16th RIO SYMPOSIUM ON ATOMIC SPECTROMETRY

Bento Gonçalves, Brazil
November 28th to 30th, 2023

BOOK OF ABSTRACTS
and
SCIENTIFIC PROGRAM

Universidade Federal de Santa Maria
SEDES SAPIENTIÆ
1960

UNIVERSIDADE FEDERAL DE PELOTAS
RS-BRASIL

16th RIO SYMPOSIUM ON
ATOMIC SPECTROMETRY

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Organization

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WELCOME

Since its first edition in 1988, the **Rio Symposium on Atomic Spectrometry** alternates between different countries of South America. In 2023, the Symposium returns to Brazil for its 16th edition. It is scheduled to take place in the city of Bento Gonçalves, in the State of Rio Grande do Sul, Brazil. Due to the last pandemic and its consequences, this will be the first meeting since the edition hosted in Mendoza, Argentina, in 2019. It is important to mention that, during the pandemic and later, atomic spectrometry has been a field of great importance for the understanding and development of new health treatments.

After the visionary project of this meeting by Professors Adilson J. Curtius and Bernhard Welz, the **Rio Symposium on Atomic Spectrometry** has been an outstanding event for scientists, students and scientific companies. Currently, the Symposium is one of the most important meetings for the discussion of state-of-the-art, new applications and developments covering all aspects of analytical atomic spectrometry. More than 200 participants from over 15 countries usually attend this biannual event, and direct contact among participants and the leading companies active in the field of atomic spectrometry is fostered.

Similar to the **Rio Symposium on Atomic Spectrometry**, the *Brazilian Meeting on Chemical Speciation* (*EspeQBrazil*) is a well-stablished scientific meeting taking place since 2008 in Brazil. This time, after many suggestions and considering the growth of speciation analysis, the 16th edition of the **Rio Symposium on Atomic Spectrometry** will be held sequentially to the 7th *EspeQBrazil,* with specific activities and programs for each meeting, but in the same week and venue. It is worth noting that the integration among researchers from the fields of atomic spectrometry and speciation analysis can promote further developments in both these areas. Therefore, we aim to bring together the scientific communities of both meetings for a five-day period in which experts can interact in a pleasant atmosphere and reinforce the connections between both fields.

The Organizing Committee is proud to welcome all the participants in the **16th Rio Symposium on Atomic Spectrometry** after this period of hiatus, and hope to inspire new interactions between researchers, as well as strengthen previous cooperations. In addition to the intense scientific program promoted by the event, the pleasant and vibrant city of Bento Gonçalves offers many tourist attractions as well as excellent hospitality and gastronomical infrastructure for the participants to enjoy.

Welcome to the 16th Rio Symposium on Atomic Spectrometry.

Érico Marlon de Moraes Flores
Chair of the 16th Rio Symposium on Atomic Spectrometry
Federal University of Santa Maria (UFSM), Brazil

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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 28th, 2023: 09:00 to 19:00 h
November 29th and 30th, 2023: 08:30 to 18:30 h

EXHIBITION AREA (Carménère Hall)

November 28th, 2023: 09:00 to 22:00 h
November 29th and 30th, 2023: 08:30 to 18:30 h

PARTICIPANT MATERIAL

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

CONGRESS BADGE

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

ACCESS TO THE 16th RSAS

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 16th RSAS will have two poster sessions, on November 29th, from 15:00 to 16:30 h, and on November 30th from 15:15 to 16:45 h. Posters must be fixed on their allocated space between 08:30 and 10:45 h, of the day they will be presented. 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 30th, at the 16th RSAS's office. After this period, the posters will be discarded.

ORAL PRESENTATIONS

Participants with oral presentations must present themselves to the room monitor at least 30 minutes before the beginning 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.

CERTIFICATES

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

CHANGES TO THE EVENT PROGRAM

The Organizing Committee reserves the right to change 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.

ATOMIC DINNER (November 29th, 2023, Dall'Onder Grande Hotel, Sauvignon Room)

The tickets may be acquired at the General Office, in the registration area. Please, ask the staff for assistance.

SIMULTANEOUS TRANSLATION

There will be no simultaneous translation.

INTERNET

The 16th RSAS will provide wireless internet to the participants of the event on the premises of the Dall'Onder Grande Hotel.

FOOD

The restaurant of 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, official agency of the 16th RSAS, will offer an exclusive service to the participants of the event, located at the lobby of the hotel.

EMERGENCY NUMBERS

Ambulance/Medical service: 192
Military police: 190
Fire department: 193

COMMITTEES

ORGANIZING COMMITTEE

Érico Marlon de Moraes Flores, UFSM (Chairman)
Fábio Andrei Duarte, UFSM
José Neri Gottfried Paniz, UFSM
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Paola de Azevedo Mello, UFSM
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Juliano Smanioto Barin, UFSM
Jussiane Souza da Silva, UFSM

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Dirk Schaumlöffel, Université de Pau et des Pays de l'Adour, France
Érico Marlon de Moraes Flores, UFSM, Brazil
Ewa Bulska, University of Warsaw, Poland
Frank Vanhaecke, Ghent University, Belgium
Heidi Goenaga-Infante, LGC National Measurement Laboratory, United Kingdom
Helmar Wiltshe, Graz University of Technology, Austria
Jan Kratzer, Czech Academy of Sciences, Czech Republic
Jiří Dědina, Czech Academy of Sciences, Czech Republic
Joanna Szpunar, French National Research Center, France
Joaquim de Araújo Nóbrega, UFSCar, Brazil

Jörg Feldmann, University of Graz, Austria
Jorge C. Yáñez, University of Concepcion, Chile
Márcia Foster Mesko, UFPel, Brazil
Maria das Graças Andrade Korn, UFBA, Brazil
Maria Montes-Bayón, University of Oviedo, Spain
Maria Tereza Weitzel Dias Carneiro Lima, UFES, Brazil
Martín Resano, University of Zaragoza, Spain
Marco Aurélio Zezzi Arruda, UNICAMP, Brazil
Patricia Smichowski, National Scientific and Technical Research Council, Argentina
Ralph Edward Sturgeon, National Research Council Canada, Canada
Ramon Murray Barnes, University of Massachusetts Amherst, USA
Ricardo Erthal Santelli, UFRJ, Brazil
Rodolfo Wuilloud, National University of Cuyo, Argentina
Ryszard Lobinski, French National Research Center, France
Viktor Kanický, Masaryk University, Czech Republic
Waldo Emerson Quiroz Venegas, Pontificia Universidad Católica de Valparaíso, Chile
Zoltan Mester, National Research Council Canada, Canada

NATIONAL SCIENTIFIC COMMITTEE

Cassiana Seimi Nomura, USP
Clésia Cristina Nascentes, UFMG
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Márcia Mesquita Silva da Veiga, USP
Maria Goreti Rodrigues Vale, UFRGS
Paola de Azevedo Mello, UFSM
Pedro Vitoriano de Oliveira, USP
Tatiana Dillenburg Saint´Pierre, PUC-Rio

Tributes

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

Daniel Lázaro Gallindo Borges

UFSC, Brazil

Francisco José Krug

CENA-USP, Brazil

Heidi Goenaga-Infante

LGC National Measurement Laboratory, UK

Jiří Dědina

Czech Academy of Sciences, Czech Republic

Ramon Murray Barnes

University of Massachusetts Amherst, USA

Opening Conference

Frank Vanhaecke

Ghent University, Belgium

Closing Conference

Heidi Goenaga-Infante

LGC National Measurement Laboratory, UK

Plenary Lectures

Maria Montes-Bayon

University of Oviedo, Spain

Ryszard Lobinski

CNRS, France

Invited Speakers

Björn Meermann
Federal Institute for Materials Research and Testing, Germany

Cassiana Seimi Nomura
USP, Brazil

Clésia Cristina Nascentes
UFMG, Brazil

Dirk Schaumlöffel
French National Research Center, France

Edenir Rodrigues Pereira Filho
UFSCar, Brazil

Éder Lisandro de Moraes Flores
UTFPR, Brazil

Fábio Andrei Duarte
UFSM, Brazil

George Luis Donati
Wake Forest University, USA

Gisele Simone Lopes
UFC, Brazil

Helmar Wiltsche
Graz University of Technology, Austria

Jan Kratzer
Czech Academy of Sciences, Czech Republic

Jefferson Santos de Gois
UERJ, Brazil

Jiří Dědina
Czech Academy of Sciences, Czech Republic

Jozef Kaiser
Brno University of Technology, Czech Republic

Juliana Severo Fagundes Pereira
UFRGS, Brazil

Márcia Mesquita Silva da Veiga
USP, Brazil

Maria Luisa Fernández Sánchez
University of Oviedo, Spain

Martín Resano
University of Zaragoza, Spain

Pablo Pacheco
Universidad Nacional de San Luis, Argentina

Patricia Smichowski
National Atomic Energy Commission of Argentina, Argentina

Ralph Edward Sturgeon
National Research Council Canada, Canada

Ramon Murray Barnes
University of Massachusetts, USA

Rodolfo Wuilloud
National University of Cuyo, Argentina

Rui Miguel Santos
University of Porto/ Analytik Jena, Portugal

Tatiana Dillenburg Saint´Pierre
PUC-Rio, Brazil

Thiago de Oliveira Araujo
INMETRO, Brazil

Zoltan Mester
National Research Council Canada, Canada

16th RIO SYMPOSIUM ON
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Bento Gonçalves, Brazil
November 28th to 30th, 2023

TABLE OF CONTENTS

Sections

SCIENTIFIC PROGRAM

Scientific Program - Schedule

November 28th, 2023

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

November 29th, 2023

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 1
16:00 – 16:30 h		Coffee-break
16:30 – 18:10 h	Session 4	

November 30th, 2023

TIME	MALBEC	CARMÉNÈRE HALL	ASSEMBLAGE HALL
09:00 – 10:30 h	Session 5		
10:30 – 11:00 h		Coffee-break	
11:00 – 12:05 h	Session 6		
14:00 – 15:15 h	Session 7		
15:15 – 16:45 h		Poster Session 2	
16:00 – 16:30 h		Coffee-break	
16:45 – 18:00 h	Session 8		
18:30 – 19:10 h	Closing Conference		
19:10 – 19:40 h	Closing Ceremony		
21:00 – 23:50 h			Bottle Party

November 28th (Tuesday)

9:00 - 17:00 h	**Registration** Carménère Hall

Short courses (10:00 - 12:00 h)

Short course 1: Analytical Method Validation

Room: Pinot Center

Speaker: Thiago de Oliveira Araujo (INMETRO, Brazil)

Short course 2: Advances in Sample Preparation for Atomic Spectrometry

Room: Pinot Center

Speakers: Fábio Andrei Duarte (UFSM, Brazil) and Éder Lisandro de Moraes Flores (UTFPR, Brazil)

Meet the Editor: Royal Society of Chemistry

Room: Pinot Center

Chair: Elizabeth Magalhães (RSC, Brazil)

Speakers: JAAS and Analytical RSC Editors

Workshops (14:00 - 15:45 h)

Workshop 1: Atomic Spectrometry for Environmental Applications

Room: Pinot Center

Coordinator: Maria Tereza Weitzel Dias Carneiro Lima (UFES, Brazil)

14:00 - 14:05 h	**Opening:** Maria Tereza Weitzel Dias Carneiro Lima (UFES, Brazil)
14:05 - 14:25 h	**Applications of multidimensional chromatography strategies in speciation analysis by ICP-MS** **Speaker:** Pablo Pacheco (Universidad Nacional de San Luis, Argentina)
14:25 - 14:45 h	**New materials applied for ultratrace determination by atomic spectrometry** **Speaker:** Jefferson Santos de Gois (UERJ, Brazil)

14:45 - 15:05 h	**Total reflection X-ray fluorescence for environmental analysis: possibilities and challenges** **Speaker:** Clésia Cristina Nascentes (UFMG, Brazil)
15:05 - 15:25 h	**Plasma-based techniques applied to airborne particulate matter characterization** **Speaker:** Patricia Smichowski (Argentinian Atomic Energy Commission, Argentina)
15:25 - 15:45 h	**Discussion**
Workshop 2: Atomic Spectrometry for Food, Beverages and Biological Applications **Room:** Pinot Center **Coordinator:** Rochele Sogari Picoloto (UFSM, Brazil)	
14:00 - 14:05 h	**Opening:** Rochele Sogari Picoloto (UFSM, Brazil)
14:05 - 14:25 h	**Photochemical and thermochemical vapor generation techniques for trace element analysis by AAS** **Speaker:** Gisele Simone Lopes (UFC, Brazil)
14:25 - 14:45 h	**Isotopic and elemental assessment in foods: from fortification to toxicity** **Speaker:** Márcia Mesquita Silva da Veiga (USP, Brazil)
14:45 - 15:05 h	**Trends and challenges of food and beverages analysis by LIBS** **Speaker:** Cassiana Seimi Nomura (USP, Brazil)
15:05 - 15:45 h	**Discussion**

Opening Ceremony

Room: Malbec

17:30 - 18:00 h	**Opening and Welcome** Érico M. M. Flores (UFSM, Brazil) *Chair of the 16th RSAS* **Tributes** Honored 1: Daniel Lázaro Gallindo Borges (UFSC, Brazil) Honored 2: Francisco José Krug (CENA-USP, Brazil) Honored 3: Heidi Goenaga-Infante (LGC National Measurement Laboratory, UK) Honored 4: Jiří Dědina (Czech Academy of Sciences, Czech Republic) Honored 5: Ramon Murray Barnes (University of Massachusetts Amherst, USA)
18:00 - 18:30 h	**Cultural presentation**
18:30 - 19:10 h	**Opening conference** **ICP-MS in the biomedical sciences: pushing the boundaries of the application range** Frank Vanhaecke (Ghent University, Belgium) Sponsored by **Thermo Fisher Scientific** and **SENS**
19:30 - 23:00 h	**Welcome cocktail** Carménère Hall

November 29th (Wednesday)

Session 1 (9:00 - 10:30 h) **Chair:** Márcia Foster Mesko (UFPel, Brazil) **Room:** Malbec	
9:00 - 9:40 h	**ICP-MS based bioanalytical strategies to study nano-iron therapies using in-vivo and in-vitro models** **Plenary lecturer 1:** Maria Montes-Bayón (University of Oviedo, Spain)
9:40 - 10:05 h	**Elemental bioimaging at micro- and nanoscale** **Invited speaker 1:** Dirk Schaumlöffel (French National Research Center, France)
10:05 - 10:30 h	**Advanced solvents and nanomaterials in microextraction techniques: a gateway to sensitive trace element determination and speciation** **Invited speaker 2:** Rodolfo Wuilloud (National University of Cuyo, Argentina)
10:30 - 11:00 h	**Coffee-break**
Session 2 (11:00 - 12:05 h) **Chair:** Dirk Schaumlöffel (French National Research Center, France) **Room:** Malbec	
11:00 - 11:10 h	**Oral presentation 1: Use of micro-plasmas for metal speciation** Zoltan Mester National Research Council Canada, Canada
11:10 - 11:20 h	**Oral presentation 2: Raman spectroscopy coupled to HR-CS FMAS for sequential determination of nitrogen species in fertilizers** Evilim Martinez de Oliveira, Edilene C. Ferreira, José A. Gomes Neto, George L. Donati, Bradley T. Jones UNESP, Brazil
11:20 - 11:30 h	**Oral presentation 3: Reactivity and analytical performance of NH_3 as reaction cell gas in inductively coupled plasma tandem mass spectrometry (ICP-MS/MS)** Beatriz M. Fontoura, Joaquim A. Nóbrega, George L. Donati, Alex Virgilio CENA-USP, Brazil

11:30 - 11:40 h	**Oral presentation 4: ICP-MS based platforms for tracing studies of isotopically labelled selenium nanoparticles in plants** Bruna Moreira Freire, Ana Rua-Ibarz, Eduardo Bolea-Fernández, Flávio Venâncio Nakadi, Maite Aramendía, Bruno Lemos Batista, Martín Resano UFABC, Brazil/ University of Zaragoza, Spain
11:40 - 12:05 h	**Challenges and advances in the analyses of oil samples by ICP-MS** **Invited speaker 3:** Tatiana Dillenburg Saint´Pierre (PUC-Rio, Brazil) Sponsored by **Perkin Elmer**
12:05 - 14:00 h	**Lunch**
Session 3 (14:00 - 15:00 h) **Chair:** Daniel Lázaro Gallindo Borges (UFSC, Brazil) **Room:** Malbec	
14:00 - 14:25 h	**Analytical approaches for PFAS sum-parameter analysis - from materials to environment** **Invited speaker 4:** Björn Mermann (Federal Institute for Materials Research and Testing, Germany)
14:30 - 14:40 h	**Oral presentation 5: Boron elemental and isotopic determination via HR-CS GFMAS: absorption of the BF diatomic molecule** André L. Marques de Souza, Flávio V. Nakadi, Maite Aramendía, Martín Resano University of Zaragoza, Spain
14:40 - 14:50 h	**Oral presentation 6: Assessing the elemental composition in transgenic soybean cells using single-cell ICP-MS** Ana Beatriz Santos da Silva, Elisânia Kelly Barbosa Fonseca, Marco Aurélio Zezzi Arruda UNESP/UNICAMP, Brazil
14:50 - 15:00 h	**Oral presentation 7: Plasma-mediated vapor generation by dielectric barrier discharge: an arsenic study using AAS** Gilberto Coelho Junior, Jan Kratzer, Jiří Dědina Czech Academy of Sciences, Czech Republic
15:00 - 16:30 h	**Poster session 1** Abstracts 001 to 050 Carménère Hall

16:00 - 16:30 h	**Coffee-break**
Session 4 (16:30 - 18:10 h) **Chair:** Marco Aurélio Zezzi Arruda (UNICAMP, Brazil) **Room:** Malbec	
16:30 - 16:55 h	**On the interaction of microwave radiation with mineral acids - fundamental considerations on microwave-assisted sample digestion** **Invited speaker 5:** Helmar Wiltshe (Graz University of Technology, Austria)
16:55 - 17:20 h	**Facing new analytical challenges in atomic spectrometry via microsampling** **Invited speaker 6:** Martín Resano (University of Zaragoza, Spain)
17:20 - 17:45 h	**Analysis of solid samples using atomic and mass spectrometry: relevant or remembrance?** **Invited speaker 7:** Daniel Lázaro Gallindo Borges (UFSC, Brazil)
17:45 - 18:10 h	**Dielectric barrier discharge hydride atomizers for trace element and speciation analysis** **Invited speaker 8:** Jan Kratzer (Czech Academy of Sciences, Czech Republic)
20:00 - 23:00 h	**Atomic Dinner**

November 30th (Thursday)

Session 5 (9:00 - 10:30 h) **Chair:** Tatiana Dillenburg Saint´Pierre (PUC-Rio, Brazil) **Room:** Malbec	
9:00 - 9:40 h	**Multi-technical atomic spectrometry approach to speciation of gadolinium in rat brain** **Plenary lecturer 2:** Ryszard Lobinski (French National Research Center, France)
9:40 - 10:05 h	**Laser-induced breakdown spectroscopy (LIBS): data analysis and contributions for agrobusiness** **Invited speaker 9:** Edenir Rodrigues Pereira Filho (UFSCar, Brazil)
10:05 - 10:30 h	**Expression of matrix metalloproteinases and their inhibitors in breast cancer tissues** **Invited speaker 10:** Maria Luisa Fernández Sánchez (University of Oviedo, Spain)
10:30 - 11:00 h	**Coffee-break**
Session 6 (11:00 - 12:05 h) **Chair:** Rodolfo Wuilloud (National University of Cuyo, Argentina) **Room:** Malbec	
11:00 - 11:10 h	**Oral presentation 8: Are toenails the ideal specimen to access the exposure to arsenic and other elements in epidemiological studies?** Camilla Faidutti, Louise Hair, Casey Doolette, Enzo Lombi, Jörg Feldmann University of Graz, Austria
11:10 - 11:20 h	**Oral presentation 9: A new magnetic nanomaterial as solid phase for trace elements analysis in Brazilian pre-salt produced water by ICP OES** Maradona C. da Silva, Tiago M. Freire, Pierre B. A. Fechine, Gisele S. Lopes, Francisco L. F. Silva, Wladiana O. Matos UECE, Brazil

11:20 - 11:30 h	**Oral presentation 10: Direct determination of Sr isotopes in rock by LA-ICP-MC/MS** Laís N. Viana, Rafael C. C. Rocha, Rafael C. M. Telles, Cleverson J. F. Oliveira, Christiane B. Duyck, Tatiana D. Saint'Pierre, Mauro C. Geraldes PUC-Rio, Brazil
11:30 - 11:40 h	**Oral presentation 11: Assessment of bromine and iodine concentrations in drill cuttings and oily sludge by ICP-MS** Renan G. Marim, Eduardo S. Chaves UFSC, Brazil
11:40 - 12:05 h	**Alternatives of sample preparation methods for biofuels analysis** **Invited speaker 11:** Juliana Severo Fagundes Pereira (UFRGS, Brazil) Sponsored by **Anton Paar**
12:05 - 14:00 h	**Lunch**
Session 7 (14:00 - 15:15 h) **Chair:** Ralph Edward Sturgeon (National Research Council Canada, Canada) **Room:** Malbec	
14:00 - 14:25 h	**Tracing authenticity: isotope ratios in cigars, wines, and cereals** **Invited speaker 12:** Rui Miguel Santos (Universidade do Porto, Portugal) Sponsored by **Analytik Jena**
14:25 - 14:50 h	**Characterization of aged microplastics covered by biofilm using advanced laser-based techniques** **Invited speaker 13:** Jozef Kaiser (Brno University of Technology, Czech Republic)
14:50 - 15:15 h	**Standard dilution analysis 2.0: automation and two internal standards for fast, accurate determinations** **Invited speaker 14:** George Luis Donati (Wake Forest University, USA)
15:15 - 16:45 h	**Poster session 2** Abstracts 051 to 103 Carménère Hall
16:00 - 16:30 h	**Coffee-break**

<table>
<tr><td colspan="2">Session 8 (16:45 - 18:00 h)
Chair: Ewa Bulska (University of Warsaw, Poland)
Room: Malbec</td></tr>
<tr><td>16:45 - 17:10 h</td><td>Inductively coupled plasma for spectrochemical analyses: what we learned from computer models
Invited speaker 15: Ramon Murray Barnes (University of Massachusetts, USA)</td></tr>
<tr><td>17:10 - 17:35 h</td><td>Pushing down detection limits of atomic fluorescence spectrometry coupled to generation of volatile species
Invited speaker 16: Jiří Dědina (Czech Academy of Sciences, Czech Republic)</td></tr>
<tr><td>17:35 - 18:00 h</td><td>Insights into the role of transition and noble metals mediating photochemical vapor generation
Invited speaker 17: Ralph Edward Sturgeon (National Research Council Canada, Canada)</td></tr>
<tr><td colspan="2"></td></tr>
<tr><td colspan="2">Closing Conference
Chair: Maria Montes-Bayón (University of Oviedo, Spain)
Room: Malbec</td></tr>
<tr><td>18:30 - 19:10 h</td><td>Closing conference:
A multi-technique strategy towards improved diagnosis and therapeutics of metal metabolism disorders
Heidi Goenaga-Infante (LGC National Measurement Laboratory, UK)</td></tr>
<tr><td colspan="2"></td></tr>
<tr><td colspan="2">Closing Ceremony
Room: Malbec</td></tr>
<tr><td>19:10 - 19:40 h</td><td>Érico M. M. Flores (UFSM, Brazil)
<i>Chair of the 16th RSAS</i>

Information and remarks of the 16th RSAS
Poster Awards
Closing</td></tr>
<tr><td>21:00 - 23:50 h</td><td>Bottle party
Assemblage Hall</td></tr>
</table>

Sponsors Technical Lectures

Diamond Sponsor technical lecture: Analytik Jena

November 30th, 2023

Room: Pinot Center - Room A

15:30 - 16:00 h	**High resolution inductively coupled plasma optical emission spectroscopy: technology and special applications** **Speaker**: Júlio Cezar Paz de Mattos (Analytik Jena, Brazil)

Gold Sponsor technical lecture: Perkin Elmer

November 27th, 2023

Room: Pinot Center - Room A

12:15 - 12:40 h	**Updates on new technologies present in Perkin Elmer systems that contribute to analyzes focused on chemical speciation** **Speaker:** Marcelo Anselmo Oseas da Silva (Perkin Elmer, Brazil)

Gold Sponsor technical lecture: Agilent Technologies

November 27th, 2023

Room: Pinot Center - Room A

14:30 - 14:55 h	**Hyphenated systems for elemental speciation: advances in HPLC and ICP-MS/MS** **Speaker:** Bruno Menezes (Agilent Technologies, Brazil)

Gold Sponsor technical lecture: Nova Analítica

November 29th, 2023

Room: Pinot Center - Room A

12:15 - 12:40 h	**Total workflow approach to sample preparation for ICP analysis** **Speaker**: Mariana Ortega Garcia (Nova Analítica, Brazil)

Gold Sponsor technical lecture: Thermo Fisher Scientific

November 29th, 2023

Room: Pinot Center - Room C

15:00 - 15:25 h	**Analytical technologies - boost your productivity** **Speaker**: Felipe Rezende (Thermo Fisher, Brazil)

Sponsor technical lecture: Vert

November 29th, 2023

Room: Pinot Center - Room C

12:00 - 12:25 h	**Simplify digestor: a reliable alternative for sample preparation aiming at elemental analysis by ICP techniques** **Speaker**: Gabriel Gustinelli Arantes de Carvalho (Vert, Brazil)

ABSTRACTS

Opening conference

ICP-MS IN THE BIOMEDICAL SCIENCES: PUSHING THE BOUNDARIES OF THE APPLICATION RANGE

Frank Vanhaecke
Atomic and Mass Spectrometry – A&MS research unit, Department of Chemistry, Ghent University, Ghent, Belgium, 9000
*e-mail: frank.vanhaecke@ugent.be

Since its commercial introduction in the 1980s, inductively coupled plasma-mass spectrometry (ICP-MS) has been used for the trace element analysis of body fluids and nowadays, it is routinely used in clinical labs for evaluating (professional) exposure to toxic metals and/or for verifying the concentration levels of essential mineral elements.

Via the development of more powerful and versatile instrument types and the use of various alternative sample introduction strategies and hyphenation of separation techniques, the application range of ICP-MS has been continuously extended and further efforts are still done to enable measurement types that were previously out of reach. In this presentation, method development carried out at the Atomic and Mass Spectrometry – A&MS research unit of Ghent University (Belgium) and the subsequent application of the methodology developed in a biomedical context will be discussed. The introduction of tandem ICP-mass spectrometry (ICP-MS/MS) and its practically unlimited capabilities to create interference-free conditions based on selective reaction between the analyte ion(s) and the reaction gas in the collision/reaction cell (mass-shift approach) offers unprecedented limits of detections, e.g., enabling the determination of ultra-trace amounts of metals stemming from deterioration of implants in the human body. Moreover, the use of a syringe-driven sample introduction system reduces the sample volume needed to sub-µL volumes.

The use of laser ablation (LA) as a means of sample introduction in ICP-MS opens the possibility to reveal the 2- and sometimes even 3-dimensional distribution of exo- and endogenous elements in tissue sections. The use of doped gelatin standards allows these “elemental maps” to provide quantitative information. Introduction of an ultrafast tube-type cell and a transfer line securing a laminar flow has led to signal response profiles (SPRs) of millisecond duration only. This has not only rendered the technique much faster, but the corresponding enhanced signal-to-noise ratio also leads to substantially improved limits of detection and/or enhanced spatial resolution (pixel size down to ≈ 1 µm). The combination of such LA-unit and an ICP-MS instrument equipped with a time-of-flight (ToF) analyzer opens the possibility to obtain a full mass spectrum for each laser shot.

Also high-precision isotopic analysis of essential mineral elements using multi-collector ICP-MS has an important role to play in the life sciences as isotope ratios have been observed to be more sensitive than the corresponding element concentration levels to changes in (human) metabolism and/or contain information that is not embedded in the element concentrations. As a result, the occurrence of a disorder can cause a systematic change in the isotopic composition of an essential mineral element in a body fluid or tissue, and thus provide information on the biochemical changes that are occurring, while also demonstrating diagnostic and/or prognostic capabilities. This approach has already been shown to provide useful information in the context of various disease types, ranging from cancer over malaria to Alzheimer’s disease.

Finally, also single-cell ICP-MS is an emerging application. In this type of measurement, a dilute suspension of cells is aspirated and introduced into the ICP and whenever a cell is reaching the ICP, a burst of ions is produced, manifesting itself under the form of a short transient signal. Adequate calibration thus permits the absolute content of exo- and endogenous elements to be determined in individual human cells, down to femtogram levels.

[This presentation is based on the work of many (former) PhD students and postdoctoral researchers of the A&MS research unit and collaborators from other departments of Ghent University and other research institutions]

Closing Conference

A MULTI-TECHNIQUE STRATEGY TOWARDS IMPROVED DIAGNOSIS AND THERAPEUTICS OF METAL METABOLISM DISORDERS

Heidi Goenaga Infante[*], Stanislav Strekopytov, Christian Ward-Deitrich, Kharmen Billimoria

LGC National Measurement Laboratory, Queens Road, Teddington, Middlesex, TW11 0LY
*e-mail: Heidi.Goenaga-Infante@lgcgroup.com

Metal metabolism disorders (MMD) are those with genetic origin and, for which the functions and levels of physiologically relevant metals in the blood are controlled by specific proteins. Inherited metabolic disorders can result in protein malfunction and therefore, deficiency or toxic accumulation of metals in the body. Wilson's disease (toxic copper levels accumulate in the liver, brain, and other organs) and hemochromatosis (the intestines absorb excessive iron, which builds up in the liver, pancreas, joints, and heart) are very important examples of MMD[1,2]. Diagnosis usually involves gene mutation testing, clinical observations and bio-chemical testing [e.g. non Ceruloplasmin (CER)-bound Cu or exchangeable Cu (CuEXC) for Wilson's disease and total blood Fe, serum Ferritin (light chain) for hemochromatosis]. Disease treatment usually involves the use of chelating agents, which may help demetallation on one hand but, on the other hand may cause toxicity.

In Wilson's disease, exchangeable Cu (CuEXC) is currently measured by nephelometry as the amount of total Cu minus that of CER-bound Cu. The main limitation of this test lies in the inaccuracy of measuring CER by immunological methods not able to distinguish between the apo-CER and the active holo-CER, thus leading to biased results. In Fe disorders, Ferritin is the main storage protein for iron in tissues and is engaged in its uptake, accumulation and release in cells. The level of serum Ferritin is normally quantified using an antibody test to diagnose iron-related disorders like hemochromatosis. WHO, which revised its global guidelines for the use of Ferritin thresholds in patient groups with iron deficiency and those at risk of iron overload, recognises that there is no specific recommendation on variability among analytical methods and commutability. From the foregoing account, there is an urgent need for reference methods for the quantification and identification of biochemical markers used for the early diagnosis and treatment monitoring of MMD.

This lecture will demonstrate the potential of novel multi-technique strategies based on the combination of plasma metalloprotein speciation (by HPLC-ICP-MS) and tissue multi-element imaging (by LA-ICP-ToFMS) to monitor both plasma CuEXC as well as effects of chelating therapies for Wilson's disease. Such information was found essential to understand observed effects of drug treatment as well as drug upload and accumulation. The lecture will also describe sample preparation protocols combined with HPLC-ICP-MS and AF4-ICP-MS methodology to selectively quantify plasma Ferritin-light chain as biomarker of hemochromatosis. Efforts to produce natural and an isotopically-enriched sulphur standards of light human ferritin towards isotope dilution quantification of such biomarker species in human serum will also be highlighted.

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Plenary Lectures

ICP-MS BASED BIOANALYTICAL STRATEGIES TO STUDY NANO-IRON THERAPIES USING IN-VIVO AND IN-VITRO MODELS

M. Montes-Bayon[a,b*], L. Gutierrez-Romero[a,b], J. G. Veneziani Kamezawa [3], A. Rodríguez Pescador[d,e,b], L.M. Sierra Zapico[d,e,b], E. Blanco[a,b]

[a] University of Oviedo, Department of Physical and Analytical Chemistry, Oviedo, Spain, 33006
[b] Institute for Sanitary Research Principality of Asturias (ISPA), Oviedo, Spain, 33011
[c] Dept. of Analytical Chemistry, Institute of Chemistry, Campinas, SP, Brazil
[d] University of Oviedo, Department of Functional Biology, Genetics Area, Oviedo, Spain, 33006.
[e] University Institute of Oncology of Asturias (IUOPA), Oviedo, Spain, 33006
*e-mail: montesmaria@uniovi.es

Iron nanoparticles are currently used in intravenous formulations to treat severe cases of anaemia. However, the possibility of using nanostructured Fe-supplements for oral administration is still an area subject to extensive investigations. Oral delivery is the most accepted drug administration route among the various delivery pathways because of its advantages: painlessness, easy self administration, high patient compliance, and feasibility for outpatients. Regarding such nano-iron formulations, it has been published that reducing the particle size may result in an increasing bioavailability and therefore, an increment of the absorption level. Furthermore, size does not only determine the way of cellular uptake, but also the clearance mechanisms from the body (via kidneys for particles smaller than 10nm and via mononuclear phagocyte system for larger particles in organs). Thus, some of the current efforts to find the ideal formulation are focused on mimicking the ferritin model to encapsulate iron in nanoparticulated forms and releasing it with minimum side effects. Recently, the development of ultrasmall iron oxide nanoparticles coated by tartaric and adipic acid (TAFeNPs) represents an interesting alternative for iron supplementation that has been already tested in children with severe iron deficiencies.[1]

In this work, we aim to develop bioanalytical strategies to characterize the fate and toxicological behavior of nano-iron supplements and in particular, TAFeNPs using a battery of in vitro and in situ experiments. The first experiments are aimed to ensure that the particles remain stable within the gastrointestinal track by evaluating their physicochemical behavior in acidic environments using TEM and newly developed HPLC-ICP-MS strategies. Furthermore, intestinal absorption experiments by SPIP in combination with TEM and ICP-MS are conducted in animal models. The separation of the different regions of the small intestine should permit to establish the area where highest absorption has taken place. The toxicological aspects concerning the damage induced in enterocytes due to the NPs uptake is evaluated by addressing cell viability and ROS formation in cell Caco-2 and HT-29 cell models and correlated with the NPs absorption levels. Lastly, studies on the potential DNA damage in different cell models and genetic mutation induced in-vivo in *D. melanogaster* by the TAFeNPs will be also highlighted in order to illustrate the behaviour of this formulation.

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MULTI-TECHNICAL ATOMIC SPECTROMETRY APPROACH TO SPECIATION OF GADOLINIUM IN RAT BRAIN

Ryszard Lobinski[a,*], Izabela Strzemińska[b], Cécile Factor[a]

[a] CNRS, Institute of Analytical and Physical Chemistry for the Environment and Materials (IPREM - UMR 5254), Pau, France, 64053
[b] Guerbet Research and Innovation Department, Aulnay-sous-Bois; France, 93602
*e-mail: ryszard.lobinski@cnrs.fr

In 2014, it was suggested that repeated administration of linear gadolinium-based contrast agents (GBCAs) lead, in healthy patients, to signal enhancement in specific brain structures in magnetic resonance (MR) imaging. Also, unexpected presence of gadolinium (Gd) in other parts of the brain was demonstrated, challenging the widely accepted assumption that GBCAs cannot cross a healthy blood-brain barrier. Although the accumulation of gadolinium in brain has not been associated with any toxicological effect or disorder; its residual presence has been attracting the attention of regulatory agencies.

The lecture discusses the contributions and their synergy of different microscopic and spectrometric techniques to get an insight into the chemical forms of Gd retained in brain and in the deep cerebral nuclei of rats administered repeatedly with gadoterate or gadodiamide 4 months after the last injection.[1-3] Gadolinium species were extracted in two consecutive steps with water and urea solution. The total Gd concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS). Soluble Gd species were analyzed by size-exclusion chromatography coupled to ICP-MS. The insoluble Gd species were analyzed by single-particle (SP) ICP-MS, nanoscale secondary ion mass spectroscopy (NanoSIMS), and scanning transmission electron microscopy with energy-dispersive X-ray spectroscopy (STEM-EDX) for elemental detection.

For gadoterate, the highest amount of Gd was found in the water-soluble fractions, and present, most likely as the intact GBCA form. In the case of gadodiamide, the water-soluble fraction was composed of high-molecular-weight Gd species of approximately 440 kDa and contained only less than 1% of intact gadodiamide. Labile complexes of dissociated Gd^{3+} with endogenous molecules were likely to be present. The highest amount of Gd was detected in the insoluble residue, which was demonstrated, by SP-ICP-MS, to be a particulate form of Gd.

Two imaging techniques (NanoSIMS and STEM-EDX) allowed further characterization of these insoluble Gd species. Amorphous, spheroid structures of approximately 100–200 nm of sea urchin-like shape were detected. Furthermore, Gd was consistently colocalized with calcium, oxygen, and phosphorous, strongly suggesting the presence of structures composed of mixed Gd/Ca phosphates. No or occasional colocalization with iron and sulfur was observed.

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Invited Speakers

ELEMENTAL BIOIMAGING AT MICRO- AND NANOSCALE

Dirk Schaumlöffel,[a*] **Iris H. Valido**,[a] **Maria Angels Subirana**[a]

[a]CNRS, Université de Pau et des Pays de l'Adour, E2S UPPA, IPREM UMR 5254, Hélioparc, 2, Avenue du Président Angot, F-64053 Pau, France
*e-mail: dirk.schaumloeffel@univ-pau.fr

For investigating of the metabolic functions, biosorption, and bioaccumulation processes of metals at the cellular and subcellular level, correlative bioimaging of trace metals in cells and tissue exhibits a great potential. The development of new instrumental and methodological analytical developments as well as the combination of analytical techniques are all crucial to scientific advancement in this area. The Nanoscale Secondary Ion Mass Spectrometry (NanoSIMS) technique is capable of achieving the highest lateral resolution down to 50 nm. This method depends on positive or negative primary ion beams sputtering secondary ions from a solid surface in a high vacuum, followed by a mass spectrometry analysis of the secondary ions. Our NanoSIMS is equipped radio frequency plasma oxygen main ion source that offers excellent sensitivity and high spatial resolution for trace metal detection at cellular and subcellular level. Furthermore, we developed the combination of NanoSIMS with Laser Ablation ICPMS for correlative bioimaging of trace elements where NanoSIMS enables a nanoscale zoom of the same areas previously imaged by LA-ICPMS at microscale. In addition, synchrotron-based X-ray techniques complete the analytical approach for imaging and in-situ speciation. This talk covers the strategy for correlative imaging using NanoSIMS, LA-ICPMS and SXRF for elemental bioimaging at micro- and nanoscale. This will be demonstrated using recent studies of our research, for example (i) the localization and speciation of arsenic in Sargassum algae; (ii) the localization and speciation of zinc in zinc-accumulating yeast; and (iii) the correlative bioimaging of Zn, Cu, and Mn in eggshells and laying hen tibia bones in the context of trace metal supplementation in animal nutrition. Finally, challenges with this correlative bioimaging approach, including sample preparation, will be addressed, along with its limits.

