic and biotic stress tolerance of plants, as well as in the regulation of growth and redox potential in systems with multiple metabolic functions.<sup>1,2</sup> GSH acts as a chelating agent<sup>1</sup> and a substrate in the phytochelatins (PCs) synthesis, responsible for forming stable complexes with heavy metals.<sup>3</sup> Phytochelatins (PCs) preferentially accumulate in roots, decreasing the translocation of free metals in plants. However, the low chemical stability of these compounds represents an analytical challenge. The present study aims to identify GSH and its derivatives in basil (*Ocimum basilicum* L. grecco a palla) roots exposed to cadmium employing Paper Spray Ionization Mass Spectrometry (PS-MS). Basil root samples were obtained after 14 days of cultivation in 5% v v<sup>-1</sup> Hoagland solution with 0 and 10 μM Cd<sup>2+</sup> (n =3, renewed every three days). Roots were washed in ultrapure water and transferred to a 10 mM K<sub>2</sub>HPO<sub>4</sub> solution. After washing and drying, 10 mg (root pool) was macerated in liquid nitrogen and sonicated. The samples were then immediately analyzed to prevent degradation. A 2<sup>2</sup> central composite design (CCD) was constructed to optimize the extraction procedure, varying the volume of methanol from 500 to 1500 μL and the extraction time from 10 to 60 min. For each analysis, 15 μL of the root extract and 30 μL of methanol, in this order, were added to the triangular paper, and a voltage of 4 kV was applied to its base for spray formation. Figure 1 shows the response surface obtained after optimization.

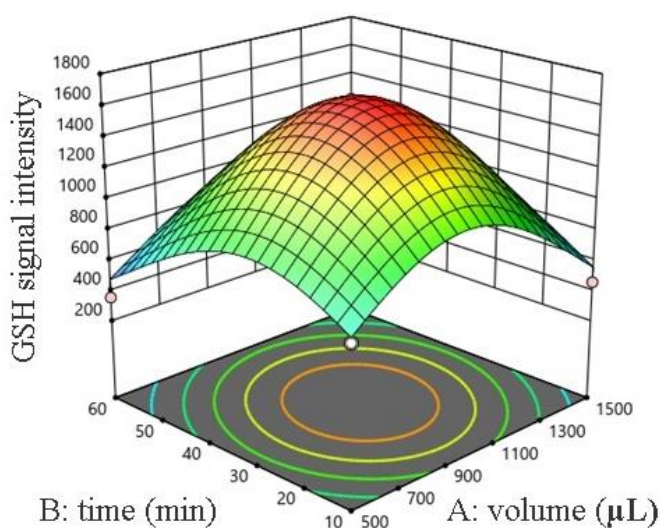


Figure 1. Response surface for GSH signal intensity (*m/z* 308) by PS-MS.

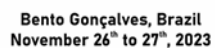
For GSH extraction (detected in its protonated form of *m/z* 308), 1 mL of methanol and an extraction time of 35 min were used. The optimization corroborated with the analysis of homogluthathione (hGSH, *m/z* 322), reduced glutathione (GSSG, *m/z* 613) and the cadmium complex (Cd-GSH, *m/z* 420) by PS-MS. The results showed similarities in the GSH signal intensity for both samples (0 and 10 μM of Cd<sup>2+</sup>) and an increased intensity for hGSH and GSSG in the contaminated root, demonstrating abiotic stress in the plant. In addition, Cd-GSH was detected in the contaminated root as a defense response to the toxic metal. The developed procedure proved efficient, simple, fast, and inexpensive, with little reagent consumption. Besides that, it is an attractive method for determining peptides in plant tissues to evaluate intoxication by toxic metals.

1 HASANUZZAMAN, M. et al. *Physiol. Mol. Biol. Plants*, 2018, 23, 2.

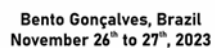
2 HOSSAIN, M. A et al. *Springer*, 2017, 1-18.

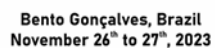
3 MOU et al. *Rapid communications in mass spectrometry*, 2016, 30, 16.

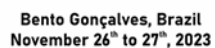
[UERR, UFAL, PPGQ-UFMG, FAPEMIG, CAPES]

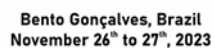
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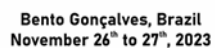








7<sup>th</sup> Brazilian Meeting on Chemical Speciation (7<sup>th</sup> EspeQBrazil), November 26<sup>th</sup> to 27<sup>th</sup>, 2023 8

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