ADVANCED SOLVENTS AND NANOMATERIALS IN MICROEXTRACTION TECHNIQUES: A GATEWAY TO SENSITIVE TRACE ELEMENT DETERMINATION AND SPECIATION

Rodolfo G. Wuilloud*

Laboratory of Analytical Chemistry for Research and Development (QUIANID), Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo / Instituto Interdisciplinario de Ciencias Básicas (ICB), CONICET UNCUYO, Padre J. Contreras 1300, (5500) Mendoza, Argentina
*email: rodolfowuilloud@gmail.com; rwuilloud@mendoza-conicet.gob.ar

Sample preparation is a crucial step during the determination of trace elements due to its very low concentration and the potential to be severely affected by the concomitants occurring in the samples under analysis. Therefore, for a precise and sensitive determination of trace elements, a preconcentration step is usually required before instrumental detection and solvents or sorption materials are normally applied. However, the toxicity and high volatility of organic solvents must be considered at the time of their application in classic liquid-liquid extraction techniques (LLA) or solid phase extraction (SPE) for the preconcentration of trace elements before total analysis or speciation. On the other hand, modern analytical methods focus on the development of simple, sensitive, and environmentally respectful practices that follow the principles of green chemistry (for example, substitution of toxic reagents, miniaturization, and automation).[1]

Alternative solvents have gained increasing attention in recent years for the preparation of samples, since they can be used instead of classical organic solvents that are considered highly toxic, volatile, and flammable. The use of alternative solvents has contributed to developing simpler, miniaturized, economic and environmentally friendly methodologies for the determination of trace elements.[2] Among them, ionic liquids (ILs), surfactants, and deep eutectic solvents (DES) have been increasingly applied to the preparation of samples in the determination of trace elements. Moreover, the combination of ILs or DES with techniques aiming miniaturization of reagents and wastes could provide significant benefits for preserving our environment when analysis is developed.

This presentation will describe useful strategies for the implementation of these solvents and their combination with different nanomaterials for separation and preconcentration of trace elements and their species. Modern liquid-liquid and solid-phase microextraction techniques based on ILs, DES and nanomaterials, such as dispersive liquid-liquid microextraction (DLLME) and dispersive micro-solid phase extraction (D-µ-SPE), will be discussed as well as the benefits of their application in combination with atomic spectrometry-based techniques.

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CHALLENGES AND ADVANCES IN THE ANALYSES OF OIL SAMPLES BY ICP-MS

Tatiana Dillenburg Saint Pierre

Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Dept. of Chemistry, Rio de Janeiro, RJ, Brazil, 22451-900
e-mail: tatispierre@puc-rio.br

The atomic spectrometry techniques employing a plasma source, i.e., inductively coupled plasma optical emission spectrometry and mass spectrometry (respectively ICP OES and ICP-MS) are complementary techniques for routine elemental analyses of most samples, due to their multi-element capability and sensitivity. Although the two techniques use different properties in detecting the elements, the systems for sample introduction and the plasma, which is the source of atoms and ions, are essentially the same. The commercially available equipments are generally provided with introduction systems for samples in liquid form, mostly highly diluted aqueous solutions. The introduction of organic solvents requires specific systems that allow the introduction of much smaller amounts of solution into the plasma, in the form of an aerosol, the adjustment of more energetic operating conditions, and the introduction of oxygen, in order to favour the decomposition of organic compounds in a homogeneous and stable manner. The analysis of organic liquid samples, such as fuels and biofuels, can be done after the sample has been decomposed in an acidic medium, usually using closed systems with controlled pressure and temperature, which, due to the flammable characteristics of the samples, is already a challenge. In addition, the introduction of carbon compounds into the plasma promotes the formation of interferences that do not occur in aqueous solutions. The preparation of samples in the form of emulsions or microemulsions was, for some time, considered the ideal alternative for the analysis of organic liquids, as it avoids decomposition and allows the use of inorganic standards. However, in order to allow the use of aqueous solution introduction systems, it is necessary that the samples are very diluted in the emulsifying medium, in addition to being susceptible to contamination by the addition of co-solvents or surfactant agents. On the other hand, the physicochemical differences between the samples require a large dilution and the use of calibration techniques that can compensate for these differences, such as the use of an internal standard, sometimes more than one, or calibration by analyte addition. Calibration strategies, such as isotopic dilution (ID) and standard dilution analysis (SDA), have been proposed as alternatives to compensate for the difficulties encountered and will be discussed in this work.

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[FAPERJ, CNPq, CAPES]

ANALYTICAL APPROACHES FOR PFAS SUM-PARAMETER ANALYSIS – FROM MATERIALS TO ENVIRONMENT

F. Simon[a], L. Gehrenkemper[a], S. Becher[b], G. Dierkes[b], N. Langhammer[a], A. Cossmer[a], M. von der Au[a], B. Göckener[c], A. Fliedner[c], H. Rüdel[c], J. Koschorreck[d], B. Meermann[a*]

[a]Federal Institute for Materials Research and Testing (BAM), Division 1.1 - Inorganic Trace Analysis, 12489 Berlin, Germany
[b]Federal Institute of Hydrology (BfG), Department G2 - Aquatic Chemistry, 56068 Koblenz, Germany
[c]Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME), 57392 Schmallenberg, Germany
[d]German Environment Agency (UBA), 06813 Dessau-Rosslau, Germany
*e-mail: bjoern.meermann@bam.de

Per- and polyfluorinated alkyl substances (PFASs) are a group of several thousand individual compounds.[1] Many PFASs are extremely persistent, bioaccumulative and toxic.[2] The analysis of PFASs is challenging because of their various chemical and physical properties as well as the high number of compounds.

Analytical methods for PFAS determination were compared – target analysis, non-target screening (NTS, LC/ESI-(HR)MS/MS), direct total oxidizable precursor assay (dTOPA) and extractable organically bound fluorine (EOF, HR-CS-GFMAS)[3,4]. Therefore, suspended particulate matter (SPM) samples from German rivers at different locations in time series from 2005–2020 were analyzed to investigate temporal and spatially resolved trends.

Fluorine mass balance analysis revealed that mean proportion of unidentifiable extractable organically bound fluorine (uEOF), i.e., proportion of EOF not determinable by target analysis, was at 93% ± 10%. The proportion of the uEOF in SPM samples of German rivers increased between 2005 and 2019. This suggests that new organofluorine compounds are introduced into German rivers, which are neither oxidizable precursors of perfluoroalkyl acids nor targets routinely analyzed. In addition, the comparison of sum parameters (EOF and dTOPA) with PFAS target analysis, revealed high gaps in organofluorine mass balances.

Sum parameter methods are a powerful and highly needed tool to identify PFAS contamination in the environment to end up with a valuable PFAS risk assessment.

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ON THE INTERACTION OF MICROWAVE RADIATION WITH MINERAL ACIDS – FUNDAMENTAL CONSIDERATIONS ON MICROWAVE-ASSISTED SAMPLE DIGESTION

Wiltsche Helmar[a*]

[a] Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Graz, Austria
*e-mail: helmar.wiltsche@tugraz.at

Microwave-assisted sample digestion using mineral acids is a well-established and widely used sample preparation technique for atomic and mass spectrometry techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Though widely used, the theoretical understanding of the interaction of microwave radiation with concentrated mineral acids is surprisingly limited. In fact, it is commonly assumed, that mineral acids absorb microwave radiation of 2.45 GHz much like water. Based upon this hypothesis, the penetration depth of microwave radiation into the digestion acid mixture is believed to be about 20 mm – much as in the case of water. Therefore, volumetric heating has been postulated. Unfortunately, these assumptions are wrong.

Due to the very high electrical conductivity of mineral acids used for sample digestion, microwave radiation is absorbed in a thin (< 1 mm) liquid layer at the digestion vessels inner surface. Heat conduction and convection have to ensure the energy transfer from this boundary region to the center of the digestion vessel and thereby limit the heat transfer. Volumetric heating, that is the heating of the entire sample volume directly by microwave radiation cannot occur. In fact, the heating mechanism is closer to a beaker glass on a hotplate than commonly anticipated. In the latter case a thin liquid layer is heated directly by the hot glass surface and the bulk volume temperature increase of the liquid phase is dominated by convection and conduction.

FACING NEW ANALYTICAL CHALLENGES IN ATOMIC SPECTROMETRY VIA MICROSAMPLING

M. Resano[a*], M. Aramendía[a], A. Bazo[a], Flávio V. Nakadi[a], D. Leite[a], R. Garde[a], J. Resano[a], K. Billimoria[b], H. Goenaga-Infante[b], J. C. García-Mesa[c], E. Vereda Alonso[c]

[a]Universidad de Zaragoza, Aragon Institute of Engineering Research (I3A), Pedro Cerbuna 12, Zaragoza, Spain, 50009
[b] National Measurement Laboratory, LGC, Queens Road, London, UK, TW11 0LY
[c] Universidad de Málaga, Department of Analytical Chemistry, Faculty of Sciences, Málaga, Spain, 29071
*e-mail: mresano@unizar.es

In atomic spectrometry, the term microsampling has been evolving in recent years. From the original meaning of simply targeting the analysis of microsamples[1] to the more complex current sense that also includes targeting individual analysis of micro/nanostructures.[2] In this regard, single event ICP-MS has enabled the development of a significant number of applications for analysis of nanoparticles (NPs),[3] cells,[4] or even micro plastics.[5] However, matrix effects often affect the quality of the results, and the application of traditional solutions in this context is not straightforward.

A novel approach for overcoming matrix effects in real samples when using single particle-ICP-MS is presented in this work. The approach is based on the standard addition method and calibration of the particle size is performed by two different methods: (i) by spiking a suspension of NPs standards of known size containing the analyte, or (ii) by spiking the sample with ionic standards; the measured sensitivity is finally used in combination with the transport efficiency (TE) for sizing the NPs. Moreover, such transport efficiency can be also obtained from these set of data, so that the particle number concentration can also be determined.[6]

Another possibility for elements with more than one nuclide is applying isotope dilution approaches. The importance of different factors to achieve the best possible precision and accuracy when using ICP-TOF-MS will be discussed in the context of AgNPs characterization.[7] Finally, another approach makes use of the mass spectrometer (quadrupole) operating in bandpass mode, enhancing the sensitivity for the monitoring of NPs while also allowing for the detection of NPs of a different type in the same measurement run, such that they can serve as an internal standard.[8] Examples of such approaches applied to the characterization of NPs in complex matrixes will be discussed.

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ANALYSIS OF SOLID SAMPLES USING ATOMIC AND MASS SPECTROMETRY: RELEVANT OR REMEMBRANCE?

Daniel L. G. Borges[a*]

[a]Universidade Federal de Santa Catarina, CFM - Chemistry Department, Florianópolis - SC, Brazil
*e-mail: daniel.borges@ufsc.br

The analysis of solid samples has always posed a challenge for analytical chemists, since most instruments are designed for the analysis of liquids, especially as aqueous solutions. Hence, obtaining quantitative trace elemental information from a solid sample frequently requires the adoption of fairly complex and time-consuming sample preparation strategies as an attempt to provide adequately digested samples for the instrument. Nevertheless, the analysis of solid samples either directly or as suspensions has been investigated for many decades and experienced a “hype” with the development of electrothermal vaporization / atomization devices and high-resolution instruments. The question remains on whether the analysis of solid samples remains relevant nowadays, considering the long years of investigation and the advancements in sample preparation strategies. A literature overview will be, therefore, provided and discussed, along with a compendium of the latest results that were obtained in our research group, directed to the quantification of a variety of metals and non-metals in solid samples using inductively coupled plasma mass spectrometry and atomic absorption spectrometry. Overall, the discussed examples should demonstrate that the analytical challenges related to solid sample analyses remain relevant and alternative sample introduction strategies and, quite often, minimum sample preparation are efficient ways to provide accurate results.

DIELECTRIC BARRIER DISCHARGE HYDRIDE ATOMIZERS FOR TRACE ELEMENT AND SPECIATION ANALYSIS

Jan Kratzer[a*], Alexandra Slota[a,b], Matěj Plecháč[a,b], Tomáš Matoušek[a], Milan Svoboda[a], Vishal Dwivedi[c], Martina Mrkvičková[c], Pavel Dvořák[c], Jiří Dědina[c]

[a]Czech Academy of Sciences, Institute of Analytical Chemistry, Brno, Czech Republic, 602 00
[b] Charles University, Faculty of Science, Prague, Czech Republic, 128 43
[c] Department of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic, 602 00
*e-mail: jkratzer@biomed.cas.cz

Dielectric barrier discharge (DBD) plasmas were intensively studied in our laboratory since 2013 to serve as atomizers of hydride forming elements (As, Sb, Bi, Se, Te, Pb, Sn) for sensitive detection of these metal(loid)s by hydride generation atomic absorption spectrometry (HG-AAS). For some analytes (As, Sb, Se, Te) DBDs were found a good alternative to quartz tube atomizers (QTA) while for the others (Bi, Pb, Sn) their performance in terms of sensitivity was significantly worse. Our recent work targeted at another hydride forming element - germanium. Concentration trends of Ge species in the environment and their mutual transformations in (bio)geochemical cycles are now in focus as the industrial consumption of Ge as a technology critical element is increasing. Low sensitivity reported in 1980´s for Ge determination by HG-AAS with flame and QTA atomizers hindered further investigations. Since new types of hydride atomizers have emerged (e.g. multiple microflame QTA (MMQTA) and DBD) and the hydride atomization theory was further developed it is worth to revise the potential of HG-AAS for Ge determination. Three types of hydride atomizers based on diffusion flame (DF), QTA and DBD were optimized for atomization of three environmentally important volatile Ge species including germanium hydride (GeH_4) and its two methyl-substituted analogues – monomethyl germanium hydride (CH_3GeH_3) and dimethyl germanium hydride ($(CH_3)_2GeH_2$). Atomization efficiency was confirmed to be comparable among the species in given atomizer. MMQTA was found to be more sensitive to Ge species compared to plain QTA owing to the controlled supply of air. Also the use of gas phase dryer improves substantially the sensitivity of Ge determination in both MMQTA and DBD atomizers. When compared to other hydride forming elements, the sensitivity observed for Ge species is two orders of magnitude worse in MMQTA, 10-50 times lower in DBD and 5 times worse in DF. Mechanistic study was carried out to get deeper insights into the atomization of volatile Ge species and the fate of free Ge atoms. Employing GeH_4 as a model analyte the fraction of Ge deposited in the atomizers was quantified by leaching with subsequent ICP-MS determination. The spatial distribution of free Ge atoms was investigated by laser induced fluorescence (LIF). Although HG-AAS cannot compete with (HG)-ICP-MS at all in determination of Ge traces the experiments conducted bridged the gap in the knowledge of atomization of volatile germanium species.

Efficient in-situ preconcentration of hydrides and their methyl-substituted analogues in DBD atomizers can be used as a simple and operator friendly approach to improve the detection limit of HG-AAS. Analyte retention (trapping) occurs in the presence of oxygen admixed to the discharge gas while analyte release (volatilization) is achieved by switching off the O_2 flow in presence of H_2 evolved spontaneously during blank measurement. Determination of four toxicologically relevant arsenic species including inorganic As (sum of arsenite and arsenate), monomethylarsonic acid, dimethylarsinic acid and trimethylarsine oxide was optimized making use of this approach. The species were separated by HPLC to be subsequently treated by post-column hydride generation followed by in-situ preconcentration in DBD and AAS detection in a fully automated procedure. The method developed was successfully validated by analysis of certified reference materials of human urine (NIST-2669, levels 1 and 2) and marine tissue samples (TORT-3). A “hybrid” mode of determination was found useful for samples with greater difference in concentration of individual As species. Only the species present at low concentrations are preconcentrated while the others can be quantified in the same run but without preconcentration.

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LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS): DATA ANALYSIS AND CONTRIBUTIONS FOR AGROBUSINESS

Edenir Rodrigues Pereira-Filho

Federal University of São Carlos, Chemistry Department, São Carlos, São Paulo, Brazil, 13565-905
*e-mail: erpf@ufscar.br

Laser-Induced Breakdown Spectroscopy (LIBS) plays an important role in the field of analytical chemistry by enabling direct analysis of solid samples without the need for extensive sample preparation steps. This instrumental technique offers the unique advantage of recording emission spectra across a broad spectral range: from ultraviolet (UV) to infrared (IR), while maintaining a high analytical throughput [1]. However, the process of extracting meaningful insights from LIBS data is a non-trivial challenge, necessitating the application of various mathematical and statistical tools, often falling under the umbrella of chemometrics [2]. This study aims to showcase the significant contributions made by the Group of Applied Instrumental Analysis (GAIA) over the past decade. The focus of our research has primarily revolved around samples of great agricultural importance, such as soils, fertilizers, seeds, and leaves for nutritional inspection [3]. The bulk of our work involves univariate and multivariate calibration methods proposition, normalization strategies, and liquid sample immobilization. The main emphasis was dedicated to the determination of both major and micronutrients, as well as the identification of some contaminants.

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EXPRESSION OF MATRIX METALLOPROTEINASES AND THEIR INHIBITORS IN BREAST CANCER TISSUES

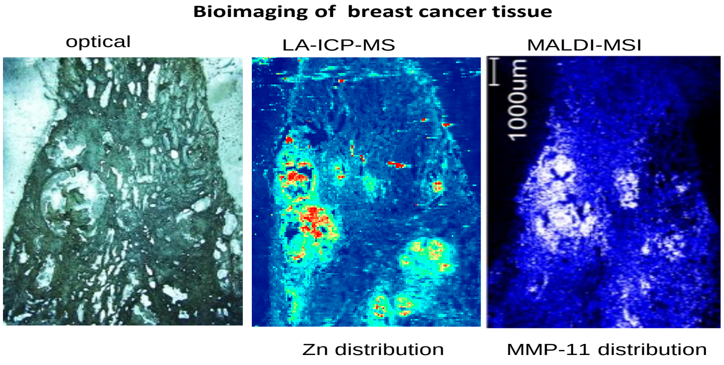
María L. Fernández-Sánchez[a], Sara Escudero-Cernud[a], Raquel González de Vega[b], María Fraile[c], Noemí Eiró[c], Francisco Vizoso[c].

[a]Department of Physical and Analytical Chemistry, University of Oviedo, Spain, 330012.
[b]TESLA-Analytical Chemistry, Institute of Chemistry, University of Graz, Graz, Austria.
[c]Research Unit, Hospital de Jove Foundation, Gijón, 33290
e-mail:marisafs@uniovi.es

Breast cancer is the most common cancer and the leading cause of cancer death in woman. Recently, many investigations support that the tumor microenvironment plays important roles in *tumor* initiation, *progression* and metastasis. The tumor microenvironment (or stroma) is made up of many cell types (immune cells, fibroblasts, and endothelial cells) as well as a complex mixture of proteins (glycoproteins and proteoglycans) known as extracellular matrix (ECM). Currently, most investigations are focused on functional characterization of ECM components and how they relate to the processes involved in cancer pathogenesis and response to therapy.

Matrix Metalloproteinases (MMPs) are a family of endopeptidases requiring Zn^{2+} for their enzymatic activity, which promotes extracellular matrix degradation. Under physiological conditions, MMPs activity is tightly controlled by endogenous tissue inhibitors of metalloproteinases (TIMPs). However, MMPs are upregulated in most human tumour cell lines and their high levels are linked to metastasis[1].The Matrix metalloproteinase 11 (MMP-11) was identified as a highly expressed protein in the stromal cells of breast cancer and has been implicated in cancer progression.

This work investigates the prognostic significance of stromal MMP-11 expression in breast cancer tissues and its role in breast cancer progression. An immunohistochemistry-assisted laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) method has been developed for the quantitative bioimaging of MMP-11 in breast cancer tissues. Results showed that MMP-11 is significantly up-regulated in breast metastatic samples compared to non-metastatic and healthy breast tissue. Furthermore, Conditioned Media or secretome from human Uterine Cervix Stem Cells (CM-hUCESCs) possesses antitumour effect on the malignant breast cancer line MDA-MB-231[2]. A semiquantitative proteomic study by ESI-MS/MS showed the presence of high levels of TIMPs in CM-hUCESCs.



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ALTERNATIVES OF SAMPLE PREPARATION METHODS FOR BIOFUELS ANALYSIS

Juliana Severo Fagundes Pereira[a*], Diogo Pompéu de Moraes[a], Paolla Hermann[a]

[a]Universidade Federal do Rio Grande do Sul, Instituto de Química, Porto Alegre, RS, Brazil, 91501-970
*e-mail: julianasfp@ufrgs.br

Nowadays, the renewable sources of energy has great interest worldwide due to the increase of energy demand, the shortage of light crude oil reserves and the reduction of carbon emissions to avoid global warming. In this way, a remarkable interesting has been given to the production of biofuels produced from renewable resources. As example, it could be mentioned the biodiesel and bio-oil. Both biofuels come from biomass and have utility in different engine in agreement with the sustainability principles. Furthermore, the low concentration of metals and sulfur, the main pollutants found in fuels from fossil, gives attractiveness to its use as biofuel.[1] Even though the use directly from bio-oil as automotive fuel is not part of the current reality, its antimicrobial potential and its improvement through hydrodeoxygenation for the obtaining a fuel with characteristics similar to biodiesel have been investigated.[2,3] Due the growing demand for alternative energy sources, there is an increasing need to control and monitor the quality of biofuels. Metal monitoring controlled by the ANP (National Petroleum, Natural Gas and Biofuels Brazilian Agency) is only intended for the majority inorganic contaminants present at the parts per million level. However, the presence of minority elements, such as Fe, Ni, Co, Cu, even in low concentrations, are harmful to the quality of the fuel, reducing its stability and, subsequently, increasing the degradation. Furthermore, damage to the metal parts of the engine can be observed and increased in the environmental pollution by the emission of particulate matter.[4] Despite direct analysis of metals could be performed in biofuels by spectrometry techniques after sample dilution in organic solvents, the use of organic solvents promotes some disadvantages, such as loading of the plasma with organic matter and limitations in the sample introduction system. Furthermore, problems due to carbon deposition and matrix interference are commonly observed. In this work the performance of microwave-assisted digestion using diluted acids was demonstrated for biofuels decomposition prior metals determination. Microwave digestion in closed vessels is a promising alternative due to the possibility of using diluted acids for digestion and several conditions were evaluated, as sample mass, concentration of acids and auxiliary (H_2O_2). Efficiency was determined by residual carbon content and residual acidity in final solutions. Sample masses higher than 400 mg could be digested using diluted acid solutions. Although biofuels digestion could be performed using concentrated nitric acid, the use of diluted acid was preferable in view of the low reagent consumption and low blanks values, achieving better LODs that is important aspect to green chemistry recommendations for trace elements analysis.

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[ANP-PRH50.1, CAPES, CNPq, FAPERGS]

TRACING AUTHENTICITY: ISOTOPE RATIOS IN CIGARS, WINES, AND CEREALS

Rui Santos

Analytik Jena, Rua do Campo Alegre 687, Porto, Portugal
e-mail: rui.santos@analytik-jena.com

The traceability of origin in consumer products, such as tobacco, beverages, and cereals, has assumed an increasingly pivotal role in the realm of quality control across diverse industrial sectors. High-quality products that bear the mark of a specific geographic origin or adhere to a specialized manufacturing process often command greater appreciation from consumers, frequently reflected in significantly higher price points than their counterparts.

Moreover, with the emergence of diseases tied to foodstuffs from particular regions, there is a compelling need to scrutinize the origin of these products to ensure consumer safety and guarantee authenticity. In this pursuit, chemical analysis, and particularly the determination of isotopic ratios, assumes a critical role in forensic endeavours. By applying various techniques to a range of food products, we can formulate methods that enable us to ascertain their geographic origins with varying degrees of certainty. The measurement of elemental concentrations and isotopic variations in premium regional products stands as the optimal analytical strategy for verifying their geographical provenance.

CHARACTERIZATION OF AGED MICROPLASTICS COVERED BY BIOFILM USING ADVANCED LASER-BASED TECHNIQUES

Jozef Kaiser[a,b*], Pavel Pořízka[a,b], Aida Fazlić[a], Daniel Holub [b], Ota Samek[c], Martin Kizovský[c], Lukas Brunnbauer[d], Andreas Limbeck[d], Ula Rozman[e] and Gabriela Kalčíková[e]

[a] Central European Institute of Technology, Brno University of Technology, Brno, Czech Republic, 61200
[b] Faculty of Mechanical Engineering, Brno University of Technology, Brno, Czech Republic, 61669
[c] Institute of Scientific Instruments, Czech Academy of Sciences, Brno, Czech Republic, 61264
[d] TU Wien, Institute of Chemical Technologies and Analytics, Vienna, Austria,1060
[e] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia, 1000
*e-mail: jozef.kaiser@ceitec.vutbr.cz

Microplastics (MPs) are a growing environmental concern due to their ubiquitous presence and potential adverse effects on ecosystems and human health. The accurate and efficient detection of MPs is essential for monitoring and mitigating their impacts. However, conventional analysis methods encounter challenges when dealing with aged MPs covered by biofilm. Therefore, this study focuses on laser-based techniques as a versatile alternative in MPs detection and characterization. In our study, we recognized the potential influence of biofilm on aged MPs during analysis. As biofilm can significantly impact the characteristics of MPs, we opted to analyze them together to better understand their interaction and behavior in the aquatic environment. Additionally, we considered other factors, such as the environment in which the MPs were aged (freshwater or wastewater), as they can also affect the properties and fate of MPs.

In this study, we investigated five types of aged MPs, specifically polyamide (PA), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), and polyvinyl chloride (PVC). These MPs were analyzed in their pristine state as well as were subjected to aging in both freshwater and wastewater environments. To analyze and differentiate the various polymer types accurately, we utilized Raman spectroscopy in conjunction with principal component analysis (PCA). This powerful combination allowed us to precisely identify and distinguish different MP compositions with exceptional accuracy. In addition to Raman spectroscopy, we employed laser-induced breakdown spectroscopy (LIBS) to gain valuable insights into the characterization of MPs. This technique provided a precise identification of the MPs and their respective compositions, enabling us to determine their unique chemical makeup with high precision. Furthermore, we conducted laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) imaging experiments to obtain essential spatial information about the distribution of inorganic elements within the MPs. Through this detailed analysis, we gained crucial insights into the potential uptake of various inorganic constituents by the aged MPs during freshwater and wastewater aging.

The outcomes of our study [1] clearly demonstrate the immense potential of advanced laser techniques for accurate and comprehensive MP analysis, even under challenging environmental conditions. By successfully differentiating polymer types, we have opened up new avenues for improved MP detection and monitoring. As we advance our understanding of the environmental behavior of MPs, this research supports broader efforts aimed at mitigating the adverse effects of microplastics on ecosystems and human health.

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STANDARD DILUTION ANALYSIS 2.0: AUTOMATION AND TWO INTERNAL STANDARDS FOR FAST, ACCURATE DETERMINATIONS

George L. Donati
Wake Forest University, Department of Chemistry, Winston-Salem, NC 27109, USA
e-mail: donatigl@wfu.edu

Calibration is one of the most consequential steps in any analytical procedure. Although widely employed in many fields, the traditional methods of external standard calibration (EC), internal standardization (IS), and standard additions (SA) present limitations associated with either poor accuracy or low sample throughput. Among the alternative approaches to EC, IS, and SA, standard dilution analysis (SDA) is one of the most successful at minimizing matrix effects. It has been used in inductively coupled plasma optical emission spectrometry (ICP-OES), ICP mass spectrometry (ICP-MS), microwave-induced plasma OES (MIP-OES), flame atomic emission spectrometry (FAES), Raman spectroscopy, and UV/Vis spectroscopy applications. SDA is faster than SA and more accurate than EC and IS, as it uses only two calibration solutions per sample, each containing the same amount of matrix. In the originally described SDA method,[1] analyte and IS signals were continuously recorded as one of the calibration solutions (S2, with 50% v/v sample and 50% v/v blank) was manually poured into a tube containing the other calibration solution (S1, with 50% v/v sample and 50% v/v of a standard solution containing the analytes and an IS species). Thus, several calibration points were generated on the fly as S1 and S2 mixed. In addition to its manual nature, one of the main limitations of the original SDA method was the requirement for judiciously selecting data corresponding to the exact moment when S1 and S2 were mixing. In this presentation, we will discuss recent developments in SDA that allowed for faster and simpler data processing, and for the autonomous mixing of S1 and S2. By adding a second IS species to S2, the entire SDA dataset could be used to build the calibration plot, which greatly facilitated data processing. In the new SDA approach,[2] the unknown concentration of analyte in the sample (C_{sam}) is calculated from the concentration of analyte added to S1 (C_{std}), the slope (*m*) and intercept (I_1) of a plot with analytical signal on the *y* axis and the first IS species (the one added to S1) on the *x* axis (**Fig. 1**), and the intercept (I_2) of another plot with the first IS species on the *y* axis and the second IS species (the one added to S2) on the *x* axis (**Fig. 2**), *i.e.* $C_{sam} = \frac{I_1 \cdot C_{std}}{m \cdot I_2}$. On the other hand, the solution mixing process has been automated by using a lab-made mixing chamber,[2] or an electronically controlled pinch valve.[3] In each case, solution mixing was carried out by the ICP-OES' own automatic sampler, for faster and accurate trace element analyses of complex matrix samples such as 40% v/v HNO_3, 40% v/v ethanol, 1% m/v Ca, 1% m/v Na, and diluted solutions of beer, cachaça, mouthwash, soft drinks, wine, etc.

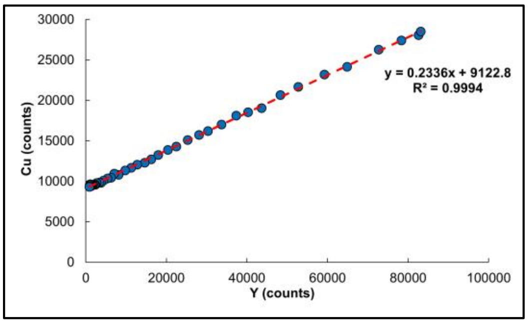

Fig. 1. SDA plot for Cu determination in apple juice using Y as IS species.

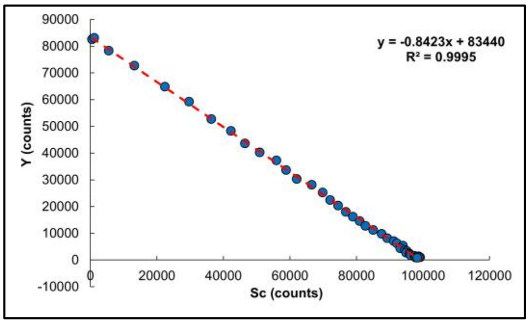

Fig. 2. SDA plot to determine I_2. Here, Y and Sc were added to S1 and S2, respectively.

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[Department of Chemistry and Graduate School of Arts and Sciences at Wake Forest University]

INDUCTIVELY COUPLED PLASMA FOR SPECTROCHEMICAL ANALYSES: WHAT WE LEARNED FROM COMPUTER MODELS

Ramon M. Barnes[a*]

[a]University of Massachusetts, USA
*e-mail: rbarnes@umass.edu

Although it took a decade from when its potential as a spectrochemical source was first described to its commercial introduction, the inductively coupled plasma (ICP) development during the early years in the 1960’s and 1970’s was full of research discoveries and instrumentation breakthroughs. Driven by low limits of detection and wide dynamic concentration range for multiple, simultaneous elemental analyses with minimum matrix effects, the ICP was examined by atomic absorption, atomic emission, and atomic fluorescence spectroscopy and subsequently by mass spectroscopy. Our early research focused on characterizing the plasma and its interactions with samples experimentally and by computer modeling. Along the way we examined various sample-handling approaches and applied them to practical problems. Some highlights from the results of computer models will be described.

In order to distribute ICP progress reports and discuss outstanding practical questions, we introduced in 1975 the monthly ICP Information Newsletter, now in its 49th year, and we started in 1980 the Winter Conference on Plasma Spectrochemistry with planning for the 23rd biennial gathering in Tucson in January.

PUSHING DOWN DETECTION LIMITS OF ATOMIC FLUORESCENCE SPECTROMETRY COUPLED TO GENERATION OF VOLATILE SPECIES

Jiří Dědina

Czech Academy of Sciences, Institute of Analytical Chemistry, Brno, Czech Republic, 602 00
*e-mail: dedina@biomed.cas.cz

Atomic fluorescence spectrometry (AFS) coupled to generation of volatile species has the potential to reach very low limits of detection (LOD). Namely the non-dispersive arrangement of the AFS apparatus provides an attractive alternative even to mass spectrometric techniques because of low purchase and operating costs. The potential of AFS to reach very low LODs can generally be fully achieved only when using very mild atomization conditions which are typically compatible with the atomization of volatile species. This is the reason why AFS is currently associated prevalently with volatile species. The simple and convenient non-dispersive AFS apparatus employs an interference filter for the selection of the detection wavelength interval placed in front of a detector, typically a photomultiplier. The other two essential components of a non-dispersive atomic fluorescence spectrometer include an atomizer and a radiation source (atomic lamp). Since the introduction of non-dispersive AFS as an analytical method mainly two types of atomic lamps have been used: electrodeless discharge lamp (EDL) or boosted hollow cathode lamp. EDLs are said to provide higher radiation intensities, however, the range of elements for which the EDLs are manufactured is limited to volatile elements. Boosted hollow cathode lamps are widely applied in the current commercial AFS instruments whereas EDLs are usually used in experimental laboratory setups of AFS.

The relevant instrumental settings for a non-dispersive AFS apparatus are namely: type of atomic lamp; atomic lamp feeding power/current and its modulation pattern; optical path parameters such as focusing of (i) radiation from the atomic lamp to the atomizer and (ii) fluorescence radiation to the photomultiplier; choice of a suitable interference filter; and selection of the optimum fluorescence line. In principle, the intensity of the fluorescence radiation is proportional to the radiation source intensity. Consequently, higher sensitivity, and lower LOD, can be reached simply by increasing the intensity of the radiation source.

Our long-time ambition is to optimize experimental parameters of non-dispersive AFS in order to reach minimum LODs for volatile species forming elements. Aim of this presentation is to outline potential of AFS for ultratrace analysis of volatile species forming elements and to illustrate the positive impact of optimizations of the relevant experimental parameters. A historical view of our activities in the field will be given. Then our recent investigations of atomic lamps focused on the lamp absolute radiation intensity and on its dependence on the modulation pattern of the lamp feeding power/current will be presented. Perspectives of the coupling of ambient low-power plasma atomizes to AFS will also be delineated.

[This research was supported by the Czech Science Foundation (grant 23-05974K) and by Institute of Analytical Chemistry of the Czech Academy of Sciences (RVO: 68081715)]

INSIGHTS INTO THE ROLE OF TRANSITION AND NOBLE METALS MEDIATING PHOTOCHEMICAL VAPOR GENERATION

Ralph E. Sturgeon[a*]

[a]National Research Council Canada, Metrology, Ottawa, Ontario, Canada K1A 0R9
*e-mail: Ralph.sturgeon@nrc-cnrc.gc.ca

It is well-known that selective introduction of gaseous atomic or molecular analyte species into sources used for atomic spectrometry provides numerous advantages, including enhanced detection power, reduction of matrix and spectral interferences, as well as speciation capabilities. Vapor generation (VG) has been utilized for more than 50 years for such purpose, with photochemically driven VG processes currently offering the broadest elemental coverage, encompassing classical hydride forming elements, the halogens and a growing number of transition metals.

Most recent advances in photochemical vapor generation (PVG) have arisen as a consequence of the addition of trace concentrations of selected transition metals to the reaction medium, principally Fe, Cd. Co, Ni and Cu. These so called “sensitizers” will be examined in light of possible catalytic mechanisms of analytical product synthesis which may account for their substantial impacts on the efficiency of PVG while continuing to respect current models1 advanced to account for the general homogeneous mechanism of PVG.

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Short Course 1

ANALYTICAL METHOD VALIDATION

Thiago de Oliveira Araujo[a]*

[a] Instituto Nacional de Metrologia, Qualidade e Tecnologia (Inmetro), DIMCI/DIMQT/LABIN, Duque de Caxias, RJ, Brazil, 25250-020
*e-mail: toaraujo@inmetro.gov.br

The development of biomaterials, nanotechnology, and other fields of science as well as decisions about commerce, health and environment are heavily based on analytical results, thus, inadequate results lead to waste of time and resources, and jeopardize the wellbeing of society. Analytical method validation is key for the guarantee of quality of data produced in laboratories. The analytical chemistry community is used to the main concepts of validation and many analytical organizations and regulatory agencies throughout the world issue method validation guides[1]. The central goal of analytical methods validation is to assure that the data produced is adequate for the intended use. Validation is a systematic approach to demonstrate objectively, with experimental evidence, that the method is fit for purpose. Many strategies to validate a methodology are available, and the most suitable for each application should be selected. The evaluation of parameters that can influence the results is the most used approach in the chemical area and common parameters evaluated to assess method performance are: selectivity, limits of detection/quantification, linearity, trueness, precision and measurement uncertainty. The experimental set-up and data treatment must be designed to evidence the compliance of the method with the intended application and the criteria used to evaluate these parameters are key for the guarantee of fitness for purpose. There is a myriad of strategies for method validation presented in the literature, with different statistical approaches and criteria to evaluate the parameters vary largely depending on application. This variability and lack of fixed criteria commonly causes great concern on analysts less familiar with the validation systematic.

The objective of this course is to contextualize method validation within quality assurance systematic, quality system standards (such as 17025), and the metrological concepts involved, such as traceability and comparability. The dynamic of the course is based on discussions with participants about the concepts of the main parameters evaluated during method validation, present different examples and strategies for some analytical problems and indicate how can they evaluate their working analytical methods, develop a validation strategy, and stablish appropriate criteria to assess fitness for purpose. The short course focus on clarifying the principles behind every validation parameter, so participants can transfer the strategies seen in class or in the literature to their own daily problems.

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[Inmetro; Pronametro]

Short Course 2

ADVANCES IN SAMPLE PREPARATION FOR ATOMIC SPECTROMETRY

Fabio A. Duarte[a*], Eder L. M. Flores[b]

[a] Universidade Federal de Santa Maria, Chemistry Department, Santa Maria, Rio Grande do Sul State, Brazil, 97105-900
[b] Universidade Tecnológica Federal do Paraná, Chemistry Department, Medianeira, Paraná State, Brazil, 85884-000
*e-mail: fabio.duarte@ufsm.br and ederflores@gmail.com

Atomic spectrometry techniques have been widely used for metals and non-metals determination in trace or ultra-trace levels in different matrices (environmental, food, geological materials, fuels, among other samples). In a few cases where only the matrix dilution is allowed, a sample preparation step is required, which can be broadly divided as digestion or extraction. may involve dry or wet decomposition of the samples in open or closed systems, using thermal, ultrasonic or radiant (infrared, ultraviolet and microwaves) energy. In the analytical sequence, the sample preparation step remains as the "Achilles' heel", being considered critical and prone to errors that can affect the accuracy and precision of the analytical results. In this short-course, the main sample preparation methods will be covered, starting from traditional dry methods (dry-ashing, and fusion) up to recent methods such as microwave-induced combustion (MIC). For wet digestion methods, on the use of microwave irradiation will be highlighted, as well as their main technological advances, such as the use of high-pressure closed vessels and recent strategies for improving the digestion efficiency, such as the combination with UV radiation. Finally, the most recent sample preparation methods for analytes extraction from the matrix without the need for total digestion will be discussed. Methods based on microextraction, such as dispersive liquid-liquid microextraction (DLLME) and reversed-phase DLLME (RP-DLLME), will be discussed highlighting their main advantages, such as reduced use of reagents, pre-concentration and the low implementation cost. Extraction methods using ultrasound and some recent applications will also be presented. In particular case of halogens determination, sample preparation based on pyrohydrolysis will be presented and the main aspects of these systems will be discussed. The participants of the short course are expected to have a broad and critical view of the fundamentals and applications surrounding sample preparation methods with a journey through the past, present and future trends in this important field of analytical chemistry.

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[**CNPq, CAPES, FINEP, FAPERGS, ARAUCÁRIA**]

Workshop 1: Atomic Spectrometry for Environmental Applications

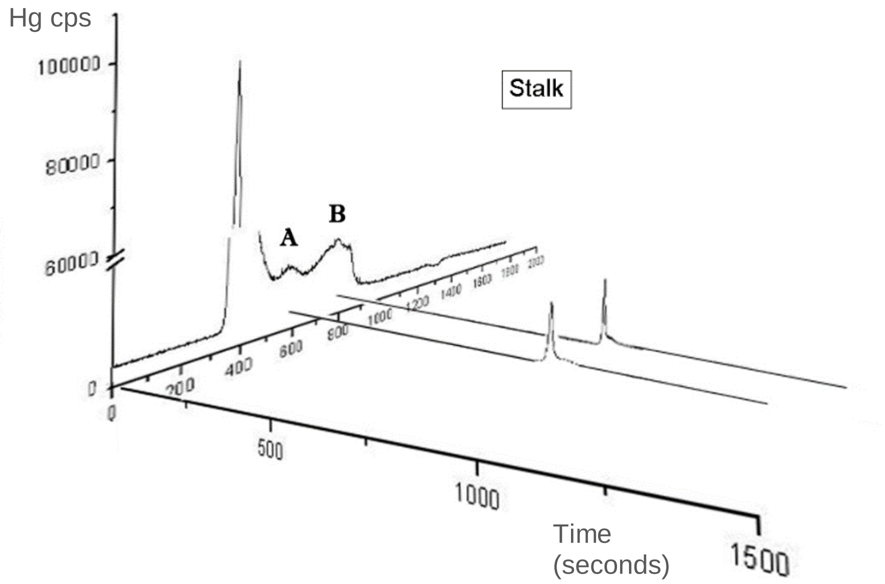
Coordinator: Maria Tereza Weitzel Dias Carneiro Lima (UFES, Brazil)

APPLICATIONS OF MULTIDIMENSIONAL CHROMATOGRAPHY STRATEGIES IN SPECIATION ANALYSIS BY ICP-MS

Pablo Pacheco[a*]

[a]Universidad Nacional de San Luis, Ejército de Los Andes 950, D5700HHW-San Luis, Argentina
*e-mail: ppacheco@unsl.edu.ar

Total elemental analysis provides limited information of Hg, As, and Se impact in environment and organisms. Individual species of these elements have different bioavailability, essentiality, and toxicity. In consequence, speciation analysis provides a deeper understanding of Hg, As and Se roles in nature. Speciation can be performed by coupling liquid chromatography to inductively coupled plasma mass spectrometry (LC-ICP-MS). Features like atomization efficiency from metabolites and macromolecules, transient signal monitoring of heteroatoms, and sensitivity, turns ICP-MS into the ideal detector for speciation analysis.[1] Biological and food samples have complex matrices, requiring successive purification steps to extract and ultimately determine specific elemental species. Liquid chromatography is compatible with speciation analysis according to its resolution capacity, non-destructive separation and versatility.[2] By introducing different chromatographic modes, low molecular weight species like inorganic species, and high molecular weight like peptides and proteins can be isolated. The non-destructive nature of LC allows the recovery of unmodified elemental species. Recovery can be performed by fractions collection according to retention times, followed by a preconcentration step through filtration with molecular weight cut off filters and lyophilization. The collected fractions can be further analyzed in LC^n modes in a multidimensional approach. Synergy between multidimensional chromatography and ICP-MS allows for the speciation of heteroatom tagged inorganic molecules, amino acids, and proteins, in samples of environmental, food, and biological interest.



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NEW MATERIALS APPLIED FOR ULTRATRACE DETERMINATION BY ATOMIC SPECTROMETRY

Jefferson S. de Gois[a*]

[a]Rio de Janeiro State University, Department of Analytical Chemistry, Rio de Janeiro, RJ, Brazil, 20550-013
*e-mail: jefferson.gois@uerj.br, jeffersonsgois@gmail.com

New materials for pre-concentration and separation/purification can contribute to the enhancement of the detection capabilities of a given analytical technique, resulting in simple, robust, with high sample throughput, and low-cost preconcentration methods that can be applied for determination at the ultra-trace level in different samples. In this lecture, we discuss the application of new materials for pre-concentration methods, such as graphene-based nanocomposites, metal oxide nanoparticles, and molecular sieves prepared by conventional routes, as well as nanoparticles synthesized by environmentally friendly routes with the use of biomass, which are unprecedented factors for processes pre-concentration of elements and determination by atomic spectrometry techniques[1]. Nanoparticles of GO/γ-Fe_2O_3, γ-Fe_2O_3, manganese oxide (OMS-2), and iron oxide-based nanoparticles obtained using biomass were synthesized by different rout of synthesis and characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS), and thermogravimetric analysis (TGA) techniques. The materials were applied for preconcentration and determination of elements in environmental samples after the multivariate optimization, method development, and validation. All statistical analyses were carried out using R software. The “rsmDesign ()” function of the ″qualityTools″ package was used to create the central composite designs. Analysis of variance (ANOVA) was used to assess the significance of each factor, and p-value < 0.05 was used to determine if the effect of the factor was significant. Shapiro-Wilk’s test was used to evaluate whether the residuals of the models had a normal distribution, being so when the p-value > 0.05. The “desirability ()” function was used for multiresponse optimization. In general, the domain of the factors pH, material mass, and adsorption time was optimized using a central composite design for all methods. The methods provided good accuracy, low detection limits, and relatively low cost for the determination of Se in fish samples by hydride generation atomic absorption spectrometry and flow injection analysis (FIA-HG-AAS); As in juvenile eyeshadow samples by FIA-HG-AAS; As, Cu, and Pb in seawater samples by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES); Pb in river water samples by graphite furnace atomic absorption spectrometry and As, Se and Pb in lignocellulosic biomass samples by ICP-OES. All methods were validated and applied to the contaminants at ultra-trace levels in case studies from Rio de Janeiro.

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[**CNPq, FAPERJ, UERJ**]

TOTAL REFLECTION X-RAY FLUORESCENCE FOR ENVIRONMENTAL ANALYSIS: POSSIBILITIES AND CHALLENGES

Clésia C. Nascentes

Federal University of Minas Gerais, Department of Chemistry, Belo Horizonte, MG, Brazil, 31270-901
*e-mail:clesianascentes@gmail.com

Total reflection X-ray fluorescence spectrometry (TXRF) is a powerful analytical technique that is widely used in various scientific and industrial applications. This technique is based on the principle of total external reflection of X-rays at the interface between a sample and a high refractive index material, usually quartz [1]. The use of TXRF is particularly important in fields such as materials science, environmental analysis, and forensic science, where accurate and precise elemental analysis is crucial. This technique required small quantities of sample and offers high sensitivity and selectivity, allowing for the detection of trace elements in complex matrix [2]. The ability to analyse a wide range of elements simultaneously makes TXRF an efficient and time-saving method for environmental studies.

In our research group, we have successfully utilized the TXRF to investigate the levels of selenium (Se) and various other elements in diverse soils across Minas Gerais state. This analysis has allowed us to comprehensively evaluate the availability of these elements in the soil and their potential impact on the environment.

Another important application was the analysis of blood and hair of wild animals to assess the environmental contamination. In non-lethal collection of small animals, the amount of sample available is minimal, limiting the use of other spectrometric techniques.

In a recent development, we have analyzed vegetal samples such as wood, leaves, and galls. By employing TXRF, we have evaluated the levels of sulfur (S), phosphorus (P), and silicon (Si) in these samples. These elements play a crucial role in physiological processes of plants and pose analytical challenges for determination.

Despite the great potential of the technique, its use requires the formation of a thin film of the sample on the reflective surface, a task that frequently poses challenges [3]. In this sense, sample preparation strategies must be carefully evaluated to obtain reliable results. Furthermore, the homogeneity and representativeness of the small amount of sample analyzed must be guaranteed.

Overall, the wide range of applications and the accuracy of results obtained through TXRF make it an important tool for environmental studies striving to understand and mitigate the impact of pollutants on ecosystems.

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[CNPq, CAPES and FAPEMIG]

PLASMA-BASED TECHNIQUES APPLIED TO AIRBORNE PARTICULATE MATTER CHARACTERIZATION

Patricia Smichowski[a,b]*

[a] Comisión Nacional de Energía Atómica, Gerencia Química, San Martín, Pcia de Buenos Aires, Argentina
[b] Consejo Nacional de Investigaciones Científicas y Técnicas, Buenos Aires, Argentina
*e-mail: patricia.smichowski@gmail.com

Atmospheric aerosols are very complex matrices. The determination of metals and metalloids in airborne particles requires the use of multielemental techniques of high sensitivity and selectivity. Plasma-based techniques are multielemental in nature, can be applied to different matrices, have an extended dynamic range and offer the possibility to be coupled to other analytical techniques (HG, FI, HPLC). In this context, inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma-mass spectrometry (ICP-MS) and sector field inductively coupled plasma-mass spectrometry (SF-ICP-MS) are useful tools in this kind of studies.

This presentation gives an overview of the research carried out for more than 20 years in the framework of national and international projects focused on the determination of a wide variety of major, minor, trace and ultra-trace elements in PM10, PM2.5, size distributed aerosols (<0.1-18 µm), ashes and road dust using different plasma-based techniques. Statistical analysis was performed in the described studies and the principal sources were assessed. Most of the studies were carried out in samples collected in Buenos Aires, Argentina.

The determination of almost 20 elements by plasma-based techniques in PM2.5 and PM10 samples collected during different periods made possible to obtain a profile of Buenos Aires aerosols. Vehicular traffic is the main source of platinum group elements (PGEs) in highly populated urban areas like Buenos Aires. For Pt and Rh determination, it was necessary to use an instrument of high resolution such as SF-ICP-MS for the ability to resolve troublesome polyatomic spectral interferences and for the higher resolving power. In these studies, a class 100 clean room was used to minimize the risk of sample contamination. Platinum and Rh were quantified in PM10 at pg m^{-3} levels. Platinum concentrations ranged from 2.3 to 47.7, with a mean value of 12.9±7, and that of Rh from 0.3 to 16.8, with a mean value of 3.9±2.8. These concentrations are by far below the levels for which adverse health effects might be expected to occur.

Mercury is present in oil vehicles fluids and engine coolants. For this reason, it is important to gain knowledge on Hg levels in APM and related matrices. For the determination of Hg in size-fractionated road dust samples, ICP-MS and CV-AAS were used and compared. Levels of Hg varied from 0.1 to 4.5 µg g^{-1} and higher values were detected in the smaller fractions.

Recently, ten size distributed aerosol with aerodynamic diameters of <0.10,0.1 0–0.18, 0.18–0.32, 0.32–0.56, 0.56–1.0, 1.0–1.8, 1.8–3.2, 3.2–5.6, 5.6–10 and 10–18 µm collected on Teflon filters by using a micro-orifice uniform deposition impactor (NanoMOUDI sampler) were analyzed for 21 elements. For elemental quantification ICP OES and ICP-MS were employed. A predominance contribution (~60%) of fine particle (PM1) was observed in the total aerosol mass.

The main characteristics as well as the pros and cons of the different instrumental techniques employed for aerosols characterization are described and discussed.

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Workshop 2: Atomic Spectrometry for Food, Beverages and Biological Applications

Coordinator: Rochele Sogari Picoloto (UFSM, Brazil)

PHOTOCHEMICAL AND THERMOCHEMICAL VAPOR GENERATION TECHNIQUES FOR TRACE ELEMENT ANALYSIS BY AAS

Gisele S. Lopes[a*], Victor M. Campos[a], Jane K. S. Brito[a]

[a]Laboratory of Applied Analytical Chemistry (LEQA), Graduate Program of Chemistry, Federal University of Ceara (UFC), Fortaleza, Ceara, Brazil, 60440-554.
*e-mail: gslopes@ufc.br

The chemical vapor generation, particularly hydrides generation (HG), emerged with the aim of improving the efficiency of sample introduction (100% efficiency) when compared to nebulization techniques. However, it has limited application, in addition to making use of unstable reagents, which makes these methods expensive and generate more waste. Photochemical vapor generation (PVG) and thermochemical vapor generation (TVG) systems can become sustainable and low-cost alternatives, as they only require low molecular weight organic acids (formic and acetic acid). Moreover, PVG presents wide applicability already reported in the literature. TVG presents only few studies reported in the literature [1-3]. Therefore, studies were carried out on different configurations of TVG reactors with a view to introducing and to analyze Hg species using spectrometric techniques. Hg speciation was accomplished in certified reference materials and total Hg was determined in tuna fish samples. Therefore, the main goal of this presentation is to show applications using PVG and TVG for trace element analysis by atomic absorption techniques. The development of prototypes of TVG reactors that can be used as accessories for Hg determination by cold vapor generation coupled to atomic absorption spectrometer will be presented as well.

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[CAPES, CNPq, INCTAA]

ISOTOPIC AND ELEMENTAL ASSESSMENT IN FOODS: FROM FORTIFICATION TO TOXICITY

Márcia Andreia Mesquita Silva da Veiga*

University of São Paulo, Department of Chemistry/FFCLRP, Ribeirão Preto, SP, Brazil, 14040-901
*e-mail: marcia.veiga@usp.br

Nutrient fortification of foods aims to maintain, correct, or prevent nutritional deficiencies in the population or specific groups such as the elderly, pregnant women, and children; in this sense, isotopic measurements for monitoring are essential to control the fortification process. Food groups such as non-conventional plants have also been evaluated for their nutritional constituents to contribute to dietary safety and diversification. However, they need attention regarding their composition due to alimentary security purposes. Toxicity studies are also fundamental to assess food safety in foods from impacted areas, such as fish in a mining area. Mercury (Hg) contaminates humans through contaminated fish consumption, affecting the riverside population, as fish is their staple food. This presentation will focus on these issues by discussing studies conducted: 1) to quantify ^{40}Ca and ^{44}Ca isotopes in clinical samples by high-resolution continuum source molecular absorption spectrometry to tracer experiments [1]; 2) estimation of essentiality and potential nutrient uptake in non-conventional food plants and impairing anti-nutrient factors; 3) effects of consuming Se-rich food on the potential bioaccessibility of Hg present in contaminated fish. The study of mineral nutrient absorption is necessary for the health of a population, particularly in the health of children, because mineral nutrition not only meets children's growth and developmental needs but can also limit or prevent disease. Analytical rigor in developing procedures ensures the reliability of results involving food safety. Suitable spectroscopic analytical techniques are crucial in detecting and correctly quantifying challenging target elements such as Hg and other essential elements.

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[**CNPq, CAPES, FAPESP**]

TRENDS AND CHALLENGES OF FOOD AND BEVERAGES ANALYSIS BY LIBS

Cassiana Seimi Nomura[a*]

[a]Institute of Chemistry, University of Sao Paulo, Sao Paulo, SP, Brazil, 05508-000
*e-mail: csnomura@iq.usp.br

Laser-induced breakdown spectrometry (LIBS) has deserved attention last decadesas one of the most promising and powerful analytical method for the direct analysis of solid samples. This method has gained popularity and found applications in several fields due to a set of unique advantages, including multi-element analysis capability, fast response, micro analytical capability (less than 100 μg of sample consumed per analysis), ease of use, and possibility of carrying out remote and in situ analysis because of the availability of portable instruments (Hahn and Omenetto, 2010). On the other hand, LIBS shows some challenges, which need to be overcome in order to be competitive with other well-established instrumental methods (Hahn and Omenetto, 2012). Quantitative measurements in complex matrices have still been considered the "Achilles heel" of LIBS due to the pronounced matrix effects caused by the complex laser-sample interaction processes. Moreover, its inherent microanalytical characteristic may hinder precision due to the natural heterogeneity of solid samples. Achieving reliable results depends on the appropriate handling of the samples and the use of adequate calibration approaches. This work shows some application of LIBS in direct analysis of food and beverages samples.

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[FAPESP, CAPES, CNPq, INCTAA]

Atomic Absorption Spectrometry

001 - ADDITIVE MANUFACTURING OF A DISPOSABLE SAMPLE HOLDER FOR HR-CS GFAAS: DETERMINATION OF Rh AND Ru

Caroline Scache Prudencio[a*], João Victor B. Santiago [a], Clovis Augusto Ribeiro [a], Edilene C. Ferreira[a], José A. Gomes Neto[a], Hernane da Silva Barud[b]

[a]São Paulo State University (UNESP), Institute of Chemistry, Araraquara, São Paulo, Brazil, 14800-060.
[b]University of Araraquara – UNIARA, Araraquara, São Paulo, Brazil, 14801-340.
*e-mail: cs.prudencio@unesp.br

Platinum group metals (PGMs: Ir, Os, Pd, Pt, Rh and Ru) are used by several industries in different applications due to their physicochemical properties. Recovery of PGMs from different sources is economically attractive due to their high value. The high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) is an interesting technique for determination of some PGMs due to possibility of analyzing solids, monitoring multiple lines, improving background correction based on least-squares algorithm, among others. Preliminary tests carried out in our laboratory showed improved sensitivity for Rh (up to 1.5 times) and Ru (up to 3 times) when the conventional graphite platform was changed by a 3D polymeric platform made of poly-lactic acid (PLA) was used. Also, the transient signal was narrower, with a faster return to baseline. The proposal of this work is the construction of a polymeric platforms (poly-lactic acid, PLA) by 3D printing[1] through the fused filament fabrication (FFF) technique allowing an alternative to conventional graphite platforms for elemental determinations by HR-CS GFAAS. The 3D printing platform projected and manufactured in work (Fig. 1) was applied to the simultaneous determination[2] of Rh (343.4893 nm) and Ru (343.6740 nm) in electronic waste (E-waste) samples.

Fig 1. Original pyrolytic graphite platform (left) and 3D polymer platform (right).

Calibration curves for Ru (5.0 – 25.0 µg L$^{-1)}$ and Rh (50.0 – 250 µg L$^{-1)}$ with good correlations (r) between absorbance and concentration were observed: r= 0.9948 (Rh) and r= 0.9953 (Ru) for 3D platfors; r= 0.9929 (Rh) and r=0.9930 (Ru) for graphite platforms. Analytes were simultaneously determined in acid digest extracts from samples of printed circuit board, monitors, fluorescent lamp glass powders and automotive catalysts samples. In general, the levels of Rh and Ru were in the 0.19 – 10.4 mg and 0.11 – 135 mg, respectively. Addition of 20 µL of 8 and 20 µg L^{-1} Rh and 80 and 200 µg L^{-1} Ru into digests furnished recoveries in the 13 - 165% (graphite platform) and 8 -125% (3D platform) intervals. Despite preliminary results in liquid samples, data suggest possibility of replacing conventional graphite platforms by polimeric disposable ones considering the low cost, rapid homemade manufacturing of pure or blend polymer devices according to the problem at hand.

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002 - DETERMINATION OF CR AND CU IN BIOFUELS BY GF AAS USING A MICROEMULSIONS AS SAMPLE PREPARATION STRATEGY

Paolla R. S. Hermann[a], Luan Ferreira Passos[a], Vinícius Pospichil Gil[a],
Alan dos Santos da Silva [a], Diogo Pompéu de Moraes[a*]

[a]Universidade Federal do Rio Grande do Sul (UFRGS), Institute of Chemistry, Porto Alegre, RS, Brazil, 91501-970
*e-mail: diogo.moraes@ufrgs.br

Bio-oil produced by fast pyrolysis of biomass is an important biofuel. Recently, a remarkable interesting have been given to the presence of inorganic contaminants in biofuels, due to environmental pollution and loss of fuel quality or proprieties. In this way, the use of microemulsion was proposed as a sample preparation method for bio-oil samples for subsequent determination of Cr and Cu by graphite furnace atomic absorption spectrometry (GF AAS). For microemulsions preparation, two emulsifiers were evaluated using ternary phase diagrams, such as *n*-propanol and Triton X-100. This study allowed the formation of water-in-oil microemulsions using about 560 mg of bio-oil, 240 mg of *n*-propanol and 200 mg of water, and oil-in-water microemulsion, using about 400 mg of bio-oil and 600 mg of Triton X-100 (10% w/v). Emulsions were characterized by measuring the diameter of dispersed drops by dynamic light scattering (DLS) technique, and, therefore, were classified as microemulsions. Pyrolysis and atomization temperatures for quantification of analytes by GF AAS were 1400 and 2100 °C for Cr, and 700 and 2000 °C for Cu, respectively. The presence of matrix interferences was evaluated by means of aqueous calibration standards and standard addition method. The results showed higher sensitivity for analytes in the presence of matrix and, for this reason, standard addition method was used for quantification step. The Cr and Cu signals were monitored one week after the microemulsion preparation and no difference was observed, demonstrating the stability of analytes. Accuracy of the proposed method was evaluated by analysis of certified reference material (HU-1 used oil) and by microwave-assisted wet digestion (MW-AD), and results were in agreement with a confidence level of 95% (t-student test). The concentrations of Cr and Cu in four analyzed samples ranged from 76.1 to 4881 and from 4.01 to 3668 μg kg^{-1}, respectively. The limits of quantification (LOQ) for Cr and Cu ranged from 2.45 to 4.58 μg kg^{-1}.

[ANP/PRH 50.1, CNPq and Fapergs]

003 - DETERMINATION OF Cd and Pb IN PETROLEUM WASTE BY HR-CS GF AAS USING Pd NANOPARTICLES AS CHEMICAL MODIFIER

Karine S. Coêlho[a], Welman Curi Elias[b], Daniel L. G. Borges [a], Rafael C. C. Rocha[c], Tatiana D. Saint' Pierre[c] and Eduardo S. Chaves[a*]

[a] Universidade Federal de Santa Catarina, Departamento de Química, Florianópolis, SC, Brasil, 88040-900
[b]Rice University, Department of Chemical and Biomolecular Engineering, Houston, TX, United States,77005
[c]Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química, Rio de Janeiro, RJ, Brazil, 22451-900
*e-mail: eduardo.chaves@ufsc.br

Nanoparticles (NPs) have been applied as an interesting alternative to conventional chemical modifiers in graphite furnace atomic absorption spectrometry (GF AAS) analysis.[1-3] Recent studies have indicated that NPs provide thermal stabilization for volatile analytes, as well as improved sensitivity and accuracy of the results obtained by GF AAS.[2,3] Thus, the feasibility of palladium nanoparticles (Pd-NPs) as chemical modifiers for Cd and Pb determination in the leached extracts from oil and gas industry residues by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS), was evaluated. Palladium NPs with different sizes and shapes were obtained according to ELIAS, 2017.[4] Hydrophilic palladium nanocubes and nanospheres with sizes varying from 3 to 22 nm were synthesized. In general, the results showed that the use of Pd-NPs chemical modifier provided a positive effect in terms of sensitivity and thermal stability for Cd and Pb. The mass of Pd-NPs introduced into the graphite tube influenced the analytes' thermal stability. However, the sensitivity of the analysis and the effectiveness of the modifier appeared to be suppressed to an important extent in the presence of matrix components of the leached extracts, which were obtained following a specific Toxicity Characteristic Leaching Procedure (TCLP). The optimum conditions were determined using 200 ng of 3 nm Pd-NPs nanospheres, a pyrolysis temperature of 800 °C for Cd and Pb, and atomization temperatures of 1800 °C (Cd) and 2300 °C (Pb). The resulting limits of detection were 0.2 µg L^{-1} for Cd and 4 µg L^{-1} for Pb and the precision, evaluated by means of the relative standard deviation (RSD) (≤ 34 % for Cd e ≤ 18 % for Pb), was considered satisfactory for the analysis of leached extracts from oil and gas industry residues. The method accuracy was evaluated by recovery tests and comparison of the results with those obtained by inductively coupled plasma mass spectrometry (ICP-MS). Recoveries ranged from 97 to 115 % and the concentrations were in good statistical agreement with those obtained by ICP-MS (paired t-test at a confidence level of 95 %). The developed method based on using Pd-NPs as a chemical modifier was effectively applied to determine Cd and Pb in leached extracts obtained from samples of oily sludge and drill cuttings. The concentrations of Cd in the analyzed extracts ranged from < 0.50 (LOQ) to 39.8 µg L^{-1} and from < 13 (LOQ) to 354.4 µg L^{-1} for Cd and Pb, respectively. These concentrations are lower than the legal limits (0.5 mg L^{-1} Cd and 1.0 mg L^{-1} Pb) established in the Brazilian Standard ABNT NBR 10004.

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[CNPq, CAPES, Petrobras and UFSC]

004 - EVALUATION OF Al, Ba, Mg AND Zn IN PROTEIN SUPPLEMENTS BY MICROWAVE-INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY

Sérgio V. F. Scholante[a*], Jéssica da R. Porto[a], Yasmin R. Bloedorn[a], Charlie G. Gomes[a], Daisa H. Bonemann[a], Wiliam Boschetti[a], Anderson S. Ribeiro[a]

[a]Federal University of Pelotas, Chemical, Pharmaceutical and Food Science Center,
Capão do Leão, RS, Brazil, 96160-000.
*e-mail: sergio.scholante@ufpel.edu.br

Proteins are indispensable in the human diet, since they act in several processes that occur in the body. Therefore, several food supplements are available to complement the protein intake, such as whey protein[1]. Whey protein is the by-product of the cheese manufacturing process, and considered a waste by the dairy industry, but due to the presence of proteins of high nutritional value, low cholesterol, carbohydrates and lactose, it acts as an excellent sports nutritional supplement[2,3]. In addition to providing proteins, these products are a source of metals, providing essential elements and potentially toxic elements, therefore, monitoring the concentration of these elements in food is extremely important[4]. Therefore, this work aims to evaluate the total concentration of Al, Ba, Mg and Zn in whey protein samples by Microwave Induced Plasma Optical Emission Spectrometry (MIP OES). For sample preparation, an acid decomposition method in a closed low-pressure system was used as described by Miranda[5]. In order to optimize the best experimental conditions for sample preparation, a compound factorial design was used, where the following independent variables were investigated: sample mass, HNO_3 volume, pre-digestion time and digestion time. The volume of reagents and mass of samples are limited due to the risk of system explosion. For sample preparation, 162.5 mg were weighed directly into the borosilicate tube, followed by the addition of 1.064 mL of HNO_3 65% (v/v) and 0.96 mL of H_2O_2 30% (v/v). The tubes were closed and after 30 minutes of pre-digestion, were placed in the digester block with a gradual increase in temperature until reaching 150°C for 155 minutes. After, the samples were transferred to polypropylene tubes and filled up to 15 mL with deionized water. The detection limits (LOD) of the proposed method was 0.252, 0.096, 0.084 and 0.451 mg kg^{-1} for Al, Ba, Mg and Zn, respectively. The accuracy of the method was evaluated using certificate reference material (NIST 1577c) and (Agro C1005a), the values obtained were in accordance with the values certified at 95% confidence through a Student's t-test for all analytes. The results of the total concentration of samples A, B, C and D were 16.15; 28.10; 35.35 and 14.14 mg kg^{-1} for Al, 1.85, 0.92, 2.68 and 1.91 mg kg^{-1} for Ba, 748, 809, 1071 and 902 mg kg^{-1} for Mg and 3.57, 27.03, 29.82 and 4.30 mg kg^{-1} for Zn, respectively. Considering that the recommended daily intake value (DRI)[6] for adults of Al, Ba, Mg and Zn is 2 mg/body weight, 0.14 mg/body weight, 260 and 7 mg, respectively, and considering the consumption of one dose, equivalent to 30 g as indicated by the manufacturer, it can be concluded that the samples contribute to the ingestion of these elements, but without exceeding the recommended value.

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[CNPq, CAPES, INCTAA]

005 - ANALYSIS OF ELEMENTS FROM THE METALLURGICAL INDUSTRY IN $PM_{2.5}$ IN MEXICO CITY

Ciro Eliseo Márquez Herrera[a*], Gilberto Esparza Martínez [a], Larissa Barbosa Sanchez[c], Octavio Gamaliel Aztatzi[d], Martha Patricia Sierra[e], Yasmin Debrai García[a], Rodolfo Sosa Echeverríai[b]

[a] Universidad Nacional Autónoma de México, Facultad de Química, Ciudad Universitaria México, CP 04510
[b] Universidad Nacional Autónoma de México, Instituto de Ciencias de la Atmósfera y Cambio Climático, Ciudad Universitaria Ciudad de México, CP 04510
[c] Instituto Nacional de Salud Pública, Cuernavaca, Morelos, México, CP 62100
[d] Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, San Pedro Zacatenco, Ciudad de México, México, CP 07360
[e] Instituto Nacional de Enfermedades Respiratorias , Tlalpan, Ciudad de México, CP 14080
*e-mail: ciromar@unam.mx

The Valley of Mexico is one of the largest cities in the world, home to more than 20 million people. More than 3 million vehicles circulate. According to data from the National Institute of Geography and Informatics of Mexico, there are more than 100 industries related to metallurgical activity. In Mexico there is legislation related to PM emission parameters, which indicate the maximum permissible values of particle emission as well as the elements considered as potentially toxic, however there is little data related to the emission of particles from a sector. specifically industrial [1,3] The present work shows the results of analysis of elements obtained from PM2.5 filters placed in 3 different areas of Mexico City (north, south and east), with the objective of relating the results of elements obtained with the possible emission of industries with metallurgical activity. 90 samples of 47 mm Teflon filters were used. Sampling was carried out in the cold dry season from November 12 to February 28, 2022, and the hot dry season from March 1 to April 1, 2022. The samples were prepared according to Compendium Method IO-3.1. EPA, using microwave digestion. The analyzes were performed using atomic emission spectrometry with ICPOES Avio 500 Perkin Elmer equipment. NIST 1648 was used as reference material.

Results:

The elements found with the highest values related to the metallurgical industry are shown in Table 1:

Table 1. Elements Founded ($\mu g/m^3$)

Al	7.419	Cr	0.735
Ni	0.1126	Fe	0.2244
Zn	0.2299	Pb	0.4629
Mn	0.1621	Cu	0.1706
Cd	0.0595	V	0.0595

The recovery values with respect to the reference material for the different elements are between 90-110%.

The values presented are comparable to those presented in other investigations for cities with high environmental impact from different industries, including metallurgy [1,2]. And it presents higher values than those found in a study carried out in the same area in 1997 [3].

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[CONACYT]

006 - OPTIMIZING THE ANALYTICAL SIGNAL CAPTURE CONDITIONS OF A LOW-COST FLAME ATOMIC EMISSION SPECTROMETER

Matheus Felipe Pedrotti[a*], Francisco Cunha da Rosa[a], Lucas Gabriel Oliveira de Aguiar[a]

[a]Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul (IFRS), Campus Feliz, Feliz, RS, Brazil, 95770-000
*e-mail: matheus.pedrotti@feliz.ifrs.edu.br

Obtaining laboratory experience is a fundamental requirement for aspiring professionals in the field of chemistry. A primary avenue for gaining this indispensable experience is through practical experiments conducted in the classroom setting.[1] However, a significant challenge arises due to the prohibitive costs associated with procuring and maintaining advanced analytical equipment, rendering them largely unavailable within educational institutions. [2] This challenge is especially pronounced for expensive techniques such as atomic spectrometry, which is often omitted from the practical curriculum, thereby depriving students of the opportunity to develop proficiency in these crucial skills essential for their future careers in chemistry. To address this issue and provide students experience with this technique, the construction of low-cost instruments becomes an important alternative to meet this demand. Therefore, this work involves the development of a Flame Atomic Emission Spectrometer (F AES) using reused electronic components and 3D-printed parts. As the detection of analytical signals in the proposed equipment relies on a smartphone, the conditions for capturing images must be evaluated and chosen appropriately. Among these conditions, camera sensitivity to light (ISO) and camera exposure time (exposure time) are crucial factors. This is important because each element emits light at a different intensity at the same concentration. Therefore, it is necessary to identify the best ISO and exposure time condition for each analyte. To do this, an evaluation was carried out for sodium (Na), potassium (K), lithium (Li), and calcium (Ca). In this evaluation, solutions were prepared in advance in the absence of analytes (blank) and solutions at 15.0 mg L^{-1} for all metals. Initially, the exposure time was set to 4 s, and ISO was varied from 50 to 3200 units. Then, with the best ISO condition observed for each analyte, exposure time was varied from 1 to 10 s. The transformation of images into analytical signals is performed using ImageJ software. The captured image was separated into red (R), green (G), and blue (B) vectors, which range from 0 to 255. To choose the best condition in each case, the conditions that showed values of G (for Na and Ca) and R (for Li and K) closest to 125 for the standards were selected. This allowed confirmation of the expected sensitivity difference for capturing the different elements. Furthermore, in all cases, calibration curves were obtained with determination coefficients exceeding 0.999 for all analytes under the chosen optimal conditions.

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007 - PLASMA-MEDIATED VAPOR GENERATION BY DIELECTRIC BARRIER DISCHARGE: AN ARSENIC STUDY USING AAS

Gilberto Coelho Junior*, **Jan Kratzer**, **Jiří Dědina**
Institute of Analytical Chemistry of the Czech Academy of Sciences, Department of Trace Element Analysis, Prague, Czech Republic, 142 20
*e-mail: coelho@iach.cz

Chemical vapor generation (CVG) is a well-known sample derivatization technique in the field of trace element analysis. Analyte is efficiently, often quantitatively, converted from the liquid into the gas phase after the treatment of acidified sample with a reductant reagent. CVG benefits include high introduction efficiency and matrix separation. However, the molecular species (*e.g.* binary hydride) has to be atomized for atomic absorption spectrometry (AAS) or fluorescence detectors, excited in case of atomic emission spectrometry or even ionized prior to its mass spectrometric detection. All these processes require energy to be delivered either by resistive heating, flame or plasma. Both steps, *i.e.* analyte vaporization and detection, are separated in time and space. One of the novel strategies is the plasma-mediated vapor generation technique (PMVG) that allows integrating of both processes, analyte volatilization and atomization, into one compartment (reactor) placed directly in the optical axis of the spectrometer. Moreover, PMVG does not require any chemical reagent to be added offering thus an elegant and environmentally friendly approach. In recent years, the dielectric barrier discharge (DBD) reactors have been used for PMVG.[1] A thorough optimization of the DBD device for As^{3+} determination based on PMVG and subsequent AAS detection was the main goal of this work. A lab-made volume discharge DBD reactor was designed with the dielectric barrier consisting of a T-shaped quartz tube. Its central arm served for sample introduction and discharge gas inlet. Two copper foil electrodes were placed on the outer surface of the main tube (optical arm) with a distance of 20 mm, which were coupled to a lab-made high voltage power supply with sinusoidal waveform modulation. The plasma was on all the time with a constant flow of He as a discharge gas. The sample solution (7 µL) was injected *via* a lab-made automated system (using a peristaltic pump, a servo motor and a microcontroller) inside the quartz tube. The solution droplet was immediately dried after the contact with the hot surface of the tube (*ca.* 200 °C), heated by the plasma. The preliminary experiments have revealed that As is trapped inside of the tube during the drying step and that it can be volatilized and atomized only in presence of H_2. It is well-known that H_2 content in the plasma plays an important role for analyte reduction.[1] Pure inert gas was employed as a discharge gas in the initial step (drying) of the measurement procedure. H_2 was admixed into the inert discharge gas 10 s after signal acquisition started in order to volatilize the analyte. He was selected as a discharge gas since the As signal was higher in He compared to Ar. Optimum flow rates of He and H_2 were 200 and 8 mL min^{-1}, respectively. The voltage delivered by the power supply was optimized to 5.8 kV. No memory or carry-over effects between consecutive measurements were observed indicating the efficiency of the PMVG procedure. The effect of acid concentration was studied from 0.001 to 1 M for HNO_3 and HCl. There was a decrease in the signal of As when using concentrations from 0.01 M (by 63% for HNO_3 and 18% for HCl). At 1 M the signals were completely suppressed for HNO_3 and by 76% for HCl. A possible explanation of acid interferences is that species such as Cl^- and NO_3^- are quenchers of radical-based reactions due to their affinity for $H^\bullet$ (recognized to be necessary for analyte reduction).[1] Calibration curves were linear in the concentration range from 50 to 500 µg L^{-1} with a limit of detection of 3 µg L^{-1} (23 pg absolute). When compared to the sensitivity obtained using conventional CVG followed by AsH_3 atomization in the same quartz tube, the PMVG proposed method achieved the same sensitivity (0.55 s ng^{-1} As), indicating high efficiency of the DBD reactor to vaporize and atomize As. In conclusion, the proposed method performed for the first time a successful As determination using PMVG based on DBD for both vapor generation and atomization. The key point is that no reagents were required.

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008 - DETERMINATION OF LEAD IN INDOOR DUST FROM TWO SOUTHEN BRAZILIAN CITIES: AVALIATION AS AN EXPOSURE MARKER.

Eduardo da Costa Ilha[a*], Cristian Da Paz Braga[a], Tatiane de A. Maranhão[a]

[a]Federal University of Santa Catarina, Chemistry Department, Florianópolis, Santa Cataria, Brazil, 8040-900
*e-mail: eduardoilha2010@gmail.com.br

The indoor environment is getting more and more important in people’s lives, as well as the concerns about its impacts on human beings' health. The house dust represents one of the mainest sources of contaminants in indoor environments, being strongly related with people's blood lead levels and, consequently, with a lot of non-carcinogenic diseases[1]. The origin of the lead contamination found in its matrix come from numerous sources, such as industrial activity, car traffic and soil particles, which enters indoors carried by people and wind[2]. In this context, the aimed of the present work was to evaluate the level of Pb contamination in 32 samples of house dust and laboratorial dust from Jaraguá do Sul, an industrialized city, and Florianópolis, the capital, less industrialized city, both from Santa Catarina, Brazil, using a Graphite Furnace Atomic Absorption Spectrometry (GF AAS). The samples were collected by 12 volunteers by the manual sweeping of the house indoor environments on three different dates, with a 6-10 day interval. The samples were sieved to separate matter other than dust, the granulometry was homogenized using a ball mill, and suspensions were prepared in the optimized condition: 2% v/v HNO_3 and 0,1% m/v Triton TX-100®. After resting for 24 hours, Lead was determined using the optimized temperature program (Tp= 900 ºC and Ta= 2000ºC) with 500 mg of W as a permanent modifier. The accuracy was available with two CRMs (Clay Soil 1 “Clay Loam Soil” and TILL-2 “Geochemical Soil”). Addition and recovery test was performed at three levels, obtaining recoveries of 103 to 113%. The limits of detection and quantification were 1.0 and 2.9 µg g^{-1}, respectively. The founded results showed concentration between 10.2-166.5 µg g^{-1} of Pb in Jaraguá do Sul and 3.7-78.5 µg g^{-1} of Pb in Florianópolis. Principal components analysis (PCA) and Hierarchical cluster analysis (HCA) were used to study the relations between the meteorological factors[3] from the sampling days (precipitation level, average wind direction, average wind speed and solar incidence) and the concentration of Pb founded in the samples. The PCA showed a grouping of samples from Florianópolis, that get separated from Jaraguá do Sul’s samples, indicating that Florianópolis has a lower contamination between both. It also showed, in accordance with the HCA, the influences of the meteorological factors in Pb concentration. The average wind direction and the solar incidence had no significant correlation with the Pb presence in dust, while the precipitation level and the average wind speed were directly correlated to the decrease of Pb concentration in the samples.

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[LEMA, UFSC, CNPq, Epagri]

Chemical Speciation Analysis

009 - DETERMINATION OF LABILE BARIUM IN SURFACE WATERS USING THE TECHNIQUE DGT.

Daniel Peloni[a], **Luiz Felipe P. P. Moreira**[a*], **Amauri Antonio Menegário**[a]

[a]UNESP CEA, Rio Claro, São Paulo, Brazil, 13506-752
*e-mail: daniel.pelloni@unesp.br luiztm94@gmail.com.br

Barium, an alkaline earth metal present in the environment, is capable of accumulating in plants, increasing the risks of toxicity through bioaccumulation processes. Its sources include anthropogenic activities, especially in the oil and gas industry, both in terrestrial and marine locations[1]. However, the accurate measurement of barium concentrations in surface waters is complex, as total determination doesn't necessarily reflect the fraction available for biological interactions [1]. To address this challenge, the technique of Diffusive Gradients in Thin Films (DGT) has been established for quantifying labile metals in aquatic environments [2,3]. In this context, the commercially available Dowex® 50WX8 cation exchange resin emerges as a promising option due to its significant ion exchange capacity, making it a viable candidate for detecting alkaline earth metals, such as barium [4]. This research aims to evaluate the applicability of this resin immobilised in agarose as a binding layer in the DGT technique, seeking to establish an effective approach for the direct and in-situ determination of labile barium in aquatic systems.

Disks were prepared by combining 1.5% (w/v) agarose and 37.5% resin (7.5 g of resin in 20 mL of agarose) under heating. The still-hot mixture was poured between two glass plates separated by a plastic spacer (approximately 0.05 mm thick). After solidification, the gel was cut into 2.5 cm diameter disks and stored in ultrapure water at 4 °C. Following gel manufacturing, an elution test was conducted by immersing the resin in agitation for 24 hours in a solution of known barium concentration, followed by elution in 2 mL of 1 mol L-1 HNO3 for 24 hours, with agitation. The eluate was analyzed by ICP-MS to determine the retention potential (%R). For the assembly of DGT devices, the Dowex 50WX8 binding layer immobilized in agarose was added, followed by a diffusive agarose layer and a cellulose nitrate filter membrane. The layers were secured by the polypropylene device cap. Subsequently, duplicate immersions were carried out in the laboratory over a period of 4 to 72 hours, evaluating the relationship between the mass of barium retained by Dowex 50WX8 and the immersion time. This relationship provided information for compliance analysis with Fick's first law and for determining the barium diffusion coefficient. The resin exhibited a retention rate (%R) of 75% for Ba. In the immersion test, it was observed that the analyte demonstrated a linearity of $R^2 = 0.97$ in its retention over time, confirming that the developed binding gel adheres to the fundamental premise of the DGT technique: Fick's diffusion law. Calculations were performed, and for the first time, the diffusion coefficient of Ba in agarose gels (the diffusion medium) was obtained as 1.32×10^{-6}.

Thus, it is possible to conclude that the applicability of the Dowex-50WX8 resin immobilized in agarose as a binding layer in the DGT technique for the direct in-situ determination of labile Ba in aquatic systems has proven effective, exhibiting a linearity of $R^2 = 0.97$.

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[CNPq, Fapesp]

010 - STABILITY THIOMERSAL IN SIMULATED VACCINE SAMPLES: A SPECIATION STUDY MADE USING COLD VAPOUR TECHNIQUES

Dayane F. Rezende-Marques[a], Jarol R. Miranda-Andrades*[b], Ricardo Q. Aucelio[b]

[a]Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Metrology, Quality and Inovation Program, Rio de Janeiro, Rio de Janeiro 22451-900, Brazil.
[b]Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Department of Chemistry, Rio de Janeiro, Rio de Janeiro 22451-900, Brazil.
*e-mail: jmirandaa83@live.com

Thiomersal ($C_9H_9HgNaO_2S$) has been used as a preservative in cosmetics and pharmaceuticals since the 1930´s, preventing contamination and ensuring long-term product stability. It has been demonstrated that thiomersal degrades forming ethylmercury (CH_3CH_2Hg) and thiosalicylic acid[1]. In recent years there has been controversy over the use of thiomersal in vaccines and pharmaceuticals, as it is considered a direct means of mercury contamination to humans and to the environment. In this work, a preliminary study on the stability of thiomersal in samples of simulated vaccines (without antigens) of hepatitis B (recombinant) and diphtheria and tetanus. The study focused on variables imposed during handling of vaccines in multidose vials in emergency care centers such as radiation exposure and variation of temperature. The stability of the simulated thiomersal solutions were monitored by measuring ultra-trace level concentrations of CH_3CH_2Hg and Hg^{2+} using gas chromatography cold vapor atomic fluorescence spectrometry (GC-CV-AFS) and by cold vapor atomic absorption spectrometry (CV−AAS). Literature reports that thiomersal concentrations in vaccines are in the ranges between 50 and 100 mg L^{-1} but for safety reasons, thiomersal solutions at 15 mg L^{-1} were used for the studies. Volumes of 10 mL of sample solutions were placed in sealed glass vials (15 mL) where appropriate quantities of specific excipients, found in real vaccines, were added. The flasks were placed in a photochemical reactor with six standard commercial fluorescent lamps (6 W each) as source of either visible or UV radiation. Periodically (every 10 min) an aliquot was collected, diluted and monitored by GC-CV-AFS (after chemical derivatization) and by CV-AAS (after chemical reduction). It was found that exposure to visible radiation, in intervals from 10 to 120 min did not increase significantly the measured concentrations of residual mercury species (CH_3CH_2Hg and Hg^{2+}) even when excipients (NaCl, KH_2PO_4, $Al(OH)_3$; $Al_2(SO_4)_3$ and formaldehyde) were mixed in solutions. In contrast, when vials were exposed to UV, an increase in the concentration of CH_3CH_2Hg (from 0.74 ± 0.28 µg L^{-1} to 4.6 ± 1.8 µg L^{-1}) was observed when thiomersal was mixed with NaCl, confirming reports from literature[2] and showing that glass does not completely shield thiomersal from UV to the point that the minor fraction transmitted through glass may be sufficient to trigger the release of CH_3CH_2Hg.

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[FAPERJ, CNPq, CAPES]

Chemical Vapor Generation

011 - DETERMINATION OF Hg, Mn AND Pb IN IMITATION JEWELRY USING PHOTOCHEMICAL VAPOR GENERATION COUPLED TO ICP-OES

Fernanda P. Braga[a], Jefferson S. Gois[a]

[a]UERJ, Instituto de Química / Departamento de Química Analítica, Rio de Janeiro, RJ, Brazil, 20550-013
*e-mail: fernandabraga.ufrrj@gmail.com

Accessing the concentration of contaminants in imitation jewelry is an important task, however it is challenging due to the complexity of the sample matrix (composed mainly of metals in high concentration). In Brazil there is no limit for Mn and Hg in imitation jewelry, but for Pb, the Inmetro established a limit of 0.03% m/m [4]. Photochemical vapor generation (PVG) coupled to inductively coupled plasma optical emission spectrometry (ICP-OES) can be purposed the determine in the concentration of these elements in samples of imitation jewelry. Therefore, this work aims to apply a lab-made PVG system for coupling to ICP-OES for the determination of Hg, Mn, and Pb in imitation jewelry after the solubilization in HCl. The imitation jewelry samples were solubilized in HCl 37% w/w (VETEC, Brazil) in a water bath at 90ºC until the complete dissolution of the samples. The PVG system was built with two UV-C germicidal lamps 15 W, 254 nm, a quartz capillary 250 cm length, 2.5 mm internal diameter, 4 mm external diameter, and 11 mL internal volume, and a gas-liquid glass separator (GLS). The levels of the factors acetic acid concentration and UV exposure time were optimized using the central composite design (CCD) for the PVG system, and the carrier gas and the radiofrequency (RF) power for the ICP-OES. The optimal conditions were obtained at 30% v/v of acetic acid, 100 s of radiation exposure time, 0.02 L min^{-1} of carrier gas flow, and 1300 W for RF power. The influence of the inorganic matrix of the sample was studied, where it was found that the presence of the main constituents in the imitation jewelry can cause the suppression of the analytical signal for the analytes, probably due to the suppression of the formation of volatile species. To circumvent this effect, chemical modifiers have been studied. The accuracy of the proposed method was evaluated by recovery tests, which ranged from 88 to 102%. Detection limits ranged from 1 to 3 mg g^{-1}. It was found in the jewelry studied a concentration of Pb between approximately fifty and eighty times higher than that allowed by Inmetro.

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[CNPq, FAPERJ, UERJ]

012 - SONOCHEMICAL VAPOR GENERATION FOR AAS DETERMINATION OF Hg: A GLIMPSE OF A POWERFUL TOOL

Karen Giacobe [a], Thaise J. Basso[a], Érico M. M. Flores[a], Ralph E. Sturgeon[b], Cezar A. Bizzi[a*]

[a] Federal University of Santa Maria, Chemistry Department, Santa Maria, Brazil, 97105-900
[b] National Research Council Canada, Ottawa, Ontario, Canada, K1A0R9
*e-mail: cezar.bizzi@ufsm.br

Mercury (Hg) determination is of paramount importance since it is a heavy metal with serious environmental issues, as well as a public health problem due to its toxicity. Hg and its compounds are generated in several industrial processes and their determination is often performed by CVG (chemical vapor generation) coupled to a spectrometric detection technique. Such approaches require use of reducing agents (usually sodium borohydride) in the presence of an inorganic acid (HCl). One can mention that these reagents are considered toxic, with associated environmental impact, are expensive, unstable and potentially give rise to high analytical blanks arising from the reducing agent.[1,2] An alternative approach based on an ultrasound system (US) was therefore evaluated for the generation of Hg^{o} from Hg(II) (sonochemical vapor generation, SVG), allowing use of diluted green reagents. A sonoreactor was directly coupled to a US probe (20 kHz) in which Hg(II) is reduced to Hg^0 and transported to a quartz cell placed in the optical beam of a F AAS instrument.[3] The parameters evaluated for the determination of Hg were: reducing agent type (organic acid: formic, acetic and propanoic acid; alcohol: ethanol, methanol and isopropyl alcohol) and concentration (0.1; 0.2; 0.5 and 1.0 mol L^{-1}), carrier gas (N_2 or Ar), gas flow rate (0.5; 1.0 and 1.5 L min $^{-1}$), sonication time (0.5, 1, 2, 2.5, 5, 7.5, and 10 min), acoustic amplitude (20, 30, 40 and 50%) and their respective delivered power density (686, 714, 1120 and 1316 W L^{-1}, respectively), and the linear range (0,1 µg L^{-1} to 1000 µg L^{-1}). Optimal SVG conditions were: 0.5 mol L^{-1} formic acid, 0.5 mL min^{-1} carrier gas (N_2), 5 min of sonication (50% acoustic amplitude, 1316 W L^{-1}), the quartz cell operating at room temperature (flame off), which presented a linear range from 0.5 µg L^{-1} to 800 µg L^{-1}.The evaluation of the efficiency of the volatile species in the systems was expressed through the calculation of characteristic mass (m_0), the proposed SVG system was compared with CVG, assembled using the same apparatus used for SVG (as well as gas flow rate, quartz cell and mass of Hg standard), using 0.05% $NaBH_4$ (in 0.1% NaOH) as reducing agent and 1 mol L^{-1} HCl. The m_0 obtained with SVG was 0.26 ± 0.02 ng, which was seven times better than that achieved by CVG ($m_0 = 1.82 \pm 0.17$ ng), showing the high generation efficiency of the proposed approach. The proposed SVG-AAS method proved to be efficient for determination of Hg at relatively low concentration, using dilute reagent, relatively short reaction time and a simple operational system (easy to assemble). Additional studies must be completed to evaluate the reduction of other Hg species, and the influence of organic matter (real samples) on the generation of Hg^{o}.

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[CAPES, CNPq, FAPERGS, and UFSM]

013 - STUDY OF DIFFERENT STRATEGIES FOR DIRECT LEAD DETERMINATION IN HONEY SAMPLES BY HG – MIP OES

Alicia Mollo[a*], Silvina Niell[b], Alexandra Sixto[a]

[a] Universidad de la República, Facultad de Química, GATPREM Grupo de Análisis de Elementos Traza y Desarrollo de Estrategias Simples para Preparación de Muestras, Montevideo, Uruguay,11800
[b] Universidad de la República, CENUR Litoral Norte, Sede Paysandú, Uruguay, 60000
*e-mail: amollo@fq.edu.uy

Honey is a complex matrix constituted mainly by glucose and fructose which mineral content is about 0.1 – 0.2 %. The presence of toxic elements may be an indicator of the environmental pollution of soils, water or air and/or the contact with stainless steel tools, containers or equipment used along its production process. In the region, the maximum allowed level (MAL) for lead in honey is 0.3 mg kg^{-1}.[1]

Hydride generation (HG) is a sample introduction technique which inherently preconcentrates the analyte and decreases its interaction with the matrix; its hyphenation with microwave induced plasma optical emission spectrometry (MIP OES) is an alternative to HG - ICP OES attaining low limits of detection and quantification. The aim of this work is to determine lead in honey by plumbane generation and MIP OES detection, in samples without previous wet digestion.

For that purpose, honey was dissolved in water (100 g kg^{-1}). The high carbohydrates content (80 % approx.) relates to changes in viscosity of the solutions prepared, thus matrix matched calibration with lead free honey samples was used. Foams in the spray chamber along with the nitrogen flow induced a carryover of the sample towards the torch creating variations in the plasma which were partially corrected by injecting high flow air to the torch. Notwithstanding, samples with low lead content were still overestimated. Arsenic (III) was used as internal standard to attempt accuracy. Plumbane was generated in 10 g of the diluted sample with 0.75 mol kg^{-1} HCl and 1.5 % w/w $K_3Fe(CN)_6$ in a multimode spray chamber (MSIS, Agilent) using 2 % w/w $NaBH_4$ as reductant in 0.5 % w/w NaOH. The solutions and nitrogen flow-rate was 0.90 mL min^{-1} and 0.75 L min^{-1} respectively; prior to the reading time (5 s), the chamber was stabilized for 30 s. Analytical determinations were performed on an Agilent 4210 MIP OES spectrometer equipped with a standard torch (viewing position: 0) at (193.695 - 234.968) nm for As and (217.000 - 405.781) nm for Pb. The analytical sensitivity at 405.781 nm is five times higher than at 217.000 nm but at low lead levels better results were found at the latter in terms of precision and trueness.

A linear response was found along the range of concentrations studied (from LOQ (10s) 5.7 µg L^{-1} up to 50 µg L^{-1}, $I_{Pb/As} = 26.825\ C_{Pb/As} - 9.6$), and LOD (3s): 1.7 µg L^{-1} in the test solutions. Trueness was assessed by recovery assay at Pb concentration close to the LOQ and MAL in wet digested honey samples. Pb concentration was determined by graphite furnace atomic absorption spectrometry (GF AAS). In both cases recoveries were between 85 – 125 %. The absence of arsenic in all the analysed samples was confirmed by GF AAS.

The HG - MIP OES methodology proposed reaches limits of detection and quantification in honey samples (0.018 and 0.057 mg kg^{-1} respectively) similar to the ones previously reported in the literature [2] avoiding the sample acidic digestion; it could be successfully applied for the determination of Pb in honey samples complying with current regulations.

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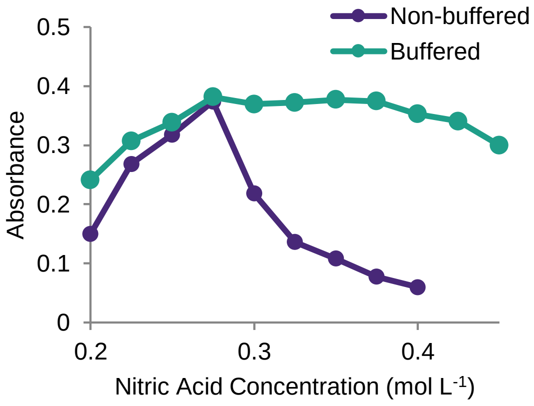
014 - IMPROVEMENT OF THE ROBUSTNESS ON A FI-HGAAS METHOD FOR THE DETERMINATION OF LEAD IN WATER SAMPLES

Jonatan Schlotthauer[a*], Leyla Mántaras[a], Lucila Brusa[a], Mirna Sigrist[a]

[a] National University of Littoral, Faculty of Chemical Engineering, Program of Research and Analysis of Chemical Residues and Contaminants (PRINARC), Santa Fe, Argentina, 3000
*e-mail: jonatanschlo@gmail.com

It is well known that plumbane (PbH_4) by hydride generation (HG) is not straightforward, which may lead to methods that are not robust enough for routine analysis. The optimum pH range for PbH_4 formation is very narrow, so strict control of the acidity of the reaction medium is required[1]. Moreover, the presence of additives, like ferricyanide, is necessary to obtain an efficient generation of PbH_4[2]. Finally, some elements, like Cu, can interfere in the HG reaction suppressing the Pb signal. Thus, the purpose of this work was to achieve a method for the determination of Pb in water samples by flow injection hydride generation atomic absorption spectrometry (FI-HGAAS) with special emphasis on robustness.

All hydride generation parameters were studied and optimized. It is not only necessary to strictly control the acid concentration in the sample, but also the NaOH concentration in the $NaBH_4$ solution. If necessary precautions are not taken, even the acid present for sample preservation could interfere with the determination, giving erroneously low results. The use of borate as a buffer significantly improved the robustness of the method towards acidity, compared to the typical non-buffered HG.



Effect of the bufferization of the $NaBH_4$ solution on the robustness towards acidity Moreover, the addition of ferricyanide to the basic tetrahydroborate solution instead of the acidic samples prevented the precipitation of Prussian blue during analysis. Furthermore, the interference Cu concentrations up to 2000 mg L^{-1} was overcome using thiocyanate as a masking agent. Other elements do not interfere at levels typically found in water samples. The limit of quantification was 0.9 µg L^{-1}, which is compatible with the current guideline value for Pb drinking water (10 µg L^{-1}).

The proposed method uses simple and relatively low-cost equipment available at most atomic spectrometry laboratories and shows a significantly increased robustness of the HG reaction. The validated method was applied to the analysis of 50 water samples. The concentrations found ranged from <LOD (0.3 µgL^{-1}) and up to 88.8 µg L^{-1}.

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015 - DIRECT HYDRIDE-GENERATION IN A CYCLONIC SPRAY CHAMBER FOR SELENIUM DETERMINATION IN PLANTS BY ICP OES

João Jou de Albuquerque Fujiwara*, **João Manoel de Lima Júnior,**
Aline Pereira de Oliveira, Pedro Vitoriano Oliveira

University of São Paulo, Institute of Chemistry, São Paulo, SP, Brazil, 05508-900
*e-mail: joao.jou@usp.br

Selenium is an essential micronutrient for humans and animals.[1] One of the main sources of this element is plant-based food, which occur at very low concentration. Consequently, highly sensitive methods to monitor Se in plants is necessary. Hydride-generation (HG) is a sample introduction technique based on the formation of volatile species of hydride-forming elements, through reaction with reductant, which has as one of its main characteristics the high sensibility of methods. HG can be used as sample introduction device in many techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS), but usually requires specific apparatus for the reagent-sample mixture and gas-liquid phase separation. However, HG can be made with conventional ICP OES using hydra-mist cyclonic spray chamber[2] and adapted flow blurring multiple nebulizer[3]. In this work, the analytical performance of direct HG in a non-modified cyclonic spray chamber as a gas-liquid separator was evaluated for Se determination in peach leaves using inductively coupled plasma optical emission spectrometry (DHG-ICP OES). The reference and sample solution and sodium borohydride reductant (1 % m v^{-1} of $NaBH_4$) flowed with the ICP OES peristaltic pump (60 rpm), mixed at a "Y" confluence, the reaction occurred in an 20 cm long coil, then nebulized in a concentric nebulizer to the cyclonic spray chamber. The aerosol solution and selenium hydride were carried out to the plasma with an argon flow-rate at 0.4 L min^{-1}. The selected wavelength of Se was 196.028 nm. To assess the sensibility improvement, analytical curves were obtained using (1.0 to 25.0 µg L^{-1}) and not using (500 to 5000 µg L^{-1}) the proposed system; then slopes ratio of curves were compared. The slope of the calibration curve for the HG was more than 200 times greater than the conventional nebulization. A much lower limit of detection was achieved using the DHG-ICP OES method (LOD = 0.14 µg L^{-1}) in comparison to the conventional sample introduction (LOD = 48 µg L^{-1}). Standard reference material of peach leaves (SRM 1547) was digested in microwave oven using diluted oxidant mixture (2 mL HNO_3 + 1 mL H_2O_2 + 3 mL H_2O). Afterward, Se(VI) was reduced to Se(IV) using 6 mol L^{-1} of HCl, heating at 90 ºC for 30 minutes. This pre-reduction step was optimized and it was necessary to guarantee precise determination of Se in sample. The final solution was analyzed by the proposed method. The obtained results showed good accuracy with 95% confidence level (t-student) with precision of 5% RSD (n = 3). This work proposes a simple and effective way to reach low detection limits using direct HG, making possible the determination of Se in plant material by ICP OES.

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3.D. Pereira et al., Microchimical Journal 112 (2014) 82-86.

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

016 - PHOTOCHEMICAL VAPOR GENERATION SAMPLE INTRODUCTION FOR DETERMINATION OF SELENIUM BY FAAS IN GREEN BEANS

Ana Clara Correia Aragão[a], Jane Kelly Sousa de Brito[a], Renato Sampaio Andrade Neto[a], Wladiana Oliveira Matos[a], Gisele Simone Lopes [a*]

[a] Federal University of Ceara, Department of Analytical and Physical-Chemistry/ Laboratory of Studies in Applied Chemistry (LEQA), Fortaleza, Ceará, Brazil, 60440-900
*e-mail: gslopes@ufc.br

Selenium can be found in foods usually in its organic form (selenomethionine and selenocysteine), such as nuts, rice and beans[1]. Beans are one of the most consumed foods in Brazil, especially in the northeast region, and can be consumed in the form of dry or immature beans (green beans). Beans are an excellent nutritional source for living beings for containing proteins, vitamins and minerals, important to supply the nutritional values of the population. In the literature, there are few works on the determination of selenium in beans, mainly with regards to green beans. The analysis of trace elements can be a challenge, considering the need to use techniques with high sensibility and low detection limits. The flame atomic absorption spectrometry (FAAS) technique can only be used with an efficient sample introduction system. Chemical Vapor Generation (CVG) has as advantages: 100% sample introduction efficiency; separation of the analyte from the sample matrix, reducing the matrix effect. However, it has disadvantages as the use of expensive and unstable reagents and high waste generation. Photochemical Vapor Generation (PVG) has the same advantages as CVG, and even more, low molecular weight organic acids (formic, acetic acids) used are degraded by UV radiation generating less waste[2]. The aim of this work was to determine the concentration of selenium in green beans using photochemical vapor generation coupled to flame atomic absorption spectrometry. CVG (hydride generation) in continuous flow injection was used to compare the results obtained using the PVG coupled to FAAS in order to verify the efficiency of the two samples introduction systems in the analysis of selenium in green beans. Green bean samples were freeze dried, macerated in a mortar and kept in a desiccator prior analysis. Three procedures for solubilization of the sample were tested: ashing in an oven, microwave-assisted digestion and solubilization with formic acid. The digestion was made using nitric and hydrochloric acids and it needed to evaporate as the nitrate and nitrite are interferents in the PVG procedure. Total Se concentration found using the CVG and $NaBH_4$ 0.2% (NaOH 0.05%) coupled to FAAS was 2.84 ± 0.24 mg kg^{-1}. Rapid volatile Se species are formed using a 19 W flow-through photochemical reactor exposing the sample to intense 185 and 254 nm radiation. Studies were carried out to find the higher absorbance signals for Se changing the concentration of formic acid, carrier gas flow (N_2) and time of exposure to UV radiation. The best results so far have been obtained using 2% v v^{-1} of formic acid, 1 min of UV radiation exposition and carrier gas flow of 25 mL min^{-1}. The results for Se in PVG coupled to FAAS and solubilization of samples with formic acid presented good agreement (95% confidence, t-test) with the CVG coupled to FAAS method. However, more 10 samples collected in market from different regions in Ceara state are under study for Se analysis and data comparison.

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[**CAPES – Proex 23038.000509/2020-82, CNPq, INCTAA**]

Chemometrics in Spectrometry

017 - EMPLOYING ENSEMBLE MACHINE LEARNING ALGORITHMS TO IDENTIFY GUNSHOT RESIDUES (GSR) USING LA-ICP-MS DATA

Isabela M. de S. Ferreira[a], Igor C. A. Lima[b], Bernardo Ferreira Braz[a], Ladário da Silva[c], Ricardo Erthal Santelli[a], Aderval S. Luna[b*].

[a] Universidade Federal do Rio de Janeiro, Departamento de Química Analítica, Rio de Janeiro/RJ, Brazil, 21941-909.
[b] Universidade do Estado do Rio de Janeiro, Instituto de Química, PPG-EQ, Rio de Janeiro/RJ, Brazil, 20550-013.
[c] Universidade Federal Fluminense, Instituto de Ciências Exatas, Volta Redonda/RJ, Brazil, 27213-145.
*e-mail: adsluna@gmail.com

Gunshot residues are significant criminal evidence, and the study of its characteristics can be used to estimate the shot's distance, identify bullet entrance/exit holes, discriminate the type of gun/caliber used, and determine the involvement of people in firearm shooting events, which may constitute judicial evidence of great importance. These particles, which are called GSR (gunshot residue), consist mainly of products from the detonation of the primer, and its analysis determines the presence of these residues on the suspect's skin and clothing and on surfaces close to the weapon used, where the particulate may have deposited. Due to the need for simple ways of classifying GSR and distinguishing between real GSR and GSR-like samples, there is considerable interest in developing elemental quantification in shooting residues, using chemometric methods for their best discrimination, promoting a modern approach with scientific robustness. Samples of fifty-three shooters were collected, being eighteen of the 0.38 caliber SPL Taurus revolver with CBC brand Full Metal Jackpot bullet (FMJ) and Solid Lead bullet (LRN) ammunition type; eighteen of the 0.380 caliber Taurus pistol using CBC brand Jacketed Hollow Point bullet (JHP) and Solid Lead bullet (LRN) ammunition type, and seventeen of the 0.40 Taurus pistol with Full Metal Jacketed bullet (FMJ) ammunition type. Samples of eighteen non-shooters, seven brake pad mechanic's workers, six people after using fireworks, and five volunteers who never used a firearm (blank) were collected using the same procedure. Measurements were performed by an ICP-MS (iCAP Qc, Thermo Fisher Scientific, Bremen, Germany) combined with an LA system (NWR 213, ESI, California, USA) equipped with a pulsed Nd:YAG laser operated in the Q-switch mode with a wavelength of 213 nm. Optimization of the analytical parameters was performed using NIST SRM 612 CRM and further with a homemade "standard" solid material with a concentration of 500 µg kg^{-1} of Pb, Ba, and Sb on a stub. The central area of the spot was chosen, at a size of 4 mm^{2}, with the ablation of 100 lines of length of 2000 µm, separated by a spacing of 20 µm, equivalent to the spot size used. The monitored nuclides were ^{208}Pb, ^{137}Ba, ^{121}Sb, ^{27}Al, ^{29}Si, ^{31}P, ^{32}S, ^{35}Cl, ^{39}K, ^{44}Ca, ^{57}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{118}Sn, ^{202}Hg, and ^{13}C as internal standard. The results obtained correspond to the elemental distribution in the analyzed area of the sample. Normalized intensities were integrated to determine the total analyte signal. With the results, a strategy for identifying GSR based on the elemental analysis by LA-ICP-MS and its differentiation of residues with similar composition to the GSR was established, presenting models of binary classification (shooters x non-shooters) and multi-class classification (different calibers), employing SMOTE (Synthetic Minority Oversampling Technique) for synthetic generation of new samples and the application of Random Forest (RF) and Extreme Gradient Boosting (XGB) algorithms. The data were normalized using min-max transformation. The binary classification (shooters x non-shooters), the RF, and XGT algorithms could differentiate with 100% accuracy. In addition, for the multi-class classification (different calibers), the same algorithms could differentiate the 0.38 and 0.380 with the same accuracy, improving current methodologies and promoting a more reliable and objective presentation of scientific results for criminal proceedings.

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[CNPq, FAPERJ, CAPES]

018 - ASSESSMENT OF MINOR AND TRACE ELEMENTS IN *Psidium cattleianum* Sabine BY ICP-MS AND CHEMOMETRIC APPROACH

Bruno L. Ferreira[a*], **Eduardo S. Chaves**[a]

[a] Federal University of Santa Catarina, Chemistry Department, Florianópolis, SC, Brazil, 88040-970.
*e-mail: f.bruno@gmail.com

Brazil is one of the most fruit producers in the world. However, many fruits are unexplored or even unknown by the general population[1,2]. Araçá (*Psidium cattleianum* Sabine) is a Brazilian native fruit rich in phenolic compounds and elements such as Ca, Mg, P, K, and Na, considered essential in the human organism in metabolic and physiological processes[3]. Nevertheless, depending on the specie and concentration, some elements can be potentially toxic to human health. Besides, the assessment of the chemical composition of a product, combined with modern techniques of unsupervised machine learning such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis, can lead to geographical differentiation through pattern recognition[4]. In this regard, this project aimed to evaluate the content of minor and trace elements in 7 samples of Araçá fruit and verify the influence of these concentrations in the PCA/HCA unsupervised methodology for geographical and chronological differentiation. The samples of Araçá (L2, L3, FR, FC, and CA from Santa Catarina state, PG from Paraná state, and TC from Rio Grande do Sul state) harvested in 2022 and 2023 by familiar producers were acquired in 2023. Samples were homogenized and digested in an open flask for 4h/130 °C + 2h/150 °C, using 4 mL of HNO_3 and 2 mL of H_2O_2. Prior to analysis, the digested sample solutions were adequately diluted, and 5 µg L^{-1} of Rh was added as an internal standard. ICP-MS (Elan 6000 PE) operating at 1200 RF power was used to determine Co, Ni, Cu, Zn, Cd, Sb, Pb, Ba, Fe, Al, Mo and Mn. The obtained LODs were in the µg g^{-1} range, the precision, evaluated by RSD, was in the mean of 10% and the concentrations in the analyses samples ranged from 0.01 ug g^{-1} (Cd) to 24.35 ug g^{-1} (Mn). Considering the normalized values, the PCA was performed, and the Euclidean distance index achieved HCA. Table 1 indicates the main results of PCA (a) and HCA (b) analysis. It is possible to observe the differences, mainly, in the samples from PG and TC, from different states. L2 and L3 samples were from the same region but 2022 and 2023 harvests. HCA clearly indicates the differences in sample regions. In conclusion, chemical composition evaluated through PCA and HCA tools is a robust approach for differentiating samples' origin.

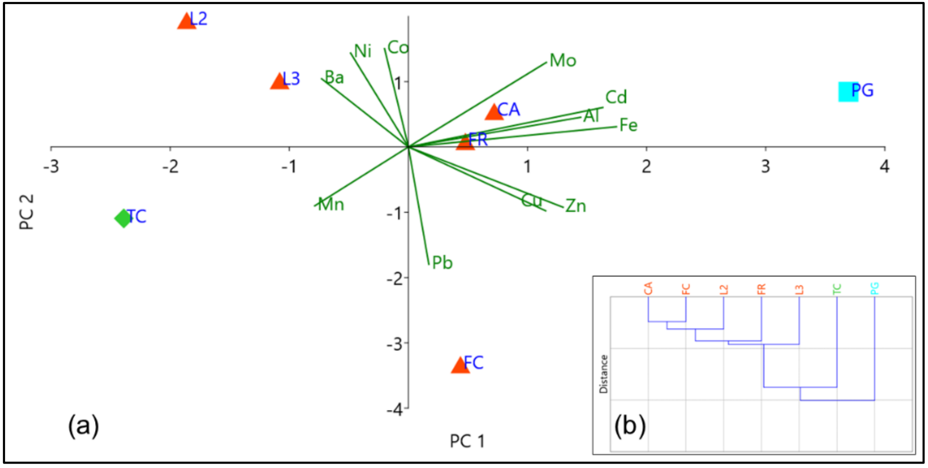

Figure 1. PCA and HCA analysis from Araçá samples of different southern Brazilian states

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[Supported by CNPq]

019 - SELF-ORGANIZING MAP AND POLLUTION INDICES FOR SPACE-TIME PATTERNS IDENTIFICATION IN A COASTAL ECOSYSTEM MONITORING PROGRAM

Luana Santos Moreira[a*], Floriatan Santos Costa[b], Lázaro Brandão Zardini[a], Lívia Davel Gomes[a], Helena Bezerra Ferrari[a], Geisamanda Pedrini Brandão[a], Renato Rodrigues Neto[c], Maria Tereza Weitzel Dias Carneiro[a]

[a] Federal University of Espírito Santo, Department of Chemistry, Vitória, ES, Brazil, 29075-910
[b] Federal University of Paraná, Department of Chemistry, Curitiba, PR, Brazil, 81531-980
[c] Federal University of Espírito Santo, Department of Oceanography and Ecology, Vitória, ES, Brazil, 29075-910
*e-mail: lnsantosmoreira@gmail.com

The breach of the Fundão dam in Mariana, MG, in 2015, caused a significant spillage of tailings into the Doce River Basin. The mud spread along the river, reaching its mouth in the northern part of the state of Espírito Santo, impacting beaches and environmentally valuable areas. After the disaster, studies have monitored the environmental impacts and considered human activities on the coast. Environmental studies involve the analysis of high datasets and variables and require forms of processing that make it possible to identify patterns. SOM is a powerful tool for exploratory data analysis, mainly in identifying patterns. In this study, twelve sampling stations were monitored along the northern coast of the state of Espírito Santo, Brazil. Superficial sediment samples were collected at the sites in ten sampling campaigns in the year 2022. The US EPA 3051A standard method was used to sediment sample decomposition before the determination of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se, V, and Zn by ICP OES and ICP-MS. SOM was used to enhance the result assessment. Based on the unified distance matrix, the data was divided into nine groups, corresponding to the sampling stations. The grouped beaches included Barra do Riacho and Putiri, Sahy and Padres, and Sauê and Santa Cruz, while the others showed individual groupings. Component planes revealed that Pontal do Piraquê-Açu, Formosa, and Grande beaches exhibited higher concentrations for most elements, except Cd. Praia Grande stood out due to its higher concentration of toxic elements like As, Cr, and Pb. Gramuté Beach demonstrated high concentrations of Cd and Hg, whereas Barra do Riacho had the lowest concentrations of all analyzed elements. The assessment of beach contamination by chemical elements utilized indicators such as the Sediment Quality Guidelines quotient (SQG-q), Threshold Effect Level (TEL), and Probable Effect Level (PEL). Beach contamination was analyzed during the rainy periods (with campaigns in January, February, March, October, and December) and the dry periods (with campaigns in April, May, June, July, and September). Among the monitored elements (As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, and Zn), only As and Ni exceeded TEL and PEL. The remaining elements stayed below TEL, except Ni in January. Arsenic exceeded PEL in all campaigns and collections, indicating widespread contamination. The average SQG-q values (0.106 in the dry season and 0.130 in the rainy season) exceeded limits, suggesting moderate contamination in the sampling locations. Only Barra do Riacho and Gramuté out of twelve beaches had SQG-q < 0.1 (non-contaminated). The Quinze and Sauê beaches had SQG-q > 0.1 in all campaigns, while Praia Grande had the highest average value (0.185). Higher concentrations were found in Al, Fe, and Mn, but toxic elements like As, Hg, Pb, and V also exhibited high concentrations. There is a strong indication of high contamination by chemical elements in the studied region. SOM was sensitive in evaluating differences in elemental concentrations, providing insights into seasonal accumulation. While SOM can complement analysis in monitoring studies, additional reference indices are advisable for a more accurate evaluation.

[UFES, FAPES, FACTO, CAPES, CNPq]

Computational Spectroscopy and Imaging Techniques

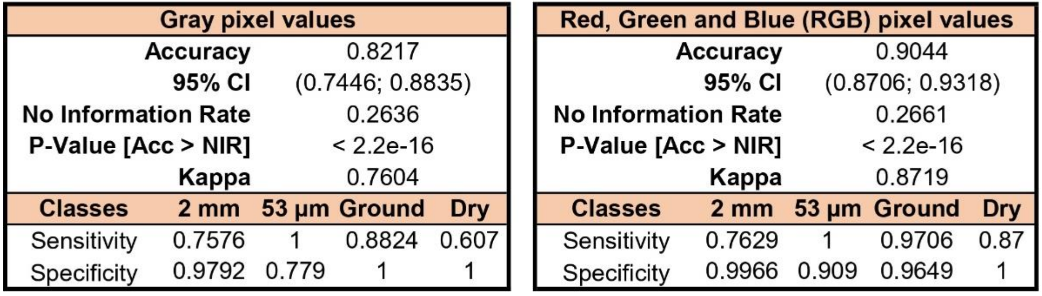
020 - ENHANCING SOIL TRACE EVIDENCE ANALYSIS: IMAGE-BASED CHARACTERIZATION FOR EFFICIENT CRIMINAL INVESTIGATIONS

Luciana R. Mendes, Caio Carraro, Rafael Romano, Márcia A.M.S. Veiga*

Departamento de Química, FFCLRP, Universidade de São Paulo, 14040-901, Ribeirão Preto, SP, Brazil
*e-mail: marcia.veiga@usp.br

Soil trace evidence is a diminished quantity of solid material deriving from contact between soil and an object during criminal activity and later recovered during an investigation. The formation process of soil evidence is random, which means that parameters such as sample representativeness and homogeneity cannot be inferred from the sample to the origin site, meaning there is no direct way to compare the likeness of two or more samples to their probable source. The second obstacle in this comparison type is the need for more resources that most Brazilian Scientific Police Bureaux face. The proposed method could aid in quick decision-making to allocate resources more efficiently and amplify the use of soil analysis in police investigations. Soil chemistry is a set of parameters that aid in individualizing a sample to compare them. Derivative of chemistry, color is a physical attribute of soil that could be measured to indirectly infer soil chemistry and allow the comparison of soil trace evidence samples. This work's methodology includes designing and constructing a black box with constant and controlled lightning, with space for the samples to be evenly distributed in a paper sampler. Twenty-two samples from different locations and soil types were collected were dried and processed by quartering with ¼ being sieved at 2 mm, ¼ being sieved at 53 µm, ¼ being ground finely, and ¼ without any further processing. Three different cameras in different mobile devices were employed to obtain images by utilizing the native Professional Camera available to each system. The images were then processed with GIMP 2.0 software, using a plugin of Batch Image Manipulation, first to select a region of interest (ROI) and then extract an array of four dimensions, each containing the red, green, blue, and gray band values for each pixel in the ROI. Those arrays were transformed into separate vectors for each dimension using Python. The vectors for the 22 samples for each dimension were concatenated into a large matrix for subsequent Soft Independent Modelling of Class Analogies (SIMCA) analysis, which was set up in a way to model four different groups according to the laboratory treatment of the sample and according to color or grayscale pixel values.

Table 1. Metrics derived from the misclassification confusion matrix derived from the SIMCA analysis.



Gray pixel values				
Accuracy	0.8217			
95% CI	(0.7446; 0.8835)			
No Information Rate	0.2636			
P-Value [Acc > NIR]	< 2.2e-16			
Kappa	0.7604			
Classes	**2 mm**	**53 µm**	**Ground**	**Dry**
Sensitivity	0.7576	1	0.8824	0.607
Specificity	0.9792	0.779	1	1

Red, Green and Blue (RGB) pixel values				
Accuracy	0.9044			
95% CI	(0.8706; 0.9318)			
No Information Rate	0.2661			
P-Value [Acc > NIR]	< 2.2e-16			
Kappa	0.8719			
Classes	**2 mm**	**53 µm**	**Ground**	**Dry**
Sensitivity	0.7629	1	0.9706	0.87
Specificity	0.9966	0.909	0.9649	1

Source 1: The authors.

The mineral-rich fraction of the sample allows for a better individualization of the sample by removing all components that might interfere with its discriminatory power. In contrast, the grinding pre-treatment allows more accurate sourcing of the probable sample origin site. The method is suitable to screen soil-type evidence recovered in crime scenes for a more efficient decision-making process while following up on leads during the investigation, as the image-acquiring devices are inexpensive and the operation overall does not require advanced training to execute.

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021 - EVALUATION OF NEBULIZATION EFFECTS IN A LOW-COST FLAME ATOMIC EMISSION SPECTROMETER

Francisco Cunha da Rosa[a*], Matheus Felipe Pedrotti[a], Lucas Gabriel Oliveira de Aguiar[a], Luís Henrique Federhen[a]

[a]Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul (IFRS), Campus Feliz, Feliz, RS, Brazil, 95770-000
*e-mail: francisco.rosa@feliz.ifrs.edu.br

Most instruments used for atomic spectrometry, whether absorption (AAS) or emission (AES), require sample introduction through a liquid medium. Since these liquids consume some of the energy for analyte desolvation when they access the energy source for atomization and excitation (flame or plasma), it is important for this process to occur quickly and with less energy consumption (more efficiently).[1] To achieve greater efficiency, spectrometers now include sample nebulization systems, with pneumatic nebulization being more accessible. In this context, this work aimed to evaluate the physicochemical effects associated with a 3D-printed nebulizer, which is part of a research project aimed at constructing and evaluating a low-cost Flame Atomic Emission Spectrometer (F AES) for the determination of metals in various samples. This spectrometer was built with the aim of enabling practical teaching of atomic spectrometry in chemistry courses that lack instruments for this purpose. In this study, the differences between direct sample aspiration by pressure differential provided with a Venturi effect and sample aspiration assisted by a peristaltic pump in the same nebulization system were evaluated. For this assessment, four different solution compositions were used: purely aqueous, acidified aqueous (2% v v^{-1} with nitric acid), aqueous with sucrose (10 g L^{-1}), and aqueous with etanol (10% v v^{-1}). To assess the effects, the concentration of the analytes (sodium, potassium, lithium and calcium) was fixed at 10.0 mg L^{-1}, and the red, green and blue (RGB) signal intensity generated from smartphone image capture and subsequent processing using the free software ImageJ® was monitored. From this evaluation, it was possible to observe that the effects of the solution matrix are smaller when a peristaltic pump is used to assist in the aspiration of the solutions. In this study, no significant differences were observed in the means compared for the same analyte with and without the use of the peristaltic pump when in the evaluated aqueous and acidified matrices. However, in the presence of matrices with high carbon concentrations, a significant reduction (t-test, 95% confidence level) in the mean of the analytical signals for elements was observed when the aspiration did not have the assistance of the peristaltic pump. In this case, in the sucrose presence in the matrix, the average signal intensity reduction reached 43% for Na and 5% for K, for example. This clearly demonstrated the importance of using the peristaltic pump to aid in the transport of the aqueous solution to the developed nebulization system, especially for matrices with a high content of residual carbon.

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[Thanks to IFRS Campus Feliz]

Electrothermal atomization/vaporization

022 - BORON ELEMENTAL AND ISOTOPIC DETERMINATION VIA HR-CS GFMAS: ABSORPTION OF THE BF DIATOMIC MOLECULE

André L. Marques de Souza[a], **Flávio V. Nakadi**[a*], **Maite Aramendía**[a], **Martín Resano**[a]

[a]University of Zaragoza, Department of Analytical Chemistry, i3A, Zaragoza, Spain, 50009.
*e-mail: fvnakadi@unizar.es

Boron trace determination in biological materials is essential across various fields of application. However, the process of sample preparation can introduce significant complications, including the potential for boron contamination stemming from acids and glassware, as well as the risk of losing analyte due to the high volatility of certain boron species. Consequently, direct solid analysis emerges as a favorable approach, effectively bypassing these challenges. The direct determination of boron in biological materials through graphite furnace atomic absorption spectrometry (GFAAS) has previously been used for this purpose, offering impressive detection limits that are often difficult to attain using alternative techniques.[1]

Nonetheless, techniques relying on the measurement of boron atomic absorption in a graphite furnace come with their own set of challenges, primarily associated with boron tendency to form resilient carbides and oxides. The use of elevated atomization temperatures is necessary and significantly extended integration times to facilitate boron atomization, thereby substantially reducing the lifespan of the graphite components within the instrument.

In this study, we have enhanced the contemporary technique of atomic/elemental boron determination by forming a volatile B diatomic molecule, boron monofluoride, and monitoring its absorbance in a GFAAS instrument.[2] Consequently, we introduce a novel method for boron determination, which involves employing GF molecular absorption spectrometry (GFMAS) directly on solid samples.

Boron has been successfully identified in the form of diatomic BF; however, promoting the presence of this molecule in the GF and measuring its absorption is not a straightforward process due to boron tendency to form highly volatile BF_3, which is lost before the absorption of the BF molecule can be recorded. A solution involving a gas-phase reaction with CH_3F has been proposed to address this issue. Although the exact mechanism for BF molecule formation is still to be confirmed, it is likely that fluorination occurs in the gas phase after boron is atomized.

Based on this strategy, a method for directly determining boron in biological materials has been developed, monitoring the BF molecule at 195.589 nm (vibronic transition $X^1\Sigma^+ \rightarrow A^1\Pi$ 0,0). This method requires lower vaporization temperatures and shorter integration time compared to the conventional GFAAS method and provides similar sensitivity. Accurate results have been achieved by directly analyzing different certified reference materials of botanic origin, with appropriate correction for spectral interferences (notably from the PO molecule) using the TAP method.[3]

Furthermore, the GFMAS method offers an additional advantage in the form of a substantial isotopic shift in the absorbance of the ^{10}BF (λ=201.160 nm) and ^{11}BF (λ=200.993 nm) molecules in the vibronic transition $X^1\Sigma^+ \rightarrow A^1\Pi$ (1,0), which can be accurately monitored. This characteristic opens up novel possibilities for isotopic analysis, which are also explored in this study.

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Hyphenated Techniques

023 - VARIATIONS IN CARBON AND NITROGEN STABLE ISOTOPES AND IN HALOGEN AND SULFUR CONTENTS TO DISCRIMINATE SEAWEED FROM THE ANTARCTIC

Luiz F. Rodrigues[a], Filipe S. Rondan[b], Roseane D'Avila[c], Adolpho Augustin[d],
Márcia F. Mesko[b*]

[a]FURG, Escola de Química e Alimentos, Rio Grande, RS, Brazil, Zip Code: 96203-900
[b] UFPel Centro de Ciências Químicas, Farmacêuticas e de Alimentos, Pelotas, RS, Brazil, Zip Code: 96160-000
[c] FURG, Centro Integrado de Análises Rio Grande, Rio Grande do Sul, Brazil, Zip Code: 96203-900
[d] Unisinos, Núcleo de Geologia e Geofísica Aplicada, Rio Grande do Sul, Brazil, Zip Code: 93022-750
*e-mail: marciamesko@yahoo.com.br

Seaweed are organisms with a great ability to absorb organic and mineral compounds from the environment and the study of chemical composition can help to understand natural and anthropogenic processes in which they are involved[1]. Carbon isotope ratio has been used to understand the carbon cycle in the high-CO_2 world (ocean acidification), whereas the nitrogen isotope ratio data can be used as environmental biomonitors for the inflow of pollutants[1]. There is little data in the literature about the monitoring of non-metals in the Antarctic continent, probably due to the difficulty in determining non-metals in a complex matrix such as seaweed. The study aimed to connect the potentiality of carbon and nitrogen isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) to halogen and sulfur content. In this way, the use of variation in carbon and nitrogen stable isotopes and the halogen and sulfur total concentration is the main goal of this work to find new proxies for accurate assessment of discrimination taxonomic groups. The samples were collected in different regions of the Antarctic and the sampled specimens belong to 2 phyla, 5 genera, and 5 species. The phyla were identified as Rhodophyta and Phaeophyta. A microwave-induced combustion method was used for the sample preparation for subsequent halogen and sulfur determination by ion chromatography with conductivity detection coupled to mass spectrometry in a single analysis. The analysis of carbon and nitrogen isotope ratios was performed using isotope ratio mass spectrometry. Seaweed can be classified into three strategies for dissolved inorganic carbon (DIC) uptake: (1) carbon concentrating mechanisms (CCM) only by active uptake HCO_3^- ($\delta^{13}C > -10$ ‰), (2) CCM active uptake HCO_3^- and diffusive uptake CO_2 ($\delta^{13}C < -11$ to -30 ‰), and (3) non-CCM CO_2 by diffusion only ($\delta^{13}C < -30$ ‰)[2]. In this work, it was observed the $\delta^{13}C$ values lower than -30 ‰ (CO_2 by diffusion only) in one seaweed of Rhodophyta and one seaweed of Phaeophyta. However, most species showed large $\delta^{13}C$ variabilities, which is evidence of a mechanism that uses a mix of HCO_3^- and CO_2 for photosynthesis. Regarding that specific group, the variability in $\delta^{13}C$, $\delta^{15}N$, Cl, Br, I, and S values in seaweed was analyzed by taxon. The Rhodophyta's values of $\delta^{13}C$ and $\delta^{15}N$ were between - 20.5 ‰ to - 12.4 ‰ and 4.7‰ to 6.2‰, respectively, while the Phaeophyta's values were -26.0 ‰ to -17.1 ‰ and 2.9‰ to 3.8‰ for $\delta^{13}C$ and $\delta^{15}N$, respectively. According to the isotope results, Rhodophyta displayed significantly higher values of $\delta^{13}C$ and $\delta^{15}N$ than Phaeophyta. In addition to isotope analysis, the results of halogens and sulfur also helped to discriminate Rhodophyta and Phaeophyta in CCM active uptake HCO_3^- and diffusive uptake CO_2 group. The range concentration of Br, Cl, and I for Rhodophyta was 137 to 327 mg kg^{-1}, 630 to 1790 mg kg^{-1}, and 54 to 411 mg kg^{-1}, respectively. For Phaeophyta, the range concentration of Br, Cl, and I were 101 to 614 mg kg^{-1}, 2328 to 11,253 mg kg^{-1}, and 215 to 455 mg kg^{-1}, respectively. Phaeophyta showed higher concentration than Rhodophyta mainly for Cl, while for Br and I, the range concentration of halogens was almost the same for both of them. However, the range concentration of sulfur was higher for Rhodophyta (11,603 to 56,350 mg kg^{-1}) than for Phaeophyta (4,586 to 10,344 mg kg^{-1}). Therefore, the use of isotope analysis ($\delta^{13}C$, $\delta^{15}N$) and new proxies such as Cl and S can be helpful in discriminating carbon concentrating mechanism that uses a mix of HCO_3^- and CO_2 for photosynthesis.

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[CAPES, CNPq, Brazilian Antarctic Program, SENS Mass Spectrometry, and INCTBio]

024 - RAMAN SPECTROSCOPY COUPLED TO HR-CS FMAS FOR SEQUENTIAL DETERMINATION OF NITROGEN SPECIES IN FERTILIZERS

Evilim Martinez de Oliveira[a*], **Edilene C. Ferreira[a]**, **José A. Gomes Neto[a]**, **George L. Donati[b]**, **Bradley T. Jones[b]**

[a]São Paulo State University (UNESP), Institute of Chemistry/Department of Analytical Chemistry, Physical Chemistry and Inorganic, Araraquara, São Paulo, Brazil, 14800-060.
[b] Wake Forest University, Department of Chemistry, Winston-Salem, NC, USA, 27109
*e-mail: evilim.martinez@unesp.br

Raman spectroscopy (RS) may be used for both qualitative and quantitative analysis with minimal to no sample preparation and the High-resolution continuum source flame molecular absorption spectrometry (HR-CS MAS) is an interesting alternative to determine non-metals via formation of diatomic molecules in flames and graphite furnaces atomizers. In this context, this study reports on a novel, rugged, simple, and environment friendly method for qualitative and quantitative determination of urea, nitrate and ammonium in NPK fertilizers by coupling HR-CS FMAS and Raman Spectroscopy in a flow system.

The identification and quantification of N species in fertilizer samples was successfully carried out using the flow system depicted in Figure 1. Sample is aspirated and passes through the Raman flow cell (FC) in which urea and nitrate are determined at 1000 and 1045 cm^{-1}, respectively. Afterwards, sample is mixied with hydrogen peroxide at the confluent point a and the mixture is injectd into the nebulization system of the HR-CS FMAS for total N determination. Ammonium is then determined by difference. External calibration for urea, nitrate and total N showed plots with linear coeffcients of 0.9989, 0.9976 and 0.9960, respectively. The limits of detection for total N, nitrate, and urea were 0.03 mg L^{-1}, 0.03 mg L^{-1} and 0.01 mg L^{-1}, respectively. Relative standard deviations were ≤ 11%. external standard calibration method provided accurate results for all analytes determined in certified reference materials, raw materials, and commercial samples of fertilizers. For comparison purposes, all samples were also analysed by traditional Kjeldahl method. The RS HR-CS FMAS method was further validated by addition and recovery experiments, which provided recoveries in the 93 – 113 % range.

The method is simple, fast, environment friendly, and adequate to perform routine, large-scale analyses of fertilizers.

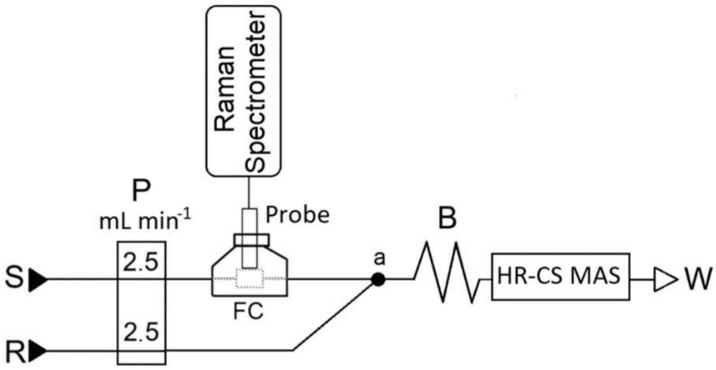

Fig. 1. Diagram representing the flow system used for speciation and quantification of nitrogen in fertilizers by coupling Raman spectroscopy and HR-CS FMAS. P: Peristaltic pump; S: blanks, standards and samples (2.5 mL min^{-1} flow rate); R: 10 % (v/v) H_2O_2 solution (2.5 mL min^{-1} flow-rate); B: mixing coil (500 mm × 0.8 mm i.d.); a: confluent point; W: waste; FC: flow cell.

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Metallomics

025 - *In vitro* BIOACCESSIBILITY OF NUTRIENTS IN COOKED FISH SAMPLES

Fiorella Iaquinta[a*], Nataly Rodríguez[a], Ignacio Machado[a]

[a]BIOESP, Área Química Analítica, Facultad de Química, Universidad de la República, Montevideo, Uruguay, 11800
* email: fiaquinta@fq.edu.uy

Several nutrients have an important role in the development of human beings. Such is the case of essential elements copper (Cu), zinc (Zn), manganese (Mn) and iron (Fe). These elements are known for its relevance in life because they are important part of many proteins. Since these elements are provided only by diet, it is important to evaluate the actual amount that can be used by the organisms. In these regard, *in vitro* bioaccessibility assays constitute a very useful strategy[1].

In this work bioaccessibility of Cu, Zn, Mn and Fe was studied in croaker fish samples (*Micropogonias furnieri*) using an *in vitro* assay. Samples were collected form Castillos Lagoon, Rocha, Uruguay, trough artisanal fishing. Once in the laboratory, samples were dissected with a stainless-steel knife to extract the muscle, which was subsequently crushed in a blade mill and stored in polypropylene tubes at -4 ºC until cooking (n=6). Fish samples were then grilled on a glass plate at 80 ºC. No other ingredients were added during the cooking process. Simulated gastrointestinal conditions were optimized adapting the INFOGEST protocol[2]. Simulated saliva fluid was prepared using 0.7 grams of amylase dissolved in 100.0 mL of ultrapure water. Simulated gastric solution was prepared with 0.3 g of pepsin dissolved in 1.0 mL of 12 mol L^{-1} HCl followed by the addition of ultrapure water to complete a volume of 100.0 mL. The pH was then adjusted to 1.3. For the simulated intestinal solution, 0.2 g of bile salts was dissolved in a solution containing 0.5 g of pancreatin previously dissolved in 8.0 mL of 0.2 mol L^{-1} NaOH. The volume was completed to 100.0 mL with ultrapure water. The pH was then adjusted to 6.8. For the optimized experiment, a portion of 0.5 g of sample was placed into a 25 mL Erlenmeyer flask with 2 mL of saliva fluid for 2 min. The solution was kept in water at 37 ºC with continuous agitation in an orbital shaker. Then 5 mL of gastric solution were added and shacked for 2 h at 37 ºC. Then, 5 mL of intestinal solution were added, and the solution was shacked for other 2 h at 37 °C. Finally, the mixture was centrifuged, and the supernatant was separated from the residue and used for bioaccessible fraction determination. Analytical determinations were performed by flame atomic absorption spectrometry, for Mn, Zn and Fe, while electrothermal atomic absorption spectrometry was used for Cu.

Trueness of the developed method was evaluated by performing the corresponding mass balances, between the amount of analyte in the supernatant and the residue. Mass balances were between 75 – 120 %, which was considered adequate for this purpose.

Bioaccesible fractions were 59.2 % for Cu, 54.7 % for Fe, 36.9 % for Mn and 84.3 % for Zn. The contribution of these metals to the RDA for adults over 19 years was estimated, as an example, considering a 150 g portion. Results showed that the average contribution to RDA for Zn was 6.7 % for men (M) and 9.2 % for women (W), for Cu was 6.0 %, for Mn was 10.9 % (M) and 14.0 % (W), while for Fe was 5.0 % (M) and 2.6 % (W), respectively.

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026 - DETERMINATION OF Cd, Hg AND Se IN LIVER OF WHALES

Guilherme dos Santos Lima[ab*], **Carlos Alfredo Suarez**[a], **Amauri Antonio Menegario**[a]

[a]São Paulo State University (UNESP), Environmental Studies Center (CEA), Rio Claro, SP, Brazil, 13506-900
[b]Postgraduate Program in Geosciences and Environment, Institute of Geosciences and Exact Sciences, Rio Claro, SP, Brazil, 13506-900
*e-mail: guilherme.s.lima@unesp.br

Aquatic environments and especially marine environments are often the final destination for a variety of chemical elements released into the environment, whether of anthropogenic or natural origin[1]. However, the increase in human activities has increased the levels of environmental concentrations and thus has altered the natural biogeochemical cycle of these elements[2]. In particular, coastal environments, as they have the largest populations of people living in these regions, suffer directly from the impact and stress generated through the accelerated dispersion of contaminants over this area[3]. Metals, metalloids and trace elements are available in the environment, enter food webs and can persist accumulating in living organisms, which may result in contamination of food chain due to their toxicity[4]. Once available in the marine environment, they can cause changes in the present ecosystem, producing serious and deleterious effects on the biota. Marine mammals, especially whales, because they are migratory and have a wide range of habitats, are key species for oceanic systems and can provide information on the health of the ecosystem[5]. As top predators are exposed to several contaminants mostly through their diet, they can thus act as sentinels of marine pollution with the potential to accumulate significant amounts of contaminants[2,6]. Thus, a point to be considered is to evaluate the use of biomonitoring tools as an approach to understanding the state of contamination of the marine environment and marine organisms at the top of the chain. In this study, Cd, Hg and Se concentrations were evaluated in liver samples from 6 different species of whales. The samples were collected by daily monitoring carried out by Santos Basin Beach Monitoring Program (PMP-BS), from stranded individuals found in the Santos Basin. Liver samples were digested in a microwave oven and subsequently, Hg was determined by cold vapor atomic fluorescence spectrometry (CVAFS), and Cd and Se were determined by inductively coupled plasma mass spectrometry (ICP-MS). The study aims to increase knowledge about the mobilization of these elements in marine organisms and to observe possible relationships between the inorganic contaminants in highly migratory species that move over great distances throughout the oceanic system. A high correlation was found between Hg-Se, Hg-Cd and Se-Hg suggesting the same origin source of Hg and Cd, and the possible role of Se in the formation of less harmful complexes. The highest correlation was between Se-Hg (R^2= 0.89), later for Cd-Hg (R^2= 0.82) and Se-Cd (R^2= 0.82). Age/size has a greater influence on concentrations within the same species, among all species, size did not show a linear correlation with concentrations. Our aim is that these results can be used to assess the extent of contamination and identify areas that need special attention in terms of environmental management. Finally, continuous monitoring of the concentrations of these top animal elements is essential for the conservation of these animals and their habitats, as they can be considered as sentinels of the health of the oceans and marine ecosystems.

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[PMP-BS, PETROBRAS]

027 - RELATIONSHIP BETWEEN MERCURY AND SELENIUM CONCENTRATIONS IN MARINE TETRAPOD LIVERS

Henrique Dias Petrovich[ab*], Daniel Fernandes Mendes[a], Amauri Antonio Menegário[a]

[a]São Paulo State University (UNESP), Environmental Studies Center (CEA), Rio Claro, SP, Brazil, 13506-900
[b]Graduate Program in Geosciences and Environment, Institute of Geosciences and Exact Sciences, Rio Claro, SP, Brazil, 13506-900
*e-mail: h.petrovich@unesp.br

Mercury is a natural and ubiquitous trace metal, considered a priority contaminant, mainly in the form of methylmercury (MeHg). In nature, it can pass from its inorganic form (Hg2+) to organic forms such as MeHg through the methylation process, mainly due to microbial activity[1]. Its presence can cause adverse effects on the central nervous and endocrine systems, leading to reproductive dysfunctions, osmoregulation, prey location, orientation, interspecific communication, among others[2], and reaching large amounts in organisms through bioaccumulation and biomagnification[3]. In some of these organisms, a defense mechanism has been developed for the elimination of this toxic mercury, through antioxidant properties mechanisms, competition for binding sites on molecules and the formation of non-toxic inert complexes through a demethylation process that occurs in the liver[4], where Hg and Se molecules bind and form insoluble, toxicologically inert crystals of HgSe[5]. For this reason, a Se/Hg molar ratio close to 1:1 or higher is expected. After the calculation of the Se/Hg molar ratio, its Neperian Logs and linear regressions were performed to determine the relationship between Hg and Se in the liver of five species of marine tetrapods, one chelonian, two cetaceans and two birds (*Chelonia mydas*, *Pontoporia blainvillei*, *Sotalia guianensis*, *Spheniscus magellanicus* and *Larus dominicanus*). In addition to an interspecific analysis, variations between sex, age and location for the species were analyzed. For sex, *P. blainvillei*, *S. guianensis* and *L. dominicanus* showed significant differences between males and females for Hg, whereas *C. mydas*, *P. blainvillei*, *S. guianensis* and *L. dominicanus* showed significant differences for Se. For age, *L. dominicanus* showed significant differences for Hg and Se, while *P. blainvillei* showed significant differences for Se. As for molar concentrations, for the cetaceans *P. blainvillei* and *S. guianensis*, the results showed a possible direct relationship between the molar concentrations of Hg and Se ($R^2 = 0.367$ for *P. blainvillei* and $R^2 = 0.203$ for *S. guianensis*), corroborating with other studies which indicate the participation of Se as a mechanism to reduce the toxicity of Hg in these animals[6,7]. In general, for *C. mydas*, *P. blainvillei* and *S. magellanicus*, it is observed that males present a direct link between molar concentrations of Hg and Se. However, for *S. guianensis* and *L. dominicanus*, females are the ones that show a direct relationship between both molar concentrations. As for age variation, *P. blainvillei* presents direct relationships between Hg and Se in its liver in both adults and juveniles, as well as juvenile individuals of *L. dominicanus* and *S. magellanicus* and tends to be a positive relationship as the age of these animals increases. In comparisons between locations, the areas that most showed a positive correlation between Hg and Se were São Paulo and Santa Catarina, mainly for the cetacean *P. blainvillei*. The mean molar ratios of *P. blainvillei* and *S. guianensis* were 6.901 and 3.260, respectively. For the species *C. mydas*, *S. magellanicus* and *L. dominicanus*, the average Se:Hg molar ratios were 21.390, 5.943 and 7.725, respectively, substantially higher than the expected 1:1 ratio, but always higher than 1, indicating that Se may be being used for the demethylation of Hg in all species studied.

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[ANP, FINEP, PMP-BS, PETROBRAS]

Plasma-based Techniques

028 - THE EMPLOYMENT OF PLASMA-BASED TECHNIQUES FOR ENVIRONMENTAL STUDIES IN THE SOUTHEAST COASTAL ZONE OF BRAZIL

Jefferson Rodrigues de Souza[a*], Maiara Krause[b], Geisamanda Pedrini Brandão(R)[b], Maria Tereza Weitzel Dias Carneiro [b]

[a]State University of the North Fluminense Darcy Ribeiro, UENF, Chemical Sciences Laboratory, Campos dos Goytacazes, Rio de Janeiro, Brazil, Zip Code 28013-602
[b] Federal University of Espírito Santo, Departament of Chemistry, Vitória, Espírito Santo, Brazil, Zip Code 29075-910
*e-mail: jefferson@uenf.br

In recent years, scientists from all over the world have turned their attention to aspects related to environmental preservation. In this regard, the development of analytical methods employing spectroscopic techniques based on plasma, such as emission spectroscopy and inductively coupled plasma mass spectrometry, has been the primary tools used for conducting studies on environmental impact aimed at quantifying potentially toxic chemical elements in environmental samples. From a strategic standpoint, coastal zones and marine environments deserve special attention due to their socio-economic significance. The coastal zone is a dynamic environment subject to external forces such as waves, continental drift, winds, etc. Consequently, accurately assessing the environmental impacts caused by the presence of potentially toxic chemical elements becomes a challenging task, and a proper elucidation of the contamination status requires a multifactorial approach that considers not only the content of chemical elements but also the use of indices that aid in identifying environmental impacts.

In 2015, the coastal zone of southeastern Brazil was severely impacted by the rupture of an iron ore tailings dam, releasing approximately 62 million cubic meters of iron ore tailings and severely polluting the coastal zone and marine environment. To identify the magnitude of contamination in the coastal environment, the concentrations of Al, As, Ba, Cr, Cu, Fe, Mn, and Pb were determined in sediment samples collected at a depth of 10 meters along the southeastern Brazilian coast. The environmental monitoring was carried out during the wet and dry season between September/2018 and January/2022. The samples were decomposed using the EPA 3051A method, and the quantification of chemical elements was carried out using ICP OES and ICP-MS. The quantification limits ranged from 0.12 mg kg^{-1} (Pb) to 8.9 mg kg^{-1} (Fe). The certified reference material NIST 2702 was used to evaluate the extraction efficiency. The results indicated that the coastal zone had a high concentration of chemical elements exceeding sediment quality guidelines, posing a risk to the coastal zone's biota.

Considering the large amount of data collected during the research and the difficulty in finding a pattern of clustering among the different studied sampling stations, chemometric methods such as principal component analysis and self-organizing maps (SOM) were employed. Thus, it was possible to classify the sampling stations into groups characterized by high levels of chemical elements located to the north of the sampling grid, indicating that the Doce River directs sediment and, consequently, pollutant loads towards the northern part of the southeastern Brazilian coastal zone.

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029 - DISTRIBUTION OF METALS AND SEMIMETALS IN CRUDE OIL

Rafael C. C. Rocha[a,b*], Eduardo R. A. Salazar[a], Cleverson J. C. de Oliveira[d], Christiane B. Duyck[c], Tatiana D. Saint'Pierre[a]

[a]PUC-Rio, Department of Chemistry, Rio de Janeiro, RJ, Brazil, 22451-900
[b] FIRJAN, IST Química e Meio Ambiente, Rio de Janeiro, RJ, Brazil, 20271-031
[c] UFF, Department of Analytical Chemistry, Niteroi, RJ, Brazil, 24020-140
[d]Petrobras, Geoquímica – Cenpes, Ilha do Fundão, Rio de Janeiro, RJ, Brazil, 21941-915
*e-mail: rafaelccrocha@hotmail.com

The concentrations of elements and their correlations can be employed for oil characterization, and as markers of the origin, biodegradation and migration of the petroleum.[1] The analytical techniques applied to determine the elements present in oil usually require the decomposition of the samples in high pressure and temperature systems, which have some limitations such as the potential risk of explosive reactions. A more direct approach is the determination of the elements in oil after the solubilization in organic solvents and the use of an adequate introduction system, which have several advantages, such as the lower risk of contamination by sample manipulation. The objective of this study was to develop a methodology for multielemental determination in crude oils by inductively coupled plasma mass spectrometry (ICP-MS) after dissolution in organic solvents. An amount of 0.1 g of the sample was dissolved in 10 g of xylene or a 60/40 (v/v) xylene / butanol solution. The solutions were analysed employing a NexIon 300X spectrometer (PerkinElmer, USA), using the standard and the DRC modes. For the DRC mode, all analytes were determined using CH_4 as reaction gas, and optimized compromise conditions. External calibration curves were used for both modes and all employed solvents. The accuracy was evaluated by the analysis of the standard reference material NIST SRM 1634c (Residual fuel oil). The obtained results were compared with those obtained by sample decomposition: 0.1 g of sample were weighed to the Teflon flasks of a DAB-2 digester block (Berghoff, Germany) and added 2 mL of sub-distilled HNO_3 and 0.5 mL of H_2O_2. After submitting to the temperature program, the resulting solutions were made up with ultrapure water to 20 mL final volume. The recovery obtained for the reference material was between 77-121%, the results are presented in Table 1.

	Certified	Acid decomposition	Organic solvent STD	Organic solvent DRC*
V	28.2 ± 0,4	28.5 ± 0,8	26.7 ± 0,8	27.4 ± 1,1
Co	0.151 ± 0,005	0.141 ± 0,016*	0.183 ± 0,006	0.155 ± 0,001
Ni	17.5 ± 0,2	18,0 ± 1,3	16.7 ± 0,5	17.4 ± 0,4
As	0.143 ± 0,006	0.147 ± 0,074*	0.142 ± 0,003	0.156 ± 0,012
Se	0.102 ± 0,004	0.116 ± 0,019*	<LOD	<LOD

STD: standard mode *DRC: Dynamic Reaction Cell mode

Table 2. Certified and obtained concentrations for NIST1634c by the three methodologies. Results are expressed in mg kg^{-1}.

When compared to the sample decomposition method, higher instrumental limits of detection (LOD) were obtained with dissolution in organic solvents, as expected. However, the limits of quantification (LOQ) of the organic method were better, due to the lower sample dilution. A set of crude oil samples were analysed employing the proposed methods and the concentrations obtained by dissolution in organic solvents for Co (0.15 to 3.3 mg kg^{-1}), Mn (0.04 to 13.7 mg kg^{-1}), Ni (2.5 to 56 mg kg^{-1}) and V (0.7 to 8.5 mg kg^{-1}) were in agreement with those obtained by sample decomposition. The organic method proved adequate when compared to decomposition method, since they present similar results.

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[CNPq, CAPES, FAPERJ, Petrobras, PUC-Rio]

030 - MICROSCALE ACID DECOMPOSITION FOR DETERMINATION OF Cu, Fe, Mg, Na AND Zn IN HAMBURGERS BY MIP OES

Ana Paula Marques [a]*, Ana Claudia B. Luckow[b], Daisa H. Bonemann[a], Charlie G. Gomes[a], Yasmin R. Bloedorn [a], Jéssica da R. Porto[a], Adriane M. Nunes[a], Anderson S. Ribeiro[a]

[a]Federal University of Pelotas, Chemical, Pharmaceutical and Food Science Center,
Capão do Leão, RS, Brazil, 96010-900.
[b]Federal University of Rio Grande, School of Chemistry and Food, Rio Grande, RS, Brazil, 96203-900.
*e-mail: ap_marques@outlook.com

Meat is a source of proteins, lipids, vitamins and essential minerals, their consumption contributes significantly to the development and functioning of the body, however, they are being replaced by processed and more accessible options[1]. Nonetheless, these products have a large amount of fat and high sodium content, so when consumed in excess, they increase the risk of developing cardiovascular diseases and various types of cancer[2]. In addition to Na, it is also necessary to monitor essential elements such as Ca, Cu, Fe, K, Mg and Zn, which also play important roles in the human body and can be found in processed meat products. Thus, the objective of this work was the application of microwave-assisted microscale acid decomposition in hamburgers samples for determination of the total concentration of Cu, Fe, Mg, Na and Zn by Microwave-Induced Plasma Optical Emission Spectrometry (MIP OES). The decomposition method applied consists of using polytetrafluoroethylene (PTFE) mini vessels for sample preparation in a closed system with microwave heating, as previously reported[3,4]. To optimize the best experimental conditions for sample preparation, a central central composite design was used, where four independent variables were evaluated: sample mass, HNO_3 volume, decomposition time and microwave power and the dependent variables correspond to the analytical signals obtained for the elements. This way, 40 mg of sample were weighed directly into mini-vessels and added 400 µL of HNO_3. After, the vessels were closed and placed in the microwave oven, using a polystyrene support with capacity for six vessels. A beaker with deionized water was placed in the center of the support. The decomposition occurred in 3 minutes and power of 475 W. The resulting solutions were transferred to polypropylene tubes and the final volume of 5.0 mL was completed with deionized water. The accuracy of the method was evaluated using certified reference material meat homogenate (NIST 1546) and lobster hepatopancreas (TORT-2), satisfactory values were observed in the application of the Z test, with Z values below 2. The limits of detection (LOD) of the method was 0.17, 0.33, 0.59, 0.86 and 0.25 mg kg^{-1} for Cu, Fe, Na, Mg and Zn, respectively. The results for the total concentration of samples A, B and C were 1.22, 1.24 and 1.22 mg kg^{-1} for Cu; 9.11, 17.6 and 10.2 mg kg^{-1} for Fe; 226.2, 261.5 and 250 mg kg^{-1} for Mg, 6031, 5994 and 6544 mg kg^{-1} for Na and 11.6, 32.5 and 8.9 mg kg^{-1} for Zn, respectively. Considering that the recommended daily intake value (DRI)[5] for adults of Cu, Fe, Mg, Na and Zn is 0.9, 14.0, 260, 2000 and 7.0 mg, respectively, and the consumption of 70g of hamburgers per day, the concentrations were below the recommended daily intake, which emphasizes the need for a diet rich in varied foods. However, it is important to point out that the Na concentration found is quite high, contributing with half of the acceptable daily concentration which corroborates the idea that these foods have a nutritional profile that can be harmful to health.

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[CNPq, CAPES, INCTAA]

031 - THE BIOANALYTICAL USE OF ISOTOPE PATTERN DECONVOLUTION ICP-QMS FOR HUMAN IRON ABSORPTION STUDIES: A NOVEL INSIGTH

Bernardo Ferreira Braz[a*], Juliana Omena[b], Vanessa Monteiro Voll[b], Marta Citelli[b], Cláudia dos Santos Cople Rodrigues[b], Fernando Henrique Cincotto[a,d], Maria Luisa Fernández-Sánchez[c], Ricardo Erthal Santelli[a,d]

a Universidade Federal do Rio de Janeiro, Departamento de Química Analítica, Avenida Athos da Silveira Ramos 149, CT, Bloco A, 5º andar, Rio de Janeiro/RJ, 21941-909, Brazil.
b Universidade do Estado do Rio de Janeiro, Instituto de Nutrição, Rio de Janeiro, Brazil.
c University of Oviedo, Physical and Analytical Chemistry Department, Oviedo, Spain.
d National Institute of Science and Technology in Bioanalytics, Campinas, SP, Brazil.
*e-mail: bernardobraz@pos.iq.ufrj.br

Iron is an essential element for human life and its nutritional status in the human body is directly linked to the human health[1]. The iron deficiency can result in anaemia, while excessive iron levels can lead to tissue and organ damage. Almost 25 % of the world population is anaemic and around 800,000 deaths per year are attributed to the lack of Fe[2]. For healthy individuals, more than 1015 atoms of Fe per second are necessary for the maintenance of haemoglobin formation. In the human body there is not a defined route of excretion of Fe, most of its excretion is done by desquamation of the intestine and skin; and, by menstrual bleeding[3]. The concentration control of Fe in the organism is given mainly by its absorption from food, therefore several protection mechanisms are activated when there is an excess of Fe in the organism. To predict the iron bioavailability three methods are normally employed: (a) fecal recovery; (b) plasma appearance; and (c) erythrocyte incorporation[2]. A major part of Fe that is absorbed from dietary source becomes incorporated into erythrocytes, so this method is often used to predict the iron bioavailability. Isotope Pattern Deconvolution (IPD) is a mathematical tool that allows isolating distinct isotope signatures from mixtures of natural abundance and enriched tracers. This tool provides the understanding of how a tracer, is incorporated into the natural signature of a sample (tracee)[4]. Hence, it is possible to know the concentrations of both, tracer and tracee, from the isotope profile, providing quantitative data about endogenous and exogenous elements and their metabolism[5]. In this work we propose a novel approach to assess the erythrocytes iron incorporation, based on the use of IPD concept. Using this approach, it is possible to obtain the distinct iron isotope signatures from mixtures of natural abundance and enriched tracers providing we can provide a most reliable way to calculate iron absorption in humans.

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[CNPq, FAPERJ, INCTBio, CAPES]

032 - DETERMINATION OF INORGANIC CONTENT BY PLASMA TECHNIQUES IN SCALLOPS (*Nodipecten nodosus)* FARMED IN RIO DE JANEIRO STATE, BRAZIL

Samara Gomes Banhos[a,b], Fabiola H. S. Fogaça[c], Amauri Rosenthal[c], Ana Rita A. Nogueira[a]

[a] Embrapa Pecuária Sudeste, P.O. Box 339, 13560-970, São Carlos-SP, Brazil.
[b] Applied Instrumental Analysis Group, Universidade Federal de São Carlos, 13565-905, São Carlos-SP, Brazil.
[c]Embrapa Agroindústria de Alimentos, 23020470 - Rio de Janeiro, RJ, Brazil
*e-mail: banhossamara@gmail.com

Scallops are bivalve mollusks of great commercial value. Farming production worldwide increased 51% between 2009 and 2019, when approximately 2.07 million tons were commercialized[1]. In Brazil, scallops are produced on an artisanal scale, and the only species cultured is *Nodipecten nodosus*, which has fast growth in culture systems[2]. Otherwise, lack of monitoring techniques, productive effectiveness, processing, and commercialization must still be overcome to expand production. The knowledge of potential contaminants and inorganic nutrients is one of the items monitored for expanding the market and consumption and guaranteeing safe and healthy products according to the legislations and regulations enforced worldwide[3]. To strengthen and increase the scallops production chain in the State of Rio de Janeiro, the diagnosis and monitoring of critical points during cultivation is essential. In this approach, analytical strategies based on plasma techniques were employed to determine the mass fractions of nutrients, and contaminants. Scallop samples produced by small producers were collected, lyophilized, ground, and microwave-digested by using diluted nitric acid. The acid digests were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) to determine the mass fraction of Ca, Fe, and Zn, and the obtained quantification limits were 57, 11, and 17 mg kg^{-1}. For the determination of the mass fraction of As, Cd, Cr, Hg, Se, Sr, and Pb, the acid digests were analyzed by inductively coupled plasma mass spectrometry (ICP-MS), and the obtained quantification limits were 0.08, 0.18, 0.23, 0.11, 0.58, 0.39, and 0.11 mg kg^{-1}.The accuracy of the methods, evaluated by using certified reference materials (IPEN and TORT-3), ranged between 74-119% for ICP-MS, and between 98-116% for ICP-OES. The method was applied to 89 scallops samples provided by small producers of Ilha Grande Bay, RJ, and the obtained values ranged from 424-1809; <11-416; 43-76; <0.08-12.8; <0.18-1.04; <0.23-1.39; <0.11; <0.58-5.1; <0.39-37; <0.11-0.22 mg kg^{-1} for Ca, Fe, Zn, As, Cd, Cr, Hg, Se, Sr and Pb, respectively. In general, except for one sample of Cd, the levels obtained are below the maximum limits allowed by legislation, being suitable for consumption[4].

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[CNPq, FAPERJ, EMBRAPA]

033 - A GREEN, SIMPLE, AND FAST DILUTE-AND-SHOOT SAMPLE PREPARATION METHOD FOR MULTIELEMENTAL ANALYSIS OF MEDICINAL CANNABIS EXTRACTS BY ICP-MS

João Victor Meirelles[a,b], Monica Costa Padilha[b], Tatiana D. Saint'Pierre[a,*]

[a] Pontifical Catholic University of Rio de Janeiro, Department of Chemistry, Rio de Janeiro, RJ, Brazil, 22451-900
[b] Federal University of Rio de Janeiro, Institute of Chemistry, Rio de Janeiro, RJ, Brazil, 21941-909
*e-mail: tatispierre@puc-rio.br

Cannabis is a highly diverse and polymorphic plant species with an extensive capacity for biosynthesis of various metabolites. The psychoactive potential of Cannabis has been known for more than 5 millennia, and the search for its use, both medicinal and recreational, is currently expanding. More than 40 different types of Cannabis-derived products are commercially available, and among medicinal items, herbal extracts stand out as a potential pharmaceutical ingredient.[1] Metals and metalloids are critical components of these inputs, representing both potentially toxic contaminants capable of bioaccumulation and essential cofactors in Cannabis biosynthesis pathways.[1,2] Elemental determination of oily extracts by spectrometric techniques is challenging, given the high organic matter content present in the matrix and appropriate sample preparation methods are critical to make it viable.[3] In this work, a green, simple and fast dilute-and-shoot based approach for sample preparation was developed for 22 elements (Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, V, and Zn) using sesame oils as sample-models, due to is common application as preparation vehicle in Cannabis extracts preparation. Butanol and isopropanol were tested as green alternatives diluents to xylene, the diluent typically used for direct analysis of oil samples by ICP-MS. Samples were diluted 10-times w/w and recovery assays were conducted at 7.5 µg kg^{-1} concentration level for diluent selection. Satisfactory recoveries (80 – 120%) were obtained in 13 elements for butanol, while only for 4 elements when xylene or isopropanol were used. Therefore, butanol was chosen for followed assays. Linearity was confirmed ($R^2 > 0.99$) between 0.1 and 100 µg kg^{-1} and working ranges of 1 – 15 µg kg^{-1} were selected. Precision was also assessed and satisfactory repeatability (<15%) were obtained for all elements at 7.5 µg kg^{-1} concentration level. Appropriate sensitivities were also observed with Limits of Quantification (LOQ) below 1 µg kg^{-1} for most analytes. Abundance elements demonstrated higher LOQs but in agreement with literature reports. Matrix effects were investigated comparing slopes of calibration curves constructed in both presence and absence of samples matrix and only ^{53}Cr, ^{24}Mg, ^{57}Fe, ^{55}Mn, and ^{44}Ca demonstrated significant interference. Subsequent trials will be conducted using Dynamic Reaction Cell (DRC) to minimize polyatomic interferences and the matrix effects. At the end of its analytical performance evaluation, this sample preparation method will be applied to the quantification of medicinal Cannabis extracts by ICP-MS.

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034 - DEVELOPMENT OF AN EASY AND ROBUST METHOD FOR THE DIRECT ANALYSIS OF MILK SOLUTIONS USING AEROSOL DILUTION AND MIP OES

João Victor S. de Araújo[a], Edmilson A. dos Santos[a], Thiago S. Santos[a], Ricardo J. Cassella[a], Christiane Duyck[a], Rafaella R. A. Peixoto[a*]

[a]Fluminense Federal University (UFF), Analytical Chemistry Department/Chemistry Institute, Niterói, RJ, Brazil, 24020-141
*e-mail: rafaellapeixoto@id.uff.br

Differently from other multielemental spectrometric techniques, such as ICP OES and ICP-MS, which employ argon plasmas, in the microwave induced plasma optical emission spectrometry (MIP OES) a nitrogen plasma is used. Nitrogen is more affordable than argon, once can it be extracted from the air in the laboratory or their proximities. However, nitrogen plasma (4220–5360 K) is colder than argon plasma (5000–10 000 K), making it less robust and more susceptible to interferences, which is an important drawback for the analysis of complex matrices[1]. Thus, samples with high organic contents, such as food, are normally treated by acid decomposition (reference method) previously to the analysis, consuming a large amount of reagents and time. In this work, a MIP OES method was developed for the analysis of milk after simple dilution. In order to make measurements in a more robust condition[2], a system of aerosol dilution (AD) was assembled and adapted in our laboratory. In this system, a nitrogen gas stream, called dilution gas (DG), was introduced between the spray chamber and the plasma torch, in a laminar flux (Figure 1).

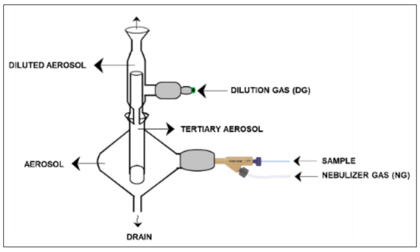

Figure 1: Aerosol dilution system assembled for sample introduction in MIP OES [self-authored].

For the dilution of the samples, formic acid was used in low volumes. The sample dilution factor, the mass of the sample, the quantity of formic acid, and the flow rates of the dilution (DG) and nebulizer gas (NG) were evaluated. The plasma robustness was monitored by using the N_2^+(391.439 nm)/OH (308.970 nm) ratio. In the optimized conditions, a dilution factor of 50-fold, 2% (v/v) of formic acid, a DG flowrate of 0.5 L min^{-1} and a NG flowrate of 0.7 L min^{-1} were selected. In these conditions, ratios of N_2^+/OH higher than 2 were obtained. The direct determination of Ca, K, Na, Mg, P, and Zn in milk samples was possible with adequate analytical performance (Table 1).

Table 1. Analytical performance parameters of the proposed method.

Analyte	Reference concentration/g kg^{-1}	Determined concentration/g kg^{-1}	Recovery/%	LOQ/mg L^{-1}
Mg	0.1 ± 0.01	0.1 ± 0.01	100%	0.006
Ca	1.08 ± 0.03	1.18 ± 0.06	109%	0.02
Na	0.72 ± 0.03	0.75 ± 0.04	104%	0.81
K	1.33 ± 0.05	1.29 ± 0.06	97%	0.37
P	0.94 ± 0.01	0.9 ± 0.2	99%	10.2
Zn* (mg L^{-1})	4.9 ± 0.4	3.5 ± 0.7	71%	0.12

To the best of our knowledge, this is the first MIP OES method that allows the analysis of a food sample without previous sample decomposition. The developed method is robust, more economically affordable, allows a high analytical frequency, and could be easily applied in routine analysis.

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035 - EVALUATION OF INTERFERENCES BY MICROWAVE-INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY IN FOOD SUPPLEMENT EXTRACTS FROM *IN VITRO* BIOACESSIBILITY PROTOCOLS

Thaís dos S. Berón[a*], Gustavo R. Bitencourt [a], Paola de A. Mello[a], Aline L. H. Müller[a], Rodrigo C. Bolzan[a]

[a]Universidade Federal de Santa Maria, Departamento de Química, Santa Maria, RS, Brasil, 97015- 900
*e-mail: paola.mello@ufsm.br

Food supplements are defined as products that complement the diet and provide essential nutrients for humans. Among the nutrients provided by food supplements, there are essential and non-essential elements. In order to access the knowledge about their nutricional action and potential toxicity, the determination of their bioaccessibility is important. Due to the composition of the extracts obtained in the bioaccessibility protocols and due to the reagent load required to carry out these protocols, matrix interferences in the determinations by spectrochemical techniques can be critical.[1] Thus, in view of this, mainly considering the large quantity of easily ionized elements (EIEs), as well as the complexity of the food supplement matrix, which contains some elements in relatively high concentrations, an evaluation of the interferences from the matrix in the determination of metals (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, La, Mg, Mn, Mo, Ni, Pb, Sr and Zn) by microwave-induced plasma optical emission spectrometry (MIP OES) was made after conducting an *in-vitro* bioaccessibility protocol (COST INFOGEST).[2] A sample of botanical-type dietary supplement was used. The total concentration of the elements was determined by inductively coupled plasma optical emission spectrometry (ICP OES) after microwave-assisted wet digestion. The COST INFOGEST protocol comprises the gastric and the gastrointestinal phase in only one stage (saliva + gastric fluid + intestinal fluid) and uses amylase, bile, HCl, KCl, KH_2PO_4, $MgCl_2$ $(H_2O)_6$, $(NH_4)_2CO_3$,$NaHCO_3$, NaCl, pancreatin, and pespsin. 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 (LOQs). When the elemental determination is performed by by spectrometric techniques a critical problem is the high concentration of EIEs elements, as Ca, K, and/or Na. However, high concentrations of those elements are common in the extracts generated after the assessment of bioaccessibility through COST INFOGEST protocol. The values found in the blank sample (containing only the reagents of the protocol) were 105 ± 4, 284 ± 9, and 3431 ± 443 mg L^{-1} for Ca, K, and Na, respectively. Thus, for the study of interferences, 100 µg L^{-1} of all analytes were added in various dilutions of a sample extract obtained after the COST INFOGEST protocol (1000, 500, 200, 100, 50, 20, 10, 5, 2 times, and without diluted). The results obtained were evaluated according to their relative intensities, comparing the values obtained in the various dilutions with that obtained for a solution containing the analytes in 5% v v^{-1} HNO_3. The results allowed to verify that elements such as Co and Cu did not suffer any effect, regardless of the dilution of the sample. The elements that had their signals intensified were: Cr and Sr (200-fold dilution), Mo, and Al (from 100-fold dilution) and La (from 5-fold dilution). On the other hand, the elements that had their signals suppressed were Mg (from 200-fold dilution), Zn (from 10-fold), Ag, Ba, Pb, and V (from 5-fold), and As, Be, Cd, Fe, Mn, and Ni (from 2-fold). Thus, in order to guarantee the accuracy of the results, a minimum dilution factor was defined, as follows: 10 times for Mn, Fe and Ba, 100 times for Sr and Al, 200 times for Cu and Mg and 500 times for Cr. In conclusion, MIP OES is a suitable alternative for the determination of the bioaccessibility of essential and non-essential elements in food supplements, being an alternative to the use of other techniques, such as the ICP OES, if necessary attention is devoted to the inherent matrix interferences.

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[CNPq, CAPES, ACS, and UFSM]

036 - TOTAL ARSENIC IN MUSCLE TISSUE OF *Zapteryx brevirostris*, *Dasyatis hypostigma* AND *Rhizoprionodon porosus* IN SOUTHEASTERN BRAZIL

Carlos José Malaquias da Silva[a*], Laís Nascimento Viana[b], Tatiana Dillenburg Saint'Pierre[b], Maria Cristina Canela[a], Cibele Maria Stivanin de Almeida[a]
[a]Universidade Estadual do Norte Fluminense Darcy Ribeiro, Laboratório de Ciências Químicas, Campos dos Goytacazes, Rio de Janeiro, Brazil, 28013-602
[b]Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química, Rio de Janeiro, Rio de Janeiro, Brazil, 22451-900
*e-mail: carlosjose@pq.uenf.br

Along the Brazilian coast, elasmobranchs are captured as bycatch and are popularly eaten as *cação* meat. The Shortnose Guitarfish, *Zapteryx brevirostris* (referred to as ZB from now on), and the Caribbean sharpnose shark, *Rhizoprionodon porosus* (RP), are frequently fished in southeastern Brazil. The ZB is classified nationally[1] and internationally[2] as Vulnerable (VU). Although it is not listed on the Brazilian fauna extinction risk list[1], RP is classified as VU by the IUCN Red List[2]. The Groovebelly Stingray, *Dasyatis hypostigma* (DH), is likewise not included in this Brazilian list[1]. The IUCN Red List[2], however, lists the species as Endangered. Because elasmobranchs are usually at higher trophic positions and are susceptible to the effects of bioaccumulation and biomagnification, they are receiving increased attention in the study of contaminants. Since *cação* is allowed for food in the state's public schools[3], concern over the consumption of these species is considerably stronger in the state of Rio de Janeiro. Arsenic is an element with high toxicity and can be found in organic and inorganic forms. Countries are developing legislation to set limits for the concentrations of this element allowed in food. For example, the Brazilian National Health Surveillance Agency (ANVISA) establishes a limit of 1mg kg^{-1} wet weight in fish. Therefore, this study aims to determine the amount of total As in muscle samples from three different species of elasmobranchs from the north region of Rio de Janeiro, southeastern Brazil. 150mg of each sample were added to 1.0 mL bidistilled HNO_3 at 100ºC for 4h. As concentrations were determined by ICP-MS. In the investigated species, there were high levels of As (Table 1), especially in the sole female of DH. Only RP had lower concentrations of As when compared to earlier assessments in Brazil. These results demonstrate the first investigation of elasmobranch As contamination in the state of Rio de Janeiro's northern region. It also illustrates the need for constant monitoring of As, a toxic element detrimental to human health, and has concentrations of total As beyond the limits set in Brazil.

Table 1. Comparisons between the total As levels determined in the present study and research conducted nationally for *Rhizoprionodon porosus*. All data are expressed as mg kg^{-1} wet weight. Missing information is denoted with dashes.

Data source	Species	Location	n	Sex	As (Min-Max)	As (means ± SD)
Present study	*Zapteryx brevirostris*	Rio de Janeiro, Brazil	2	Male	11.6-23.3	17.5 ± 6.7
			4	Female	8.71-29.4	19.1 ± 10.4
	Dasyatis hypostigma		4	Male	1.75-10.9	5.2 ± 3.8
			1	Female	36.8	37 ± 4
	Rhizoprionodon porosus		3	Male	1.10-1.73	1.44 ± 0.29
			1	Female	1.40	1.40 ± 0.26
Maciel et al.[3]	*Rhizoprionodon porosus*	Rio de Janeiro, Brazil	20	Female	4.00-10.4	6.32 ± 2.41
				Male	3.96-12.8	7.21 ± 2.10
Souza-Araujo et al.[5]	*Rhizoprionodon porosus*	Pará, Brazil	5	-	2.19-15.4	9.58 ± 5.27
Souza-Araujo et al.[6]	*Rhizoprionodon porosus*	Amazonas, Brazil	2	-	6.5-13	9.78 ± 1.07

SD = Standard Deviation

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[FAPERJ, CAPES, CNPq, UENF, GPEQ]

037 - LONG-TERM STABILITY OF GREEN COFFEE BEANS REFERENCE MATERIAL ASSESSED BY TQ-ICP-MS

Cláudio Luís Gonzaga*, Elisabete A. De Nadai Fernandes, Gabriele Rossini Moreira, Márcio Arruda Bacchi, Silvana Regina Vicino Sarriés, Maria Isabel Vega Martinez

University of São Paulo (USP), Nuclear Energy Center for Agriculture (CENA), Radioisotopes Laboratory (LRi),
Avenida Centenário 303, 13416-000 Piracicaba-SP, Brazil
*e-mail: claudio@cena.usp.br

Metrological traceability is a fundamental pillar in the field of analytical chemistry. The reliability and comparability of chemical measurement results are essential for the most diverse areas, ranging from food safety to assessment of environmental impacts. In this context, certified reference materials (CRM) are a critical component of the laboratory's quality system, from the calibration of measurement systems to the validation of methods, ensuring accuracy in testing[1]. In 2018, at the Radioisotopes Laboratory, CENA/USP, as part of a postdoctoral research, the reference material of organic coffee beans CRM-Agro C1007a - Café Verde was produced, meeting a demand from the Brazilian coffee sector. The chemical characterization of the material to assign the reference values was carried out in 2018 using 3 analytical techniques: NAA (Br, Ca, Co, Cs, Fe, K, Na, Sc, Sb, Rb, Zn), ICP-OES (P, S, Ca, K, Mg) and ICP-MS (B, Ba, Co, Cu, Mn, Rb, Sr). In 2023, the Radioisotopes Laboratory carried out the long-term stability study to assess the material's property values 5 years after production. Six determinations were performed for each analyte of interest under reproducible conditions[2]. The samples were submitted to the procedure of digestion in an acid medium assisted by microwave radiation, using HNO_3 and H_2O_2 in a closed system, at 200 °C and 1800 W of power. For analytical quality control, NIST certified reference materials were used: SRM 1568b Rice Flour, SRM 1570a Trace Elements in Spinach Leaves and SRM 1573a Tomato Leaves. The chemical elements B, Ba, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, P, Rb, Sr and Zn were determined by inductively coupled plasma mass spectrometry with triple quadrupole (TQ-ICP-MS). The mass fraction results obtained were consistent with the reference values of the characterization process in 2018, showing recoveries between 80-102% for all determined analytes, ensuring the stability of the reference material CRM-Agro C1007a - Café Verde over 5 years. This characteristic of the material was corroborated by the results obtained in the collaborative exercise CRM Agro CV_012021, promoted by CRM-Agro Reference Materials for Agriculture, Livestock and Toxicology at CENA/USP, with the participation of 56 national and international laboratories, which used 14 analytical techniques. Assessment of long-term stability is crucial for evaluating reference material lifetime for accurate, reliable and metrologically traceable analyses.

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038 - PRELIMINARY EVALUATION OF MINERAL BIOVAILABILTY IN SAMPLES OF *Pereskia acuelata* (ORA-PRO-NÓBIS), BY GASTROINTESTINAL EXTRATION

Zanata B.Amorim[1,2], Suellen G. Cordeiro[2], Maria Tereza W. D. C. Lima[2], Hildedardo S. França[1], Geisamanda P. Brandão[2]

[1]D-Bio, (IFES – VV) - Federal Institute of Espírito Santo, Brazil.
[2] Atomic Spectrometry Laboratory, Chemistry Departament/Federal University of Espírito Santo, Brazil.
*e-mail: zanata.amorim@ifes.edu.br

The unconventional food plant (Panc), *Peraskia acuelata* popularly known as ora-pro-nóbis or poor man's meat, is a Cactaceae that has a high content of proteins, vitamins and minerals, and is widely used to combat malnutrition [1]. However, a poorly studied property is the composition and bioaccessibility, which is the fraction of an element that is soluble in the gastrointestinal tract or in the lungs and available for absorption. It is known that the cacti of the genus *Pereskia* have important nutritional qualities related to the presence of essential minerals [2], and that the use of mineral concentrates through bran or powder from leaves, flowers or fruits, act as a form of supply of essential nutrients to maintain health, which can help prevent and combat pathologies arising from dietary risk [3]. For the initial evaluation of *Peraskia acuelata* used in this work, an acid decomposition assisted with microwave radiation using HNO3 and HCl was carried out. Subsequently, the analysis of Al, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn was carried out by mass spectrometry with a collusion cell. The figures of merit were verified and the working range established from 0,05 $\mu g.L^{-1}$ to 10 $\mu g.L^{-1}$. The linearity evaluated from the coefficients of determination, obtained during the construction of the analytical curves, in the determination of elements that was greater than 0.999 for all elements. The limit of detection and quantification values obtained were adequate to detect and quantify the analytes in the different calibration strategies. To evaluate the accuracy of the method, the certified reference material (NIST-1547) – Peach leaf and addition and recovery tests were used. For the evaluation of bioaccessibility, an in vitro digestion test was performed using the physiologically based extraction method (PBET), which simulates the effect of gastrointestinal conditions in a human being [4]. In this way, this study tends to add mineral/nutritional information from this Panc, which may lead to greater consumption and thus the fight against food risk.

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[IFES/D-Bio, PPGQUI/UFES, LabPetro, FAPES, CAPES, PMV, UNIMETRO/IASES, SEBRAE, SEAG, MPES and SEJUS]

039 - METALLIC PROFILING OF MOST CONSUMED SEAWEEDS IN URUGUAY

Nataly Rodríguez[a,b*], **Fiorella Iaquinta**[b], **Ignacio Machado**[b]

[a]Programa de Posgrado en Química, Facultad de Química, Universidad de la República, Montevideo, Uruguay
[b] Grupo BIOESP, Química Analítica, Facultad de Química, Universidad de la República, Montevideo, Uruguay
*e-mail: natalyr@fq.edu.uy

Seaweeds have a rich chemical composition, including vitamins, minerals, and antioxidant compounds, that make them a very promising functional food. However, they pose the ability to bioaccumulate metals and metalloids that may contribute to their nutritional value in some cases, but may also increase the associated toxicological risk, depending on the element that is accumulated. Although some seaweeds species have been made popular in Uruguayan culinary preparations, these products are not properly controlled nor regulated. In this regard, it is important to start surveillance programs that assure the safe consumption of these products and promote its use in the food industry.

In this context, the present study focused on the development and validation of an analytical method, aiming to characterize national seaweeds in terms of their metal content. For sample preparation, a microwave assisted acid digestion using a CEM Mars 6 digestor was performed. Briefly, 0.5 g of sample and 10.0 mL of 3 mol L^{-1} nitric acid (HNO_3) were added in the reaction vessel. The program employed was as follows: temperature was increased to 200 °C in 15 min and held for 10 min, while the maximum pressure equalled 500 psi, and power varied between 400 and 1800 W. The use of dilute HNO_3 during the digestion process aligned with the principles of Green Analytical Chemistry, minimizing the production of acid residues. After appropriate dilution, the resulting solutions were used for the sequential determination of chromium (Cr), iron (Fe), manganese (Mn), nickel (Ni), copper (Cu) and zinc (Zn) by Microwave Induced Plasma Optical Emission Spectrometry (MIP OES), using an Agilent 4210 spectrometer equipped with a double-pass glass cyclonic spray chamber system and a standard torch. The plasma gas flow was fixed at 20 L min^{-1} and the auxiliary gas flow at 1.5 L min^{-1}. The analytical lines were 425.433 nm (chromium), 371.993 nm (iron), 403.076 nm (manganese), 431.476 nm (nickel), 324.754 nm (copper) and 213.857 nm (zinc).

The method was validated according to Eurachem Guide. The figures of merit evaluated were linear range, limit of quantification, precision, and trueness. The linear range was demonstrated up to 13 µg L^{-1} for Cr, up to 3 mg L^{-1} for Fe, Mn, and Zn, up to 2 mg L^{-1} for Ni, and up to 60 µg L^{-1} for Cu. Limits of quantification were 0.043, 0.45, 0.09, 0.25, 0.91, 0.67 mg kg^{-1} for Cr, Fe, Mn, Ni, Cu and Zn, respectively. For trueness and precision evaluation the certified or indicative value from standard reference material strawberry leaves LGC7162 was used. No significant differences were found at the 95% confidence level between the certified and obtained values. Precision (repeatability) expressed as relative standard deviation was better than 11.2 % in all cases.

The validated method was subsequently applied to the analysis of six edible commercial seaweed samples (*Ulva spp., Saccharina japonica; Undaria pinnatifida; Sargassum fusiforme;* and two different samples of *Porphyra umbilicales L.)* available in local markets of Montevideo, Uruguay. The obtained results ranged between not detectable - 2.3 mg kg^{-1} (Cr), 52.7 - 466.8 mg kg^{-1} (Fe), 3.2 – 90.6 (Mn), not detectable – 6.3 (Ni) 1.4 – 17.6 (Cu), and 6.1 – 69.8 (Zn), which are in accordance with previous results obtained in the region[1]. These constitute the first results in edible seaweeds samples in Uruguay. This novel information will be It will be the starting point to perform more in-depth studies from the nutritional and toxicological point of view.

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[PEDECIBA-Química, Agencia Nacional de Investigación e Innovación]

040 - EVALUATION OF POSSIBLE MATRIX EFFECTS IN THE ANALYSIS OF WINES BY MIP OES

Charlie G. Gomes[a*], Jessica da R. Porto[a], Yasmin R. Bloedorn[a], Mariana M. da Cunha[a], Wiliam Boschetti [a], Anderson S. Ribeiro[a], Mariana A. Vieira[a]

[a]Federal University of Pelotas Graduate Program in Chemistry, Center for Chemical, Pharmaceutical and Food Sciences, Capão do Leão, Rio Grande do Sul, Brazil, 96160000.
*e-mail: charlieggomesii@gmail.com

Wine is one of the oldest and most appreciated beverages by humanity. In addition to its cultural and social significance, wine is also of great scientific interest due to its matrix complexity and the numerous variables involved in its production. Therefore, its chemical composition can result in the presence of elements essential to the human organism such as K, Ca, Mg, Fe, F, I, Cu, Mn, Mo, Se, and Zn.[2] In addition to that, the composition can be an indicative of where the wine was originated, which in some cases can drastically change the final added value of the product. As a result, the search for easier and more practical methods of analysis is important.[1,3] There are reports in the literature measuring concentrations of elements in wines, using direct analysis, but a few studies reporting the use of microwave-induced plasma optical emission spectrometry (MIP OES), a faster, cheaper, and reliable alternative for this sort of measurements.[3,4] The presence of high levels of organic matter can result in several interferents and, the matrix effect, can generate noises, overlapping instrumental responses, and causing instability in the plasma and also promote mechanical deterioration. Thus, the objective of this work was to evaluate the possible matrix effects of red wine in the preparation of calibration curves for multi-elementary analysis using the MIP OES technique. Three calibration curves in different conditions were prepared and the calibration range for the analytes Al, B, Ba, Cd, Co, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, Pd, Sb, Si and V was 0.5 to 2.5 mg L^{-1}. Curve (1) was prepared in aqueous medium, without the sample, only with standard and ultrapure water. Curve (2) was prepared using a sample after undergoing chemical treatment, using nitric acid and hydrogen peroxide, and finally, curve (3) was performed under wine sample diluted with ultrapure water and addition of standards. To analyze the results, a t-test was performed to evaluate whether there is a significant difference between the angular coefficient values obtained for each analyte in the three types of calibration curve investigated. Table 1 displays the relative deviations among the found slope coefficients, where values below 10% can be observed, indicating a considerable linearity among the obtained lines.

Table 1. Relative standard deviations among the angular coefficients for each analyte.

Analyte	Al	B	Ba	Cd	Co	Cu	Fe	Li
RSD	6,08	9,39	4,90	5,06	8,03	8,12	4,44	14,64
Analyte	Mn	Mo	Na	Ni	Pd	Sb	Si	V
RSD	7,37	9,49	3,12	8,80	7,10	4,21	7,66	7,21

RSD: Relative standard deviation (%)

As a result, it was found that the calibration curves are parallel to each other, indicating that, despite the organic content of the sample, the MIP OES spectrometer's plasma was sufficient to overcome potential interferents, meaning that the sample matrix does not influence the analytical response, and therefore, the curve in an aqueous medium can be used. In this way, analyte concentration measurements in wine samples can be performed using the diluted sample or after some type of sample preparation.

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[INCTAA, CNPq e CAPES]

041 - CHLORIDE IN FUEL ETHANOL BY ICP-OES AFTER MINIATURIZED SAMPLE PREPARATION

Flávia F. Oliveira[a], Ana Luiza G. Mendes[a], Alice P. Holkem[a], José Neri G. Paniz[a], Paola A. Mello[a*]

[a] Universidade Federal de Santa Maria, Chemistry Department, Santa Maria, RS, Brazil, 97105-900
*e-mail: paola.mello@ufsm.br

The National Agency for Petroleum, Natural Gas and Biofuels (ANP) establishes the specifications for ethanol to be used as a fuel. Among the required quality control parameters, the chloride content is a critical issue because, even in low concentrations, it may drastically reduce the useful life of vehicle spare parts (such as engine, fuel pipe, and tank due corrosion). The, ANP establishes a maximum of 1 mg kg^{-1} of chloride in hydrated fuel ethanol. According to ASTM D7319 (ANP NBR 10894) the quantification of chloride is carried out using ion chromatography (IC).[1] In spite of its suitability, IC is relatively time consuming and presents relatively high cost to be used as a laboratory routine technique. Spectrometric techniques are common choices for contaminants in fuels, such as gasoline, diesel/biodiesel oil, and ethanol. However, they present some drawbacks for chlorine, mainly the poor limits of detection and matrix interferences due to the limitations to carry out effective digestions.[2] In this work, an extraction protocol was investigated as sample preparation for further chlorine determination in fuel ethanol by inductively coupled plasma optical emission spectrometry (ICP-OES). A spectrometer (Spectro Ciros CCD®, Spectro Analytical Instruments, Germany) equipped with a cross-flow nebulizer coupled to a double pass-Scott type spray chamber was used. As sample preparation strategy, a dispersive liquid-liquid microextraction (DLLME) method was optimized. For comparison, chloride determination was performed by IC (819 IC Detector model, Metrohm, Switzerland) with conductivity detection (according to ASTM D7319 standard method). Initially, several solvents were evaluated as extractant (toluene, chlorobenzene, hexane, cyclohexane, xylene, methanol, dichlorobenzene, carbon tetrachloride, and tetrachlorethylene) and as dispersant (1-undecanol, octanol, dichloromethane, tetrahydrofuran, dimethyl sulfoxide, chloroform, acetone, and acetonitrile). Based on the droplet formation, a mixture of hexane and cyclohexane (1:1, v v^{-1}) was defined. For extraction, 1 mL hexane and 1 mL cyclohexane were added to 2 mL of fuel ethanol containing 1% of sodium acetate (to improve the phase separation as recommended by the literature[3]). After dispersing, a centrifugation step (2 min at 5000 rpm) was carried out (model Sigma 3K30 centrifuge, Germany). The sedimented phase was collected using a syringe, transferred to a 15 mL vessel, heated in a water bath (90 min at 100 ºC) and made up to 1-5 mL with ultrapure water. A spiked sample (5 mg kg^{-1} of Cl^{-}) was used to evaluate the method accuracy. The obtained results showed good accuracy in spite of the precision was poor (about 29%), probably due to contamination. The limit of quantification (LOQ) was 0.75 mg L^{-1} for ICP-OES and 0.15 mg L^{-1} for IC.

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[CAPES, CNPq, PRH ANP 52.1 and UFSM]

042 - MULTI-ELEMENTAL ANALYSIS OF TOXIC METALS IN SALIVA AND HAIR OF PROFESSIONAL MUSICIANS

Vanessa dos Santos Oliveira[a,b*], Rafael C. C. Rocha[b,c], Tatiana D. Saint Pierre[b]

[a]UFRJ, Licenciatura em música/Escola de Música, Rio de Janeiro, RJ, Brazil, 20031-170
[b] PUC-Rio, Departament Química, Rio de Janeiro, RJ, Brazil, 22451-900
[c] FIRJAN, IST Química e Meio Ambiente, Rio de Janeiro, RJ, Brazil, 20271-031
*e-mail: vanessaoliveiramecanica@gmail.com

The musician's health, since the beginning of his journey in the woodwind and brass sections in orchestras, is neglected, both in the external issue due to Work-Related Musculoskeletal Disorders and Repetitive Strain Injury (L.E.R), and in the internal issue involving biochemicals factors such as contamination by copper (generates vomiting, diarrhea, and seizures), zinc (causes abdominal pain, nausea, vomiting, and gastric ulcer), silver (causes changes in the metabolism of copper and selenium), tin (causes problems in the respiratory and gastrointestinal systems), nickel (causes rhinitis, sinusitis, and dermatoses) and chromium (causes lesions on the skin, mucous membranes, and lower airways), which depreciate the musician's working health, and may cause dysfunctions and even serious illnesses. In this work, we intend to verify the levels of metals and other toxic elements in the saliva and human hair of professional musicians, with the aim of understanding the effects of using wind instruments on the musician's occupational health. In this research, the target audience consisted of musicians who experience a professional musical career, whose interaction with their daily work tool is very intense (between 2 h and 4 h / day of rehearsal, at least). Routines for studying the repertoire and techniques that include the positioning of the mouth on the instrument, the fingers on the instrument, the way the air column is formed from inside the instrumentalist to the instrument, the amount of saliva produced and the cleaning of the instrument moments before and after the presentations were observed, as well as the structure of the instruments, which was also highlighted in this investigation, since corrosion in the instruments can indicate possible exposure. Qualitative analyzes were performed using questionnaires, and quantitative analysis, through the multielemental determination in saliva and hair samples from musicians, using inductively coupled plasma mass spectrometry (ICP-MS). Saliva samples were analyzed after acid decomposition on a heating plate: approximately 0.05 g of the sample were digested with 0.5 mL of bi-distilled conc. 65% HNO_3 and 0.2 mL H_2O_2 for 6 h, and then, made up to 10 mL with ultrapure water. The preparation of the saliva samples was adapted from the US EPA 3052 and the ICP-MS analysis followed the US EPA 6020. The hair samples were analyzed following the protocol established at Labspectro (PUC-Rio) for the capillary mineralogram. The accuracy was evaluated through the analysis of a certified hair sample and by recovery tests. The recovery results obtained for saliva samples were between 80% and 120% of the added concentrations. The results obtained for saliva samples collected before and after musical practice were compared and significantly higher concentrations were obtained for copper, nickel, iodine, lead, silver, gold, and zinc, which may indicate exposure of musicians to these elements, which may be present in the metal alloys of wind instruments that are in contact with the musician's mouth during rehearsals. Interestingly to observe that the concentrations of some of these elements in the musicians' hair were also significantly higher than the reference values.

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[UFRJ, PUC-Rio, CAPES, FAPERJ and CNPq]

043 - INVESTIGATION OF POSSIBLE SOURCES OF PARTICULATE MATTER USING CHEMICAL ELEMENTAL DETERMINATION

Bruna M. Dalfior[a], Carolina S. Provete[a*], Beatriz P. Lima[a], Rafael Mantovaneli[b], Renato Neto[c], Maria Teresa W. D. C. Lima[a], Geisamanda P. Brandão[a].

[a] Atomic Spectrometry Laboratory, Chemistry Departament/Ufes, Vitória, Espírito Santo, Brazil, 29075-910
[b] Laboratory Coordination/Ifes, Alegre, Espírito Santo, Brazil, 29520-000
[c] Oceanography Department/Ufes, Vitória, Espírito Santo, Brazil 29075-910
*e-mail: cprovete@hotmail.com

Atmospheric pollution is a phenomenon caused mainly by human activities and contributes significantly to the deterioration of air quality[1]. In Brazil, air quality is monitored according to the legislation described by CONAMA (National Environmental Council). However, some pollutants found in the composition of particulate matter (PM), such as As, Cd, Fe, Ni, Sn, V and, Rare Earth Elements (REE), among others, can cause damage to human health and are not mentioned in the legislation. Therefore, it is necessary to monitor and characterize the PM in terms of elemental composition, searching for associations with the possible anthropogenic sources that contribute to this material in the atmospheric air. To evaluate this, the following particulate matter samples were evaluated: PM with 2.5 (PM2,5) and 10 (PM10) µm of diameter, total suspended particles (PTS) and settled dust (PS). The samples evaluated as possible sources of PM were: asphalt, cement, iron ore (with and without suppressive resin), and sand. The sample preparation procedure used HNO_3, HCl and HF and heating by microwave radiation. In addition, PM samples (PM2,5 PM10, PTS and PS) were subjected to the same sample preparation procedure. To verify the methodology, the analytical figures of merit linearity (R^2), limit of detection (LoD), limit of quantification (LoQ) and analyte recovery were evaluated. According to the criteria of DOC-CGCRE (Inmetro), the proposed method showed good analytical figures of merit. The concentrations of Al, As, Cd, Co, Cr, Cu, Mg, Mn, Mo, Ni, Pb, Zn and REE (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Sc, Sm, Tb, Th, Tm, U, Y, and Yb) were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The highest concentrations were observed for cement and asphalt samples, with considerable differences observed between some elements. To verify the correlations between the presence of the elements in the samples of the possible sources and in the samples of PM, a Principal Component Analysis (PCA) was performed. To simplify the visualization of the results, two groups were formed: major elements (Al, As, Cd, Co, Cr, Cu, Mg, Mn, Mo, Ni, Pb and Zn) and REE. For the first group, most of the samples (PM and sources) with low concentrations of these elements were grouped together. The exception was the sample of PM10-E4 which was collected at a station close to an intense traffic of vehicles. The same behavior with PM10-E4 was observed for the PCA with REE, in addition to the separation of asphalt and cement samples due to high contents of Dy, Sc, Tb, La, Gd, Eu, Ce, Nd and Sm and Ho, Er, Y, Tm, Yb, Th and Lu, respectively. The PCA with REE showed a correlation between the samples of PM10-E4 and asphalt, which can be explained by the high vehicle traffic in the vicinity. Considering all the results, asphalt and cement were strongly influenced by REE. On the other hand, the PM samples (PM2,5, PM10 and PTS) were grouped together and influenced mainly by Al and Zn, while PS was influenced by Ni and Mn. The similarities found in the PCA among PM samples and iron ore and sand samples could infer that these were the main sources of the elemental composition of PM samples. Chemometrics proved to be an important tool in the analysis of the results. However, there is a need for further studies, as only a small number of possible sources of PM have been used.

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[FAPES, CNPq, Petrobras, CAPES, PGGQUI/Ufes and LabPetro/UFES]

044 - TRACKING THE IONIC AND NANOPARTICULATED TITANIUM RELEASED *IN-VIVO* FROM METAL DENTAL IMPLANT USING (SINGLE-PARTICLE)-ICP-MS

Diogo Pompéu de Moraes[a*], Sara Gonzáles-Morales[b], Jorge Toledano-Serrabona[c],
M. Ángeles Sánches-Garcés[c], Mario Corte-Rodríguez[b], Jörg Bettmer[b], María Montes-Bayón[b]

[a] Universidade Federal do Rio Grande do Sul (UFRGS), Institute of Chemistry, Porto Alegre, RS, Brazil, 91501-970
[b] University of Oviedo, Department of Physical and Analytical Chemistry, Oviedo, Spain, 33006
[c] University of Barcelona, Department of Oral Surgery and Implantology, Barcelona, Spain, 08907
*e-mail: diogo.moraes@ufrgs.br

Despite their wide use and tolerability, titanium-based prosthetic implants may develop some problems leading to implant rejection. In particular, dental implants are especially prone to bacterial growth and infection causing several implant-related diseases, such as peri-implantitis. Implantoplasty consists of polishing and smoothing the dental implant exposed surface, reducing bacterial adhesion, and facilitating hygiene by the patient. However, implantoplasty produces a great amount of metal debris, part of them macroscopic that can be easily removed from the surrounding tissues, but part of them in the micro- and nanometer scales, which are impossible to completely eliminate from the tissues and will stay there after the treatment, affecting the surrounding tissues and potentially producing systemic effects.[1] In this study, ICP-MS was applied to study the release and biodistribution of Ti, Al and V from implant debris implanted in rats, after acid-digesting the blood, liver, spleen, lung and brain of the animals. For this aim, sample preparation for total Ti, Al, and V determination was carefully optimized using microsampling inserts to minimize dilution during the acid attack of the lyophilized tissues. The presence of a small percentage (0.005%) of hydrofluoric acid revealed to be mandatory for quantitative recovery (> 85%) of the ionic Ti in the spiked samples analyzed using ICP-TQ-MS. Additionally, since implantoplasty may also produce nanoparticulate debris, single-particle-ICP-MS (sp-ICP-MS) and other complementary techniques were used to search and characterize titanium nanoparticles in the different tissues that may have been transported from the implant site. In these organs, the possible presence of Ti-containing nanoparticles mobilized from the dental implants was tested using enzymatic digestions. Applying proteinase K in the presence of sodium dodecyl sulfate (SDS) as solubilization media resulted in better reproducibility and highest recoveries. The presence of Ti-containing nanoparticles was observed in all the analyzed tissues, however, differences on the Ti mass per particle were found between the blanks and the enzymatic digested tissue and between control and experimental animals in some organs. Although the significant content of nanoparticulated Ti in control rats from environmental sources hampered the correct determination of the nanoparticles with an origin in the implanted debris, the mass of Ti in the obtained events seemed to point out the presence of different Ti nanoparticles in brain and spleen samples distinguishable to those in the control counterparts. The removal of this kind of particles from the solutions used for the sample preparation represents the next challenge to achieve such kind of studies. For Al and V concentrations in the different organs no significant differences were observed between control and experimental groups with a confidence level of 95% (*t*-test, $p<0.05$), with average concentration of 1000 and 10 ng g^{-1}, respectively.

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[CAPES/Print and CNPq]

045 - ELMENTAL ANALYSIS AS A BASIS FOR THE DESIGNATION OF ORIGIN OF BRAZILIAN RED WINES.

Cibele Maria Stivanin de Almeida[a*], Tatiana Dillenburg Saint'Pierre[b], José Marcus de Oliveira Godoy[b]

[a]Universidade Estadual do Norte Fluminense Darcy Ribeiro, Laboratório de Ciências Químicas, Campos dos Goytacazes, Rio de Janeiro, Brazil, 28013-602
[b]Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química, Rio de Janeiro, Rio de Janeiro, Brazil, 22451-900
*e-mail: cmsa@uenf.br

The elemental determination of red wines was performed to discriminate Brazilian wines by region of origin (Campanha Gaúcha n=10, Serra Gaúcha n = 30, Vinhedos Valley n = 30 and the São Francisco Valley n = 10) in commercial samples of fine red wine for evaluation of possible fingerprints already reported in the literature and investigation of the quality of these wines. Data were obtained by inductively coupled plasma optical emission spectrometry (ICP OES) and mass spectrometry (ICP-MS). The wine samples were decomposed following a simple gravimetric method: 1 g of wine and 1 g of concentrated HNO_3 was weighted in polypropylene tubes fifty milliliters and this mixture reacted for twenty-four hours in a sealed tube. After this time, the solutions were adjusted to ten grams with the addition ultrapure H_2O. The preparation of the wines was performed in triplicate. Aliquots of this solution were twenty times diluted to analysis by ICP-MS semiquantitative manner using Rh as an internal standard and one hundred times to ICP OES analysis. The evaluation by multivariate statistics involving commercial red wine samples showed Al, Sc, Fe, Ba, Mg and P elements as better choice for fingerprinting, different from those already described for Brazilian red wines obtained directly from wineries already reported in the literature[1]. These elements together clearly define the southern regions (Serra Gaucha, Vinhedos Valley and Campanha Gaúcha) of the wines of the northeast - São Francisco Valley. Following the analysis of the factors, we have that Al, Fe and Sc separate the Serra Gaúcha wines from the wines produced in Vinhedos Valley and in Campanha Gaúcha. These two regions have very similar Ba, Mn and P contents, which is why it is not possible to make a distinction. Finally, the wines from the São Francisco Valley present such close concentrations that they were an extremely homogeneous group.

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[CAPES, CNPq, UENF, PUC-Rio, GPEQ]

046 - DIRECT DETERMINATION OF Sr ISOTOPES IN ROCK BY LA-ICP-MC/MS

Laís N. Viana[a*], Rafael C. C. Rocha[a,b], Rafael C. M. Telles[c], Cleverson J. F. Oliveira[d], Christiane B. Duyck[e], Tatiana D Saint'Pierre[a], Mauro C. Geraldes[c]

[a]Pontifical Catholic University of Rio de Janeiro, Department of Chemistry, Rio de Janeiro, RJ, Brazil, 22451-900
[b]Industry Federation of the State of Rio de Janeiro, Rio de Janeiro, RJ, Brazil, 20270-002
[c]Rio de Janeiro State University, Dept of Mineralogy and Igneous Petrology, Rio de Janeiro, RJ, Brazil, 20550-013
[d]Leopoldo Américo Miguez de Mello Research and Development Center, Rio de Janeiro, RJ, Brazil, 21941-915
[e]Federal Fluminense University (UFF), Department of Chemistry, Rio de Janeiro, RJ, Brazil, 24020-141
*e-mail: laisnviana@yahoo.com.br

Natural processes fractionate Sr isotopes and alter their relative abundances in rocks, for example, with an increase in the abundance of ^{87}Sr with the age of the rock, due to the radioactive decay of ^{87}Rb into ^{87}Sr. Then, the Sr isotope ratio can be used in geochronology and is a useful geochemical tracer.[1] Determining isotopes for geochronology studies requires a high-resolution technique, which separates and quantifies isotopes with high precision, such as in inductively coupled plasma multi collector mass spectrometry (ICP-MC/MS). This work developed a method for determining Sr concentrations and isotope ratios from crude oil-related rock samples. A fragment was manually separated from each of the 40 rock samples and about 5 fragments were mounted in epoxy and stood for 24 h at 60 ^{o}C in a stove. The mounts were then submitted to scanning electron microscopy (SEM) imaging, employing a Quanta 250 microscope, followed by analysis using a Neptune Plus (Thermo Scientific, USA) Laser Ablation ICP-MC/MS (LA-ICP-MC/MS). All Sr isotopes (^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr) were monitored, as well as the ^{85}Rb to correct the isobaric interference of ^{87}Rb on ^{87}Sr. Ten replicates of each sample were obtained, with 100 readings each. Data acquisition was performed using a bracketing method, where blank and reference material data were used to correct the analytical data of unknown samples. The concentrations of Sr were calculated against a calibration with standard reference materials (NIST SRM 610 and NIST SRM 612, synthetic glass reference materials). The method's accuracy was checked by the analysis of the NIST SRM 688, which was prepared by fusion with lithium borate in an oven.[3] The measured Sr concentration was 177.9 ± 10.5 mg kg^{-1}, which corresponds to 111 % of the certified Sr concentration (169.2 ± 0.7 mg kg^{-1}). In addition, the NIST SRM 688 was also analysed by ICP-MS after digestion with nitric acid in a digester block (Berghoff, Germany). About 0.5 g of the sample was added with 9.0 mL of bi-distilled HNO_3 and submitted to a temperature program. Then, the solution was transferred to a Falcon tube and made up to 50 mL with ultrapure water. The solution was analysed against a 6-point calibration curve using a NexIon 300X (low resolution) ICP-MS spectrometer (PerkinElmer, USA). The obtained Sr concentration (128.2 ± 4.4 mg kg^{-1}) corresponds to 76 % of the certified concentration. Recovery results for the NIST SRM 688 are promising as they indicate that the direct analysis by LA-ICP-MC/MS, which is more environmentally friendly, allows the determination of the Sr isotope ratios with high precision and minimum sample treatment.

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047 - MULTIELEMENT DETERMINATION IN WHOLE BLOOD BY ICP-MS USING MULTI-ISOTOPE CALIBRATION

**Poliana Borges de Oliveira[a*], Maiara Krause[a], Luiza Valli Vieira[a],
Geisamanda Pedrini Brandão[a], Alex Virgilio[b], Maria Tereza Weitzel Dias Carneiro[a]**

[a]Departament of Chemistry, Federal University of Espírito Santo, Vitória, ES, Brazil, 29075-910
[b] Center for Nuclear Energy in Agriculture, University São Paulo, Piracicaba, SP, Brazil, 13416-000
*e-mail: poliana.oliveira@edu.ufes.br/polianaborges05@hotmail.com

This study proposes the application of multi-isotope calibration (MICal) method for Cd, Cr, Hg, Mo, Ni, Pb, Se, Sn and Zn determination in whole blood using inductively coupled plasma mass spectrometry (ICP-MS). MICal is a calibration strategy for ICP-MS, based on the concept of monitoring various isotopes of the same analyte in a single run and utilizing multiple signal analyses to enhance accuracy. MICal employs a matrix matching strategy, utilizing only two calibration solutions per sample, which improves accuracy and sample throughput compared to the standard addition strategy. In MICal, solution A comprises a proportion of the sample and a standard solution containing the analytes, while solution B consists of a proportion of the sample and a blank[1]. MICal allows for the evaluation of the optimal standard concentration to be added to the solution. Due to the complex characteristics of the matrix, the proportion used to prepare the MICal solutions was 5% (volume/volume) of the sample and 95% (volume/volume) of standard or blank.

This optimization is crucial in achieving better linearity of the curve, as improved responses are obtained when the slope approaches 0.5.[2] Another characteristic of MICal is its ability to identify outliers, that is, potential isotopes that may exhibit uncorrected interferences. These outliers can then be removed, resulting in enhancements in the linearity of the curves and the coefficient of determination. In the study, certain elements (Cd, Cr, Hg, Ni, Se, and Zn) had to undergo the removal of some of their isotopes due to the presence of polyatomic and isobaric interferences. This removal resulted in a significant improvement in the represented curve, which highlights an advantage of MICal compared to strategies that use least squares to construct the analytical curve. With MICal, outliers can be easily identified and removed.

A comparative study of the performance of MICal with the external calibration (EC), internal (IS), and standard addition (SA) strategies was carried out, using a control material Clinchek Whole blood Level III (Recipe – Germany), where accuracy, precision, linearity, and limits of detection and quantification were evaluated. The results were evaluated by statistical tests, such as ANOVA, Fisher's test and Tuckey's test with 95% significance and MICal performed better than CE and IS, and similar to SA, with the advantage of needing only two solutions per sample, while SA requires the preparation of a curve per sample, generating longer analysis time, a greater amount of solution, being costlier, and using more reagents.

Another remarkable aspect is the application of MICal in diluted samples. In previous studies[3-5], where MICal was tested, the samples underwent a decomposition process, making them easier to analyze. In this study, it was proposed to analyze whole blood samples using a simple dilution, enabling the evaluation of MICal's performance when dealing with samples of complex matrices. Based on the recoveries, which ranged between 70% and 110% for the determined analytes, it can be confidently stated that MICal is an effective strategy to be applied in this type of sample preparation.

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[NCPQ, PPGQUI/Ufes, CAPES, CNPq, Tomasi, FAPESP and LabPetro/Ufes]

048 - USE OF MICRO-PLASMAS FOR METAL SPECIATION

Zoltan Mester[a*]

[a]NRC Canada, Ottawa Canada
*e-mail: zoltan.mester@nrc.ca

Speciation applications often require the collection of not only elemental but also molecular and structural information. Analytical use of micro plasma based sources enables the direct interrogation of solid, liquid and gaseous samples, multi phase systems with high dissolved material content, often in extreme pH conditions. The robustness exhibited by plasma ion sources offers a unique alternative to conventional electrospray (ESI) / atmospheric pressure chemical ionization (APCI) MS insources which are not able to tolerate these extreme conditions.

In this lecture analytical use of various micro-plasma ion sources will be discussed. Examples of the use of Direct Analysis in Real Time (DART) and Atmospheric Pressure Glow Discharge (APGD) ionization in conjunction with orbitrap mass spectrometry for the detection of organometallic compounds and metal hydrides and intermediates will be presented. Mass spectral behaviour including in source fragmentation, adduct formation, oxidization will be discussed.

049 - EVALUATION OF THE TOXICITY OF RARE EARTH ELEMENTS AND THEIR POTENTIAL CARCINOGENIC RISK

Suellen G Cordeiro [a*], **Ana Cláudia H Pereira[b]**, **Denise C Endringer[b]**,
Maria Tereza W D Carneiro[a], **Jefferson S Rodrigues[c]** **Geisamanda P Brandão[a]**

[a] Atomic Spectrometry Laboratory, Chemistry Departament /Ufes, Vitória, ES, BraZil, 29075-910.
[b] Pharmaceutical Sciences Deparatament/UVV, Vila Velha, ES, Brazil, 29102-920
[c] Chemistry Sciences Laboratory/Uenf, Campos dos Goytacases, RJ, Brazil, Zip Code
*e-mail: suellengcq@hotmail.com.br

Rare earth elements (REEs) constitute a group of 16 elements that make up the lanthanide series, along with scandium and yttrium. Although they have been considered rare for many years, it is established that this group of elements is more abundant than several metals and is increasingly being utilized in the technological, industrial, agricultural, and medical sectors. The concern regarding the potential damage caused by REEs has increase, as they are considered emerging contaminants due to the lack of information in the literature regarding their resilience, bioaccumulation, and potential toxicity in the environment. In light of this scenario, bioaccessibility tests for REEs were carried out, in addition to complementary tests for cytotoxicity and bioaccumulation for the elements La, Ce, Eu, and Gd. In the bioaccessibility and bioaccumulation assays, concentrations of REEs were determined using inductively coupled plasma mass spectrometry whith collision cell. The selected bioaccessibility test was based on the method described by Boisa et al for marine sediment matrices. Based on the concentrations obtained from the bioaccessibility tests, an evaluation of human health risk through dermal absorption and oral ingestion was conducted using the hazard quotient (HQ). Following gastric digestion simulation (SBET), it was observed that the elements Ce and Nd exhibited higher absorption capacities in the human body (> 2 µg/g). Elements La and Y presented intermediate concentrations (close to 1 µg/g), while the remaining elements displayed concentrations below 0.5 µg/g. In the gastrointestinal extraction stage (PBET), the REEs maintained a similar absorption capacity to that observed in SBET. The results of the bioaccumulation test conducted with fibroblast cells (L929) indicated that La and Eu had a 25% probability of intracellular accumulation, whereas Ce and Gd showed 1%. The cell viability test, exposed to a standard REE solution in 2% HNO_3 medium (100 µg/mL) and an aqueous solution of La_2O_3, $Gd(NO_3)_3$, $Ce(NO_3)_3$, and Eu_2O_3 (1000 µg/mL), did not demonstrate cytotoxic effects on L929 fibroblast cells. Using the HQ, the evaluation of human health risks, both in adults and children, indicated that all REEs were considered safe for oral ingestion and dermal absorption. However, the higher HQ_{derm} values obtained suggest that REEs pose greater risks to human health through dermal absorption than oral ingestion. Based on the tests conducted in this research, it is possible to infer that incorporating these elements into the environment is considered a potential source of contamination. While not demonstrating cytotoxicity in L929 fibroblast cells, some REEs exhibited cellular bioaccumulation capacity. Furthermore, gastric and gastrointestinal simulation revealed the ability of these elements to enter the food chain and consequently the human body. The results obtained up to the current moment raise an alert for the need for additional research to be conducted on other cell lines, and for competent authorities to give proper attention to these potentially contaminating elements by formulating appropriate regulatory policies.

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[UFES, UVV, FAPES, CAPES, CNPq, FEST/RENOVA]

050 - MATRIX EFFECTS IN SALINE SOLUTIONS ANALYZED BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: REVISITING NON-SPECTRAL EFFECTS

Renata Nascimento Caetano*, **Daniel L. G. Borges**

Federal University of Santa Catarina, Chemistry Department, Florianópolis, SC, Brazil, 88040-900
*e-mail: renata.nascimento@posgrad.ufsc.br

Inductively coupled plasma mass spectrometry (ICP-MS) is currently amongst the most frequently used techniques for elemental analysis. The multi-elemental capability at ultra-trace levels is an unsurpassed characteristic of the technique, although careful sample preparation approaches and/or peculiar calibration protocols are critical to achieve accurate results.[1] Samples with relatively high contents of dissolved solids, particularly salts, have long been related to severe spectral and non-spectral interferences, frequently covered by the general term “matrix effect”. High concentrations of matrix components frequently lead to changes in sensitivity, inducing signal suppression or enhancement and requiring special operating conditions in order to overcome interferences.[2] Thus, this work aims at investigating the signal suppression or enhancement effects caused by saline solutions under different experimental conditions. The analyte and matrix solutions were prepared using deionized water and 0.5 % (v/v) HNO_3 or alkaline media adjusted to a pH of 9.0 with KOH, NH_3 or tetramethylammonium hydroxide. The initial assessment demonstrated that the pH of the sample solutions was not responsible for significant shifts in analyte sensitivity and, hence, additional investigation was carried out using 50 $\mu g\ L^{-1}$ solutions containing Al, Ba, Cd, Co, Cr, Fe, Mn, Mo, Ni, Pb, Sb, V and Zn. Beryllium, Bi, In, Rh, Sc, Tl and Y, as internal standards (IS), were also investigated. Saline solutions with variable ionic strengths were prepared using NaCl, $NaNO_3$ and NH_4NO_3. Hence, the effect of Na^+, Cl^- and NO_3^- on analyte signals was assessed with concentrations varying from 2.4 $\mu mol\ L^{-1}$ to 24 $mmol\ L^{-1}$. The results showed that significant signal suppression was observed with increasing concentration of the salts. In addition, the suppression effect appeared to be mass-dependent, since heavier elements (notably Bi and Pb) were significantly less affected and the sensitivity for these elements actually increased in the presence of the electrolytes. This is somehow opposite to what would be typically described as a space-charge effect, but may be associated to shielding of the electric fields produced by the ion optics[2]. It is also possibly related to improved collisional focusing in the ion lens or, perhaps, in the ion extraction process in the interface. In the presence of NH_4NO_3, generalized signal suppression was observed, although to a far less extent, which is likely due to the efficient decomposition of the salt in the plasma environment, generating smaller ions. Multivariate approaches are being planned to assess the statistical significance of the interaction amongst the ion lens voltage, salt nature and concentration and plasma RF power, which should provide additional support to investigate the origin of the mass-dependant non-spectral effect. Rhodium and Y seem to provide reasonable correction for signal suppression when used as IS, although they are effective only at lower concentrations of the electrolytes. Both IS were also more effective for heavier than for lighter elements. Similar behaviour was observed when In, Bi and Tl were investigated as IS. In contrast, Be and Sc were more effective IS for lighter elements. In addition to mass-dependent effects, investigations associated to the ionization energy have also been established, although a general trend was not clearly observed. It is evident that the proper choice of IS under these conditions should focus primarily on m/z similarity with the analytes. Additional experiments will include investigations associated to the plasma RF power and to nebulization systems.

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[CAPES, CNPq]

051 - ASSESSMENT OF INORGANIC CONTAMINANTS FOR ENVIRONMENTAL DIAGNOSIS EIGHT YEARS AFTER THE FUNDÃO DAM COLLAPSE

Nathália R. Oliveira[a*], Bianca L. Valle[b], Fernanda C. Pinheiro[a], Mariana R. Almeida[a],
José F. B. Neto[b], Letícia M. Costa[a]

[a] Universidade Federal de Minas Gerais, Department of Chemistry - ICEx, Belo Horizonte, Minas Gerais, Brazil, 31270-901
[b] Universidade Federal de Minas Gerais, Department of Genetics, Ecology and Evolution - ICB, Belo Horizonte, Minas Gerais, Brazil, 31270-901
*e-mail: nroliveira1989@ufmg.br

In recent years, events such as the rupture of the Fundão dam in Mariana, Minas Gerais, have sparked a warning signal for the stability of mining activities. Rich in metals and metalloids, the wave of tailings produced by the dam rupture followed the Doce River until reaching its mouth, totaling approximately 663 km traveled downstream[1]. The Doce River basin is an area of great social and environmental importance which contains 229 cities, an estimated population of 3.5 million people and an area of great economic importance, especially in electricity generation, mining, and industrial activities[2]. To evaluate the concentration of metals and metalloids in surface waters along the Doce River and the Santo Antônio River (reference river), within Minas Gerais state, quarterly sampling was carried out (January, April, July, and October) at 21 different points for a period of one year. Nine mL of each sample was microwave-assisted digested (Ethos Lean, Milestone, Italy) using 800 µL of concentrated HNO_3 and 200 µL of HCl, followed by the determination of inorganic contaminants using inductively coupled plasma mass spectrometry (ICP-MS, 7700, Agilent Technologies, Japan). Internal standardization was applied to minimize and correct matrix effects, and the method was validated. Accuracy was tested with certified reference material trace in natural water (NIST1640a). The determination of total metal and metalloid concentrations (Ag, As, B, Ba, Be, Cd, Co, Cr, Hg, Li, Mn, Ni, P, Pb, Se, Sb, Tl, U, V, and Zn) and dissolved metals (Al, Fe, and Cu) were compared with the maximum limits proposed by CONAMA 357/2005 resolution for freshwater Class 2. Among the 23 analytes, ten elements (Al, As, Co, Cr, Fe, Mn, Ni, P, Pb, and Se) presented concentration values that exceeded the limits established by Brazilian legislation. Considering the concentration values determined and parameters as (1) the physicochemical data collected in the sampling; (2) the river flow; and (3) the geoprocessing study carried out in the specific's periods and sampling points, it was possible to suggest the probable sources of contribution for the concentrations increasing, when compared to the CONAMA limits. In addition to the impacts generated by the rupture of the Fundão dam, forestry, mining, and agriculture stand out among the probable sources of contamination. The comparison of analyte concentrations determined over the years by literature and government agencies allowed us to compare and identify new sources of natural and/or anthropogenic inorganic contamination of the Doce River.

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052 - REACTIVITY AND ANALYTICAL PERFORMANCE OF NH_3 AS REACTION CELL GAS IN INDUCTIVELY COUPLED PLASMA TANDEM MASS SPECTROMETRY (ICP-MS/MS)

Beatriz M. Fontoura[a], Joaquim A. Nóbrega[b], George L. Donati[a], Alex Virgilio[c]*

[a]Wake Forest University, Department of Chemistry, Winston-Salem, NC, United States, 27109
[b]Federal University of São Carlos, Department of Chemistry, São Carlos, SP, Brazil, 13565-905
[c]University of São Paulo, Center for Nuclear Energy in Agriculture, Piracicaba, SP, Brazil, 13416-000
*e-mail: alexvirgilio@cena.usp.br

Tandem ICP-MS has been considered the state of the art in quadrupole-based instrumentation, owing to its superior ability to minimize/remove spectral interferences. Despite the possibility of operating in collision mode using He as cell gas, the octopole reaction system is more versatile through the reaction mode due to its better control over chemical processes and increased selectivity.[1] Different gases such as H_2, N_2O, CH_3F, O_2, NH_3 and others have been used as reactants, with emphasis on the last two, which have been further applied to ICP-MS analysis.[2,3] In this work, ammonia's reactivity and analytical performance have been further investigated considering the accuracy, sensitivity and limits of detection achieved for 18 selected analytes (Al, As, Ba, Bi, Cd, Ce, Cr, Cu, Fe, La, Mo, P, Pb, Se, Si, Ti, V and Y). Different gas flow rates (0.5 – 1.5 mL min^{-1}) and operation modes (*i.e.* on-mass, where Q2 = Q1, and mass-shift, where Q2 = Q1 + mass associated with the reaction gas) were evaluated. Both each analyte (E) and their respective products formed by H_2 elimination [E-NH], atomic H elimination [$E\text{-}NH_2$], ammonia clustering [$E\text{-}(NH_3)_n$] and combinations of these reactions (*e.g.* [$E\text{-}NH(NH_3)_n$] and [$E\text{-}NH_2(NH_3)_n$]) were monitored. In terms of reactivity, the analytes could be divided in four groups: (*i*) non-reactive elements such as ^{27}Al, ^{31}P, ^{78}Se and ^{28}Si; (*ii*) NH_3-clustering elements such as ^{114}Cd, ^{52}Cr, ^{63}Cu, ^{56}Fe, ^{208}Pb and ^{209}Bi; (*iii*) moderately reactive elements such as ^{137}Ba and ^{98}Mo, and (*iv*) highly reactive elements such as ^{75}As, ^{140}Ce, ^{139}La, ^{48}Ti, ^{51}V and ^{89}Y. Concerning the analytical parameters, the elements in groups (*i*), (*ii*), and (*iii*) presented higher sensitivities and lower LODs when on-mass mode was used. In these cases, mass-shifts to $E+^{14}NH_2$, $E+^{14}NH_3$ and $E+(^{14}NH_3)_2$ presented reduced sensitivity in comparison with E itself (on-mass) and when the ammonia gas flow rate was increased. For more reactive elements such as those found in group (*iv*), sensitivities were generally higher in on-mass mode, although background signals and, consequently, LODs were significantly lower when mass-shift was used. In these cases, compounds with up to six NH_3 molecules bound to the analytes were observed during the reactions in the octopole reaction system. Accuracy was checked by means of addition and recovery experiments using a tap water sample enriched with 1 µg L^{-1} of analytes in a high carbon (0.25% m/v) and HCl (2% v/v) medium. For elements described in groups (*i*)-(*iii*), quantitative recoveries in the 82-104% range were typically obtained for on-mass mode, while systematically low recoveries were found for mass-shift mode. On the other hand, group (*iv*) elements generally presented recoveries in the 95-108% range when mass shift mode was employed. As for the reactive gas flow rates, the best recoveries were observed for NH_3 gas flowing around 1.0 mL min^{-1}.

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053 - DETERMINATION OF Ba, Cu, Mn AND Pb IN PLANT-BASED MEAT BY MICROWAVE-INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY

Jéssica da R. Porto[a*], Kaiane de Q. Ribeiro[b], Charlie G. Gomes[a], Daisa H. Bonemann[a], Wiliam Boschetti[a], Anderson S. Ribeiro[a]

[a]Federal University of Pelotas, Chemical, Pharmaceutical and Food Science Center,
Capão do Leão, RS, Brazil, 96010-900.
[b]Federal University of Rio Grande, School of Chemistry and Food, Rio Grande, RS, Brazil, 96203-900.
*e-mail: jporto8.jp@gmail.com

Plant-based meat is gaining attention as alternative to the consumption of animal meat, studies indicate that these products have lower levels of cholesterol and higher levels of carbohydrates, in addition to being sources of minerals. Despite the many benefits they bring to human health, plant-based meat may contain, in addition to essential elements, potentially toxic and harmful elements, therefore, monitoring the concentration of metals in foods is of extreme nutritional and toxicological importance[1,2]. Multielemental atomic emission techniques, such as Microwave Induced Plasma Optical Emission Spectrometry (MIP OES), have been employed for monitoring elements in different kinds of samples, especially in food samples. MIP OES is a technique with low operational cost because the plasma is maintained with nitrogen removed from the atmospheric air, making it an excellent alternative to other plasma techniques[3]. Therefore, this work aims to evaluate the total concentration of Ba, Cu, Mn and Pb in cooked plant-based meat by MIP OES. For sample preparation, an acid decomposition method was used in a digester block with a reflux system[4]. The samples were cooked according to the manufacturer's instructions, in a preheated oven at 200°C for 30 minutes. In order to optimize the best experimental conditions for sample preparation, a central compound factorial design was used, where the following variables were investigated: HNO_3 concentration, H_2O_2 volume, decomposition time and temperature. For sample preparation, 1.28 g of sample were weighed directly into the borosilicate tube, followed by the addition of 5 mL of HNO_3 6.5 mol L^{-1} and placed in a digester block for 180 minutes; then 2 mL of H_2O_2 30%(v/v) was added for another 60 minutes. After cooling, the samples were transferred to polypropylene tubes and filled up to 20 mL with ultrapure water and refrigerated until the time of analysis. The accuracy of the method was evaluated using a certified reference material (NIST 1577c) and the concentrations obtained were in accordance with the values certified at 95% confidence through a Student's t-test for Cu and Mn. For Ba and Pb, recovery tests were performed with results between 81 and 96%. For limit of detection (LOD) and quantification (LOQ) calculations, it is recommended to use the analytical signal/background signal ratio (SBR) and background equivalent concentration (BEC), especially in complex samples in order to observe any changes in the operating conditions of the equipment[5]. The (LOQ) was 0.130; 0.859; 0.019 and 0.880 mg kg^{-1} for Ba, Cu, Mn and Pb, respectively Thee samples were analysed and the results of the total concentration of samples A, B and C were 1.15, 1.17 and 1.33 mg kg^{-1} for Ba, 2.70, 3.63 and 2.24 mg kg^{-1} for Cu, 3.03, 12.93 and 13.96 mg kg^{-1} for Mn and <LQ, <LQ and 1.27 mg kg^{-1} for Pb, respectively. Considering that the recommended daily intake value (DRI)[6] for adults of Ba, Cu, Mn and Pb is 0.14 mg/body weight, 0.9; 2.3 and 0.9 mg, respectively, and the consumption of 100g of plant-based meat per day, it can be concluded that the samples contribute to the ingestion of these elements without exceeding the recommended values.

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[CNPq, CAPES, INCTAA]

054 - ANALYSIS OF TOXIC METALS IN BRAZILIAN DARK CHOCOLATE BARS BY ICP-MS AFTER MICROWAVE-ASSISTED DIGESTION

Naomi Akiba[a*], Arthur Campos[a,b], Mariana Ortega[a], Maciel Santos Luz[c], Valeska Meirelles[a]

[a]Nova Analítica, Trace Elements Analisys, Diadema, SP, Brazil, 09925-000
[b] Presibiterian University Mackenzie, São Paulo, SP, Brazil, 01302-000
[c] Institute for Technological Research, Laboratory of Metallurgical Process, São Paulo, SP, 05508-901
*e-mail: naomi.akiba@novanalitica.com.br

Cocoa, known scientifically as "Theobroma cacao," translates to "Food of the Gods" in Latin. Native to the regions of North Brazil, Colombia, Costa Rica, and more, cocoa's cultivation has extended to tropical areas of Africa and Asia[1]. Today, it thrives on multiple continents, a global industry into cocoa powder, and the universally adored chocolate. While cocoa has gained recognition for its potential health benefits, a notable issue has emerged that warrants significant attention – the elevated food safety concerns linked to the prevalence and concentrations of toxic metals. Different toxic metals exhibit distinct distribution patterns. Metals like Bismuth (Bi) and Lead (Pb) tend to accumulate in the discarded bean shells, while Chromium (Cr) and Cadmium (Cd) appear in higher concentrations in the final cocoa products. These metals can accumulate in cocoa beans through absorption from the soil and during various stages of production, including drying, shipping, and processing[3]. Recently has been measured the amount of heavy metals in 28 dark chocolate bars. Cadmium and lead were detected in all of them. For 23 of the bars, the levels concentrations are high for at least one of those heavy metals. Five of the bars were above those levels for both cadmium and lead. And only five brands are safe to be consumed.

The purpose of this study is to determine the levels of toxic metals (Al, Ag, As, Cd, Co, Cr, Hg, Mo, Pb, Sb, Se, Sn, Sr, Ti, and V) in Brazilian dark chocolate bar by method based on microwave assisted acid digestion technique followed by analysis using the Thermo Scientific™ iCAP™ ICP-MS. The sample digestion was evaluated in different HNO_3 concentrations (14, 7, and 3.5 mol/l) and H_2O_2 volume (0, 0.5, and 1.0 ml). The heating program for the sample digestion was 10 min ramp up to 200ºC and 20 min maintained at 200 ºC. The digestion procedure was evaluated by comparing total organic carbon (TOC) that was determined using an OI Analytical TOC analyser. The levels of toxic metals (Al, Ag, As, Cd, Co, Cr, Hg, Mo, Pb, Sb, Se, Sn, Sr, Ti, and V) were determined in dark chocolate bars by Inductively Coupled Plasma Mass Spectrometry, by pneumatic nebulization (MicroMist, 400 µL min $^{-1}$) combined with a cyclonic mist chamber. The interface was assembled using a nickel cone and a skimmer cone with insert version for high matrix (high matrix, 3.5 mm). Helium and oxygen were also used in the instrument collision/reaction cell. A minimum of seven data points will be used to establish a calibration curve that covered the full concentration range of interest, ensuring accurate sample analyses. The validation process of the developed method involved precision, accuracy, linearity of the calibration curve, detection (LOD) and quantification limit (LOQ). Three replicates of each sample were analysed and blank assays were also carried out. The TOC increase (36 to 264 mg C /kg of sample) with the decreased HNO_3 concentration and the best volume of H_2O_2 was 0.5 mL. The proposed method was successfully employed for analysis of heavy metals in bars chocolates. Through this method, some of these chocolate bars were found to contain detectable levels of certain toxic metals, including Arsenic (As), Cadmium (Cd), Lead (Pb), and Mercury (Hg).

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055 - ASSESSING THE ELEMENTAL COMPOSITION IN TRANSGENIC SOYBEAN CELLS USING SINGLE-CELL ICP-MS

Ana Beatriz Santos da Silva[a*], Elisânia Kelly Barbosa Fonseca[b], Marco Aurelio Zezzi Arruda[b]

[a] Environmental Studies Center (CEA), São Paulo State University (UNESP), Rio Claro, SP, 13506-900, Brazil
[b] Spectrometry, Sample Preparation and Mechanization Group, Institute of Chemistry, University of Campinas – Unicamp, Campinas - SP, Brazil, 13083-970
*e-mail: ana.bs.silva@unesp.br

Cell heterogeneity has impacted many biological processes, from cancer cell formation to bacteria physiology. From this perspective, the single-cell ICP-MS has been considered an important technique for extracting information about the elemental composition of animal cells and unicellular organisms.[1] In this context, for the first time, single-cell ICP-MS was evaluated to determine P, Zn, Mn, Fe, Cu, and Zn in single transgenic soybean cells (RR and Intacta). The protocol for soybean cell cultivation was based on somatic embryogenesis, where the stem was employed as an explant, and the Murashige and Skoog solid medium was used for callus induction and propagation. After establishing in vitro culture, soybean callus was chopped and transferred to a liquid medium to obtain the soybean cell suspension (Figure 1a). The sample preparation involved was composed of the remotion of the medium by centrifugation and washing with deionized water. The cells were counted using a Neubauer chamber, and the cell concentration of 10^4 cells mL^{-1} was introduced using self-aspiration. The data treatment was previously performed using interactive Python-based data processing, and the background noise was discriminated using Gaussian and Poisson-based data filtering (Figure 1b). Finally, the intensity of the cell was correlated with the calibration curve, and other parameters (transport efficiency, dwell time, and sample flow rate) and the amount of an analyte was found. In this sense, the average amount of P, Fe, Zn, Mn, and Cu was 108, 6, 1.5, 0.9, and 0.3 fg $cell^{-1}$ for the Intacta soybean cell, respectively. On the other hand, for soybean cells from round-up-ready, the mass estimated was 0.3 fg $cell^{-1}$ (Cu), 1.4 fg $cell^{-1}$ (Zn), 138 fg $cell^{-1}$ (K), 1 fg $cell^{-1}$ (Mn), 6 fg $cell^{-1}$ (Fe) and 71 fg $cell^{-1}$ (P). These values were compared with those obtained for the cell bulk analysis, and a good agreement was found between them. Moreover, considering the single cell as a sample and employing statistical models, such as a Principal component analysis (PCA), it is possible to visualize the role of trace elements in the soybean transgene at a cellular level (Figure 1c). Overall, the single-cell ICP-MS is a powerful technique for analyzing plant cells, thus demonstrating its potential in plant biotechnology.

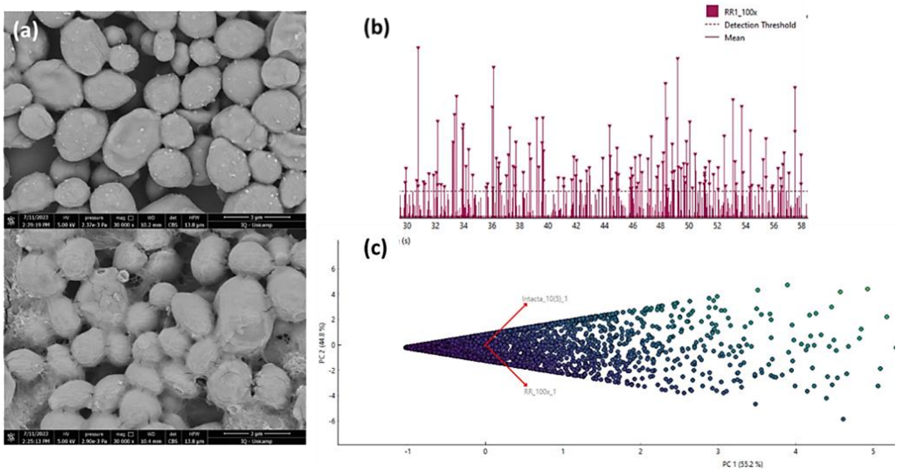

Figure 1. Summary of single ICP-MS analysis steps: (a) soybean suspension cells; (b) raw data; and (c) PCA for RR and intacta soybean cells.

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056 - TOTAL CONCENTRATION DETERMINATION OF Cu, Fe, K and Mg IN SHEEP MEAT SAMPLES BY MIP OES

Mariana M. Da Cunha [a*], Daisa H. Bonemann [a], Charlie G. Gomes [a], Mariana A. Vieira[a], Anderson S. Ribeiro[a]

[a]Federal University of Pelotas, Center for Chemical, Pharmaceutical and Food Sciences, Capão do Leão, RS, Brazil,96160-000
*e-mail: cunha.mariana2003@gmail.com

Sheep meat is a tasty delicacy that include some types of animals, lamb and sheep, which although they are less consumed in relation to beef, is an important production that extends throughout the national territory and contributes significantly to agribusiness in Brazil, being a strong source of income and substance.[1] This food has been increasingly valued, standing out for its sensory characteristics such as juiciness, odor and taste, in addition to having an essential role in improving the health of individuals by the fact that it has in its composition several vitamins, minerals and essential polyunsaturated fatty acids.[2] Because of this, it is important to develop and validate analytical methods for the knowledge of the composition of sheep meat with regard to the amount of essential elements, because the consumption of sheep meat can lead to the contribution of the ingestion of these elements in the human body. In this way, the present work aims to optimize a method of acid decomposition in a reflux system to determine the total concentration of Cu, Fe, K, and Mg by Microwave-induced Plasma Optical Emission Spectrometry (MIP OES) in sheep meat samples submitted to three heat treatments (cooking in water, microwave and conventional oven). The sheep meat samples were acquired from different cities near Pelotas/RS: Arroio Grande (samples A and B) and Capão do Leão (sample C). The heat treatment of these samples followed the methods previously described[3] which consist of cooking in water (AC), in a microwave oven (M) and in a conventional oven (F). For the sample preparation, the acid decomposition with reflux system[4] was used and the decomposition conditions were optimized through a multivariate design that evaluated the independent variables and the best conditions were sample mass (250 mg); H_2O_2 (1.8 mL); digester block temperature (140ºC) and decomposition time (187 min). The volume of HNO_3 was fixed at 5 mL. The accuracy of the results was evaluated using certified reference materials (NIST 1546a and NIST 1577c) and the statistical comparison by t-test (95% confidence level) showed no significant difference between these results. The highest concentrations of Cu were found in sample C, submitted to heat treatment in a conventional furnace (0.816 mg kg^{-1}). For Fe, the highest concentrations were observed in sample C (of 47.4 mg kg^{-1}), submitted to heat treatment by microwave. In sample C, submitted to cooking in water, the highest values for K (4,684 mg kg^{-1}) were found. Finally, for Mg, the highest concentrations were obtained in sample C treated with a conventional oven (298 mg kg^{-1}). Considering the intake of 100 g of sheep meat, all elements are below the recommended daily intake (RDI) for these elements, which are 0.9 mg for Cu, 14 mg for Fe, 4700 mg for K and 260 mg for Mg. With this, there is a need for control in sheep meat samples, since if it is ingested assiduously, it will bring health benefits.

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[CNPq, CAPES, INCTAA]

057 - DETERMINATION OF TOXIC AND POTENCIALLY TOXIC ELEMENTS IN HAIR DYES BY ICP-MS

Jessica S S Lira [a*], Tatiana D Saint'Pierre[a]

[a]Pontifical Catholic University of Rio de Janeiro, Department of Chemistry, Rio de Janeiro, RJ, Brazil, 22451-900
*e-mail: lira.jessica@live.com

Hair dyes are among the most commonly used cosmetics in the world. They are used by people of all genders to cover grey hair or change the hair colour. Since hair dyes are so widely used, it is important to ensure that they do not contain harmful substances[1]. The Brazilian health authority ANVISA has set limits on the amount of metal impurities allowed in hair dyes. For lead, the maximum allowable concentration is 20 parts per million (ppm). For other "heavy metals", the maximum allowable concentration is 100 ppm.[4] This study determined the concentrations of Al, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mo, Ni, Pb, Sb., Sn, Sr, Ti, and Zn in hair dyes. A total of nine samples of different brands including the colours black, blond, red, blue and pink were analysed. About 350 mg of each sample were decomposed in closed flasks in a digester block (Berghoff, Germany) with 10 mL of nitric acid 65% for 6 h at a temperature of up to 215 ºC. The solutions were then diluted to 50 mL and analysed by inductively coupled plasma mass spectrometry (ICP-MS), employing a NexIon 300X spectrometer (PerkinElmer, USA). Analytical curves were prepared using multi-elemental and mono-elemental standards in 10% nitric acid. The limit of quantification of the method (LOQ) were from 0.6 µg kg^{-1} (Hg) to 19.7 mg kg^{-1} (Ti). No sample presented a concentration of lead above 20 mg kg $^{-1}$, that was found in low concentrations (13 µg.g^{-1} to 273 µg.g^{-1}) in almost all samples, except in brand 3 in colours black and red in which Pb was not detected. The first brand presented the low concentrations of elements except for Zn that was found in colour "blue shine" at the concentration of 18.5 mg kg $^{-1}$. High concentrations of Cr and Zn were found in all three colours of brand 2 (2.2 to 7.5 mg.kg^{-1}) and (9.0 to 12 mg.kg^{-1}) respectively. Colour red had high concentrations of elements, with Al being the highest, at 112 mg.kg^{-1}. The blond colour had the highest concentration of Al theoretically failing ANVISA criteria, as it has a concentration greater than 100 mg kg $^{-1}$. Aluminium and its compounds can stabilize emulsions and control viscosity[5], but they can also induce granulomatous reactions[6]. Brand 3 (black colour) had the lowest concentrations of potentially toxic elements, with the highest concentration being Sn at 182 µg.kg^{-1}. For assessment of the accuracy of the method, samples were fortified in two levels with analytical standards, before the treatments, and recoveries were within 80 and 110%. The obtained results show that most analysed hair dye samples are safe for use, according to ANVISA's resolution, except for brand 2 (blond) due of its high concentration of Al.

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[CAPES, CNPq, FAPERJ, PUC-RJ]

058 - OPTIMIZATION OF INSTRUMENTAL PARAMETERS FOR WATER ANALYSIS USING MIP OES

Yasmin R Bloedorn[a*], **Lucas L Ferreira**[a], **Charlie Gomes**[a], **Jéssica Porto**[a], **Anderson S Ribeiro**[a], **Wiliam Boschetti**[a]
[a] Federal University of Pelotas, Center for Pharmaceutical and Food Chemical Sciences,
Capão do Leão, RS, Brazil, 96010-900.
*e-mail: yasminbloedorn@gmail.com

The anthropogenic dissemination of metals due to intense industrialization and urbanization processes into surface water resources is a main ecological and public health concern at various scales, ranging from regional to global. Coastal lagoons and channels are sensitive ecosystems with high productivity and biodiversity[1]. Because of this problem, water quality control is of extremely importance, since elements like Al, Ba, Ca and Li are found omnipresent in aquatic systems and due to its bioaccumulative potential they demand monitoring. Therefore, it is necessary to use analytical techniques capable of quantifying these chemical elements. The plasma-based spectrometry techniques are most used in this context. Microwave Induced Plasma Optical Emission Spectrometry (MIP OES) has drawn attention mainly for having a self-sustaining atmospheric pressure microwave plasma, which significantly reduces the costs of analyses, using a nitrogen gas source that is extracted from atmospheric air through a nitrogen generator[2]. Previously, the optimizations of instrumental conditions were evaluated. A standard solution containing Al, Ba, Ca, and Li, as well as a sample, were used to assess parameters such as nebulization flow, visualization position, reading time, pump rotation, and the number of pixels. The objective was to achieve the most intense analytical signal with the lowest relative standard deviation, devoid of interference, and with a lower signal-to-noise ratio. The plasma is axially oriented, resulting in a more energetically favorable analytical zone in the central part of the plasma, while having lower energy at its sides. Instrumental conditions for nebulization flow and viewing position were automatically assessed by the manufacturer's software. Reading time, pump rotation, and the number of pixels were manually optimized. The reading time affects signal strength by influencing the residence time of the analyte in the plasma and the number of affected pixels, which in turn affects signal width expansion on the detector. Nebulization flow and pump rotation are parameters with a direct impact on plasma temperature. It was observed that elements with high ionization energy required a lower nebulization flow, resulting in a more energetic plasma. If these parameters were to continue to increase, they would lead to plasma cooling.

Table 1. Comparison of different instrumental conditions for MIP OES.

Elements	Viewing position	Nebulization flow (L min^{-1})	Reading time (s)	Pump rotation (rpm)	Pixels
Recommended instrumental conditions					
Al	0	0,95	3	15	3
Ba	0	0,65	3	15	3
Ca	0	0,6	3	15	3
Li	0	0,75	3	15	3
Optimized instrumental conditions using a water sample					
Al	120	0,3	30	45	3
Ba	0	0,3	10	30	3
Ca	20	0,35	5	45	3
Li	10	0,3	5	30	3

Table 1 shows a comparison between the recommended and optimized instrumental conditions. During the optimization process, it was observed that elements such as Li increased their signal intensity by up to 90% with higher pump rotation and reading time. Ba exhibited a similar behavior, increasing its signal by approximately 30%, compared to the conditions recommended by the manufacturer. In the case of all elements, an increase in signal intensity was observed. These results emphasize the importance of optimizing the instrumental parameters prior to analysis. As the next steps, calibration curves will be constructed, and the method accuracy will be verified.

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[CNPq, CAPES, INCTAA]

059 - PAPER SOLID SUPPORT AS CALIBRATION STRATEGY FOR Ni DETERMINATION IN HEAVY CRUDE OIL BY LA-ICP-MS

Eduarda Q. Machado[a,b*], **Rodrigo M. Galazzi**[c], **Cleverson J. F. de Oliveira**[b], **Marco A.Z. Arruda**[a,b]
[a]University of Campinas, Dept. of Analytical Chemistry, Institute of Chemistry, Campinas, SP, Brazil, 13083-862
[b] National Institute of Science and Technology for Bioanalytics, Institute of Chemistry, University of Campinas, SP, Brazil, 13083-970
[b] PETROBRAS - Research Center Leopoldo Américo Miguez de Mello, Rio de Janeiro, RJ, Brazil, 21941-915
[c] Analytik Jena GmbH, Moema, SP, Brazil, 04029-100
*e-mail: eduardaqm@gmail.com.br

Nickel is most commonly present in crude oil samples as porphyrins. These compounds are present in heavier fractions of crude oil due to their mass and complexity of structure. Porphyrins are constituted of a tetrapyrrole group coordinated with a metal in the center of the structure, as Ni. Additionally, they may have other groups attached, associated with heteroatoms as N, S and O. For determination of Ni in crude oil samples, generally, spectrometric and chromatographic methods are used, in which is necessary a sample preparation step that are more susceptible to contamination, time-consuming, and requires the consumption of reagents[1]. An alternative to these limitations is the use of direct analysis of crude oil by graphite furnace atomic absorption spectrometry or by laser ablation coupled to mass spectrometry (LA-ICP-MS) being the samples directly introduced into the plasma as a solid aerosol, with minimum sample preparation. Nonetheless, for LA-ICP-MS, the calibration step is a challenge once, in fact, a solid sampling analysis is carried out. Generally, the calibration step is performed with external calibration, internal standards (IS), certified reference material, and matrix-matching; however, for crude oil analysis, this step is prone to matrix effects, due to the complexity of the matrix[2]. For this reason, the aim of the work was to develop a method for Ni determination by LA-ICP-MS in heavy crude oils using filter paper as a solid support for calibration[3] standards and samples. For that, three strategies are adopted: aqueous and oil-based calibration using the filter paper and normalization with IS. In this way, for standards, 4 µL of the solution are deposited directly on the filter paper. For Ni determination from samples, they are previously heated in an oven to 90 °C for 60 min and directly deposited on a filter (heated for 5 min in a hot plate for better dispersion). The analyses are performed with a laser ablation system (New Wave, UP-213) and ICP-MS (PerkinElmer, Elan DRC-e). For ablation, were used 110 µm-spot size, 60%-laser intensity, and 110 µm s^{-1}-scan speed, and for the ICP-MS, 1.2 and 1.1 L min^{-1}-nebulizer and auxiliary gas, respectively, and 1200 W-power applied in a radiofrequency (previously optimized for monitoring ^{60}Ni isotope) were used. For the aqueous standards, the analytical curve $y = 597.99x + 518.83$, $R^2 = 0.9972$, and limit of quantification (LOQ) of 0.805 mg L^{-1} were obtained. When the intensities of each point of the curve are normalized with ^{13}C (IS) the analytical curve is $y= 0.0101x + 0.0055$, $R^2= 0.9981$ and LOQ of 0.731 mg L^{-1}. Using the oil-based standards, $y= 350.41x + 1278.3$, $R^2= 0.9183$ and LOQ of 0.216 mg L^{-1} and with normalization, the curve $y= 0.0021x + 0.0167$, $R^2= 0.8056$ and LOQ of 0.253 mg L^{-1} was obtained. The aqueous curve with IS normalization was considered the best because of its better linearity and lower LOD and LOQ. The difference between results with and without normalization is significant when applied to four samples of heavy crude oil, as presented in Table 1. The results are compared with those previously obtained for microwave digestion and determination by ICP-MS for accuracy check.

Table 3. Results obtained after application of aqueous calibration curves, mg L^{-1}

Samples	**^{60}Ni**	**^{60}Ni/^{13}C**	**Agreement ^{60}Ni, %**	**Agreement ^{60}Ni/^{13}C, %**
A1	2.43 ± 0.29	18.17 ± 1.75	14.15	105.76
A2	51.06 ± 2.21	42.94 ± 1.76	119.78	100.74
A3	1.61 ± 0.18	9.72 ± 0.30	18.77	113.31
A4	3.22 ± 0.10	20.88 ± 0.58	13.55	87.91

These results showed the matrix influence of sample. In almost all results without normalization, lower intensities are achieved, showing the great influence of the organic material delivered into the plasma, which causes a high Ni signal suppression. For the corrections of the results, the IS using ^{13}C is then the best option. Through all of these results, this work showed the possibility of Ni determination in heavy crude oils by LA-ICP-MS using filter paper as solid support, and using the ^{13}C as IS for correction of the matrix interferences.

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[FAPESP, PETROBRAS, CNPq (140809/2021-0)]

060 - REVERSED-PHASE DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR TRACE ELEMENT DETERMINATION IN OILY SAMPLES BY ICP-MS: A STUDY OF CARBON INTERFERENCES

Cristian R. Andriolli[a], **Ariadne G. L. P. Gonçalves**[a], **Alessandra S. Henn**[a],
Erico M. M. Flores[a], **Rochele S. Picoloto**[a*]

[a]Federal University of Santa Maria, Chemistry Department, Santa Maria, RS, Brazil, 97105-900
*e-mail: rochele.picoloto@ufsm.br

The reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) method has been applied for oily samples, such as biodiesel, diesel, fish oil, vegetable oils, hydrogenated vegetable fat, oily pharmaceutical excipients, among others for further trace element determination by spectrometric techniques.[1-4] The RP-DLLME method is based on the analyte extraction from the organic phase (oil sample) to the aqueous phase using a mixture of dispersant (alcohol) and extractant (diluted acid solution) solvents. However, has been observed that a relatively high amount of carbon dissolved can remain in final solutions after the extraction method and can cause carbon interferences during the analyte determination. In this sense, a study of carbon interferences during As, Cd, Co, Cr, Cu, Mo, Ni, Pb, and V determination by inductively coupled plasma mass spectrometry (ICP-MS) using solutions obtained after RP-DLLME, was developed. Experiments regarding the carbon interferences were performed by using a ICP-MS instrument (Elan DRC II model, Perkin Elmer-SCIEX, Canada) and carbon determination in solutions obtained after the RP-DLLME method was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) using an optical axial view spectrometer (Ciros CCD, Spectro Analytical Instruments, Germany). For the RP-DLLME procedure, a water bath (model CE-160/22, Cienlab, Brazil), capacity of 9 L, and temperature control (up to 80 °C) was used. A corn oil sample was used in this study. The carbon concentration in solutions after the RP-DLLME method was up to 40 g L^{-1} and its effect on ^{75}As, ^{111}Cd, ^{114}Cd, ^{59}Co, ^{53}Cr, ^{63}Cu, ^{65}Cu, ^{98}Mo, ^{96}Mo, ^{60}Ni, ^{62}Ni, ^{207}Pb, ^{208}Pb, and ^{51}V measurements by ICP-MS was evaluated. For this, standard solutions containing 0.1 or 0.5 µg L^{-1} of all analytes in 5% HNO_3 solution and carbon concentrations in the range of 25 to 500 mg L^{-1} (from methanol, ethanol, *n*-propanol, and isopropanol) were prepared. Initial experiments were developed by using *n*-propanol. As results, for carbon concentration higher than 50 mg L^{-1}, an enhancement of the relative signal intensity (around 15%) was observed for ^{111}Cd, ^{59}Co, ^{53}Cr, ^{63}Cu, and ^{207}Pb (both analyte concentrations: 0.1 or 0.5 µg L^{-1}). Moreover, by using solutions containing 100 mg L^{-1} of carbon, an enhancement of 15% of the relative signal intensity for ^{75}As, ^{114}Cd, ^{65}Cu, ^{208}Pb, ^{62}Ni, ^{98}Mo, ^{96}Mo, and ^{51}V was observed. Additionally, a suppression of the signal intensity for ^{53}Cr (28 and 37% for 0.1 and 0.5 µg L^{-1}, respectively) was observed using solutions containing carbon concentration of 100 mg L^{-1}. In addition, when a solution containing 250 mg L^{-1} of carbon was evaluated, an increase of 15% in the signal intensity for ^{60}Ni was observed (0.1 or 0.5 µg L^{-1} of analytes).These results were in agreement with those already reported in literature.[5] Due to the interferences from carbon observed during the determination by ICP-MS, the final solutions obtained after the RP-DLLME method were diluted up to 400 times before ^{75}As, ^{114}Cd, ^{59}Co, ^{53}Cr, ^{65}Cu, ^{98}Mo, ^{60}Ni, ^{208}Pb, and ^{51}V determination. Moreover, with a suitable dilution of the final solution obtained after the RP-DLLME method, carbon interferences during trace element determination by ICP-MS were minimized or eliminated. Thus, the obtained results in this study emphasized the importance of monitoring the carbon concentration in the extracts obtained after the RP-DLLME method, in order to avoid to obtain over-or underestimated results.

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[CAPES, CNPq, and UFSM]

061 - THE PSEUDO-TOTAL DECOMPOSITION METHOD AND THE PRODUCTION OF REFERENCE MATERIALS WITH SEDIMENT MATRIX

Clícia Azeredo Gomes[a,b*], Jefferson R. de Souza[b], Cibele Maria S. de Almeida[b]

[a]Instituto Federal Fluminense, campus Campos-Centro, Campos dos Goytacazes, RJ, Brazil, 28030-130
[b] Universidade Estadual do Norte Fluminense Darcy Ribeiro, Campos dos Goytacazes, RJ, Brazil, 28013-602
*e-mail: cliciaagomes@gmail.com.br

Animals, plants, and soils are efficient at accumulating contaminants. Therefore, environmental monitoring analyzes, in most cases, occur in complex matrices[2]. Sediment is a suitable matrix for this type of analysis, as studies have reported that it is in the sediment that contaminants accumulate the most[3]. Therefore, the production of reference materials (RM) with sediment matrix, which is more accessible and produced with the use of pseudo-total methods for the decomposition of the matrix, is a branch to be explored since the use of MR is essential in environmental monitoring analysis, bringing greater reliability to the results and to the laboratory that reported them[3,4]. In most cases, studies carried out for environmental monitoring are interested in reporting and monitoring the most bioavailable contaminants and, therefore, use less aggressive decomposition methods in their research. However, when evaluating the accuracy of the method used, researchers are faced with high-cost RM and certificates with total decomposition methods, which interfere with the desired evaluation[2,3]. Thus, this work seeks to produce an RM for metal analysis with a marine sediment matrix using the EPA 3051 A[5] method for sample decomposition. The marine sediment was collected on Regência beach, ES, where the Doce River flows, which received the tailings from the Fundão dam, in Mariana, after its rupture in 2015[1]. The production has already undergone the initial treatment that includes drying the sample to air, crumbling, grinding, and sieving (63 µm). In preparing the batch, 200 amber bottles of 50 mL were filled with approximately 13 g of the sample each. Subsequently, the flasks were sterilized by gamma radiation at CETER/IPEN, stored in aluminum foil bags, and kept in a freezer at -20 ºC. Two tests are essential in the production of an RM: The homogeneity test, to verify whether the lot is homogeneous in relation to the properties of interest, and the stability test (short and long term), to verify whether under conditions different from those adopted as standard, the properties of interest remain stable[3]. The homogeneity test was performed by analyzing triplicates of 12 flasks drawn at random. After the decomposition and dilution steps, the samples were analyzed by inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). The results were analyzed against the calibration curve and linear regression analysis was used to verify if there was a tendency in the filling of the bottles, and analysis of variance (ANOVA) was used for the evaluation of the homogeneity between the units (Fcal for $\alpha = 0.05$). The metals that were homogeneous in the batch were Ba, Co, Cu, Zn, Fe, and Mn. Therefore, the next tests will continue with the analysis of these elements. The short-term stability test lasted one month and was performed isochronously. At temperatures of 30 ºC and 60 ºC, eight randomly selected flasks were submitted. After the determined period, the samples were decomposed, properly diluted, and analyzed by ICP-MS and ICP OES. The results are being analyzed, and the next steps (sample characterization by ICP OES and ICP-MS, interlaboratory tests, and statistical analysis) will follow with the metals that appear to be stable. At the end of the work, it is expected that the tests carried out demonstrate a homogeneous and stable material in relation to its physical and chemical properties and that a batch of MR with a marine sediment matrix for metal analysis is properly obtained.

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[UENF, IFF, CAPES, FAPERJ, CNPq]

062 - ARSENIC CONTAMINATION ON LIVER OF GROOVEBELLY STINGRAY (*DASYATIS HYPOSTIGMA)* IN NORTHERN RIO DE JANEIRO STATE

<u>Anne Caroline da Silva Nunes</u>[a*], Carlos José Malaquias da Silva[a],
Laís Nascimento Viana (R)[b], Tatiana Dillenburg Saint'Pierre[b], Maria Cristina Canela[a],
Cibele Maria Stivanin de Almeida[a]

[a]Universidade Estadual do Norte Fluminense Darcy Ribeiro, Laboratório de Ciências Químicas, Campos dos Goytacazes, Rio de Janeiro, Brazil, 28013-602
[b]Pontifícia Universidade Católica do Rio de Janeiro, Departamento de Química, Rio de Janeiro, Rio de Janeiro, Brazil, 22451-900
*e-mail: acsnunes@pq.uenf.br

Fish have the ability to store trace metals present in the environment. Organisms at the top of the food chain, such as elasmobranchs (sharks and rays), are more susceptible to most of these metals through processes such as biomagnification and bioaccumulation[1]. Determining the concentrations of metals in these organisms is essential for assessing their effect on ecology and biodiversity conservation. According to the IUCN Red List[2], the groovebelly stingray (*Dasyatis hypostigma*) is evaluated as EN - Endangered. ICMBio[3] (2010–2012) identifies the species as DD - Deficient Data and MMA Ordinance[4] No. 148 of the Ministry of the Environment does not include the species on the Official List of Brazilian Fauna Threatened with Extinction. The objective of this work is to evaluate the impact of anthropogenic arsenic contamination on the liver of the Dasyatis hypostigma species collected at Praia do Farol de São Tomé, in the Northern region of the State of Rio de Janeiro. Liver samples were collected from five individuals of groovebelly stingrays. Decomposition was performed with HNO_3 in 150 mg of sample (in triplicate) at 100ºC, for 4h. Samples were analyzed by Inductively Coupled Plasma Mass Spectrometry, ICP-MS. Concentrations were found in males between 4.3 ± 0.2 mg kg^{-1} and 12 ± 1 mg kg^{-1} and in the only female, 6.8 ± 0.5 mg kg^{-1}. Another important analysis is the determination of recent accumulations of metals in the liver, and for this, the hepatosomatic index (HSI) provides us with energy data. Regarding the HSI, the values found (1.11–1.8 for males and 1.42 for females) are equivalent to the bibliographic ones in this period, a maximum of 1.8 for males and 1.2–2.8 for females[5], with the lowest HSI for females because the material from the liver is transferred to the production of vitellus for the future embryos. The low HSI, due to the production of vitellus and the concentrations of toxic metals present in the liver, can lead to problems related to the embryos and, consequently, to the presence of species in the environment. This was the first study of these species in the region, which resulted in initially worrying data. The results obtained indicate that individualized studies should be carried out to confirm the panorama.

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[FAPERJ, CAPES, CNPq, UENF, GPEQ]

063 - HOMOGENEITY OF ORGANIC COFFEE LEAVES REFERENCE MATERIAL EVALUATED BY TQ-ICP-MS

Letícia de Lima[*], Elisabete A. De Nadai Fernandes, Cláudio Luis Gonzaga, Gabriele Rossini Moreira, Silvana Regina Vicino Sarriés, Márcio Arruda Bacchi, Robson Campos de Lima

Nuclear Energy Center for Agriculture, University of São Paulo, Piracicaba, São Paulo, Brazil, 13416-000
*e-mail: leticiadelima@usp.br

Brazil occupies a prominent position worldwide as the main producer and exporter of Arabica coffee. Approximately 16% of the coffee exported in 2022/23 had superior quality and sustainable management certification, with main destinations being United States, Germany, Belgium, Netherlands and United Kingdom.[1] For the production of superior quality coffee, the nutritional demands of coffee trees must be met, regardless of the cultivation method, whether conventional or organic. Nutrient levels are usually assessed through soil and leaf analysis to determine the actual need for supplementation. To ensure the metrological quality of the results provided by any measurement method, certified reference materials (CRMs) similar in matrix to the samples should be used as part of the analytical protocol. As established by ISO Guide 35,[2] CRMs are materials with physical, chemical or biological characteristics suitable for the measurement procedure. They should be homogeneous and stable, and be accompanied by a certificate that provides the target properties values, associated uncertainties and metrological traceability statement. For developing a candidate reference material of organic coffee leaves, 30 kg of leaves of *Coffea arabica* cv Catuaí Vermelho (IAC 99) were collected, following agronomic recommendations, from a certified organic farm located in the municipality of Ibiraci, Minas Gerais state, Brazil. After superficial cleaning, the leaves were freeze-dried, ground in a rotor mill, sieved to 250 µm and filled in amber polyethylene bottles. The 180 bottles produced, each containing 20 g of the material, were irradiated with gamma-rays dose of 15-20 kGy. Triplicate 200 mg samples were taken from ten randomly selected bottles for the homogeneity assessment. The samples were submitted to microwave assisted acid digestion, using HNO_3 and H_2O_2. For analytical quality control, certified reference materials were used: SRM1515 Apple Leaves, IAEA 336 Trace and Minor Elements in Lichen, INCT-MPH-2 Mixed Polish Herbs and CRM-Agro C1005a Sugar Cane Leaves. The chemical elements As, B, Ca, Ce, Cd, Co, Cr, Fe, K, La, Mg, Mn, Mo, Na, P, Pb, Rb, Sc, Sm, Sr and Zn were determined using triple quadrupole inductively coupled plasma mass spectrometry (TQ-ICP-MS). For the CRMs, recoveries between 80% and 120% were obtained for all elements, except Al, Cu, Ni and S. For the CRMs, recoveries between 80% and 120% were obtained for all elements, except Al, Cu, Ni and S. Statistical analysis using the ANOVA, Kruskal-Wallis and Wilcoxon tests demonstrated that all chemical elements determined are homogeneously distributed on the reference material of organic coffee leaves at a 5% confidence level.

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064 - THE CHALLENGES FOR THE QUALITY CONTROL OF DIETARY SUPPLEMENTS BY MIP OES: A STUDY OF INTERFERENCES

Gustavo R. Bitencourt[a], **Thaís S. Béron**[a], **Érico M. M. Flores**[a], **Aline L. H. Müller**[a], **Paola A. Mello**[a*]

[a]Universidade Federal de Santa Maria, Departamento de Química, Santa Maria, RS, Brazil, 97105-900
*e-mail: paola.mello@ufsm.br

Several nutrients can be added to dietary supplements as suppliers, such as essential and non-essential elements. In addition to those elements added to supply, elements can be present as contaminants, introduced from several sources (e.g. raw materials, manufacturing, among others). Thus, quality control of dietary supplements is essential. For this, plasma-based techniques, such as inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS), have been widely used.[1] In this same way, microwave-induced plasma optical emission spectrometry (MIP OES) has received special attention, mainly due to its non-dependence on argon (nitrogen is used as plasma gas, which can be obtained from atmospheric air using a nitrogen generator), which reduces long-term costs. However, although similar limits of detection (LODs) can be reached compared with those by ICP OES, the use of nitrogen as plasma gas turns the MIP OES more prone to non-spectral interferences.[2] Thus, the purpose of this work was to evaluate the suitability of MIP OES for the determination of essential and non-essential elements in dietary supplements. Aiming for a reliable method for the quality control of these products, a study of non-spectral interferences was carried out, comprising common concomitant elements normally present at high concentration in dietary supplements (C, S, Na, K, and Ca). For this, twelve dietary supplement samples of several classifications (vitamins/minerals, minerals, amino acids, and botanicals) were digested by microwave-assisted wet digestion (MAWD) for the determination of essential (Ca, Co, Cu, Fe, K, Mg, Mn, Mo, Na, and Zn) and non-essential (Ag, Al, B, Ba, Be, Cd, Cr, La, Li, Ni, Pb, Sr, and V) elements by MIP OES (4210 MP AES, Agilent Technologies, USA). The study of interferences on the determinations by MIP OES was carried out using solutions containing 100 µg L^{-1} of all analytes spiked with 25, 250, or 5000 mg L^{-1} of each concomitant (C, S, Na, K, and Ca). In addition, spiked solutions of all analytes were also prepared containing from 10 to 50% v v^{-1} HNO_3. Results obtained for a solution containing 100 µg L^{-1} of all analytes in 5% v v^{-1} HNO_3 were considered as reference values. The study of non-spectral interferences demonstrated relatively good robustness of MIP OES for elevated concentrations of C and S, since few elements were impacted even with a relatively high concentration of interferent (5000 mg L^{-1}). On the other hand, the study showed the great influence of easily ionizable elements (EIEs) on the measurements by MIP OES, being observed signal suppression or enhancement effects for several elements operating with a concentration from 250 mg L^{-1} of Na, K, or Ca. Thus, considering the high concentration of these concomitants in dietary supplements, a minimum dilution factor should be employed in order to obtain a free-interferences response and reliable results. Based on this study, it was possible to determine several essential and non-essential elements in dietary supplements by MIP OES. The accuracy was demonstrated using SRMs, and no statistical difference was observed between found and certified values (*t*-test). Therefore, the results obtained demonstrated the feasibility of MIP OES for the quality control of essential and non-essential elements in dietary supplements. In addition, on the study of interferences, the effects induced by Ca must be highlighted, since a high concentration of this element is normally found in dietary supplements (as well as other matrices) and there is a lack of studies in the literature exploring its effects in optical emission plasma-based techniques.

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[INCT-Bio, CAPES, CNPq, CAS, C&EN, and UFSM]

065 - ICP-MS BASED PLATFORMS FOR TRACING STUDIES OF ISOTOPICALLY LABELLED SELENIUM NANOPARTICLES IN PLANTS

Bruna Moreira Freire[a,b*], Ana Rua-Ibarz[b], Eduardo Bolea-Fernández[b], Flávio Venâncio Nakadi[b], Maite Aramendía[b], Bruno Lemos Batista[a], Martín Resano[b],

[a]Federal University of ABC (UFABC), Center for Natural and Human Sciences (CCNH), Santo André, São Paulo, Brazil, 09210-580
[b]University of Zaragoza, Department of Analytical Chemistry, Aragon Institute of Engineering Research (I3A), Zaragoza, Spain, 50009
*e-mail: bruna.freire@ufabc.edu.br

In the last years, metal-containing nanoparticles (NPs) have been increasingly used in many fields, including agriculture[1]. Studies reported that the use of NPs during crop cultivation has benefits to plants, such as nutrient biofortification, improvement in growth and productivity, and reduction of oxidative stress. However, the study of NPs interactions with plants is still a challenge, as established extraction procedures and measurement protocols have yet to be standardized[2]. This study aims to elucidate the uptake and biotransformation of selenium NPs (SeNPs) in rice tissues by inductively coupled plasma mass spectrometry (ICP-MS) and single-particle ICP-MS (SP-ICP-MS). Determining the most abundant Se isotopes (^{78}Se and ^{80}Se) in plants by single quadrupole instruments suffers from multiple isobaric and polyatomic spectral interferences[3]. However, the use of collision/reaction cells to cope with these interferences may cause a loss of sensitivity in bulk analysis, in addition to extending the NP event duration in SP-ICP-MS[4]. To overcome this limitation, isotopically labelled SeNPs enriched with ^{82}Se, subjected to less interferences, were synthesized and used throughout the experiments. Rice plants (*Oryza sativa*) were cultivated under greenhouse conditions during the vegetative period (approximately 45 days) with foliar applications of ^{82}SeNPs at 10 mg L^{-1} of Se. Plants of each group (n=3) were sprayed until the solution was uniformly distributed on the leaves surface. At the end of the experiment, the plants were harvested, washed with tap water and then with high purity water 5 times, and oven-dried (50 °C) until constant weight. To study the uptake and accumulation of ^{82}SeNPs, samples from different plant tissues (roots, shoots, and leaves) were acid-digested on a hot plate, and the determination of total Se was performed by ICP-MS. To elucidate the biotransformation and size distributions of ^{82}SeNPs, plant tissues were subjected to enzymatic digestion with macerozyme R-10, followed by analysis by SP-ICP-MS. Plants treated with gold nanoparticles (AuNPs) were initially used to optimize enzymatic digestion since sizing gold nanoparticles by SP-ICP-MS is straightforward. Results showed a tendency for nanoparticles (both AuNPs and SeNPs) to accumulate on leaves when applied by spraying. Selenium concentration in rice leaves increased from 0.6 (control group) to 15.8 mg L^{-1} (^{82}SeNPs group), a 26-fold increase. Optimization of the enzymatic digestion procedure showed an increase in NPs extraction efficiency with increasing sonication time, with the best extraction efficiency at 120 minutes of sonication. It was proven that the sonication time did not influence the diameter of the nanoparticles. Finally, it was observed that while part of the ^{82}SeNPs remains intact in plant tissues, another part seems to be converted to ionic Se.

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066 - TOTAL CONCENTRATION AND BIOACCESSIBLE FRACTIONS OF Cu, Fe, Ni AND Pb IN NUTS BY MIP OES

Catarine Cavada[a*], Caroline D. Clasen[a], Clarissa M. Moreira dos Santos[a], Mariana A. Vieira[a]

[a]Federal University of Pelotas, Center for Chemical, Pharmaceutical and Food Sciences, Capão do Leão, RS, Brazil,96160-000
*e-mail: cathycavada@hotmail.com

Food plays a key role in providing the necessary macronutrients and micronutrients to maintain our health. Currently, many people are seeking to adopt healthier eating habits, which has aroused a greater interest in consuming foods that offer a high nutritional value.[1] An example of this are Brazil nuts, cashew nuts and pecan nuts, oilseeds rich in essential vitamins and minerals such as Ca, Cu, Fe, K, and others. However, it is important to note that these foods can also contain potentially toxic elements. Therefore, it is crucial to perform elemental analysis on these foods to better understand the nutritional and toxicological profile of chestnuts and nuts, thus ensuring food safety and quality.[2] Thus, this work aims to determine the total concentration and bioaccessible fractions of essential and potentially toxic elements in Brazil nuts, cashew nuts and pecan nuts by microwave-induced plasma optical emission spectrometry (MIP OES). For determination of total concentration, the samples were decomposed in a digester block with a reflux system under conditions optimized. The accuracy of the results was evaluated using addition and recovery tests, and recoveries ranged from 95 to 107%. The evaluation of the bioaccessible fractions was performed using an in vitro digestion method, proposed by Minekus et al.[3] The bioaccessibility accuracy was evaluated through a mass balance. The total concentrations obtained for the analytes in Brazil nut, cashew nut and pecan nut samples were: 22.35; 29.80 and 14.91 mg kg^{-1} for Cu, 31.14; 60.95 and 26.51 mg kg^{-1} for Fe; 10.42; 7.45 and 3.72 mg kg^{-1} for Ni and 3.72; 1.86 and 1.86 mg kg^{-1} for Pb, respectively. Differences in analyte concentrations observed in this kind of samples can be attributed to climate and soil influences on nutrient uptake. Among the elements considered essential in our diet, Cu and Fe presented the highest percentages of bioaccessible fraction in Brazil nuts and cashew nuts samples, with 61% and 73% for Cu, 24% and 35% for Fe, respectively. Among those elements considered toxic, Ni showed the highest percentages of bioaccessible fraction in the pecan and cashew nut samples, with 73 e 71%, respectively. The Pb element showed higher percentages in the Brazil nut and cashew nut samples, with 35% and 88%, respectively. According to the National Health Surveillance Agency (ANVISA), the maximum tolerated limits of inorganic contaminants in chestnuts and nuts is 0.80 mg kg^{-1} for Pb.[4] For Ni, there is no reported limit. The bioaccessibility values observed for Ni and Pb, reinforce the need for their control in different nuts, since these analytes can become a health risk if their concentration exceeds the maximum permitted limit of daily consumption.

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[CNPq, INCTAA and CAPES]

067 - MATRIX EFFECT OF ACID SOLUTIONS COMMONLY OBTAINED AFTER SAMPLE DIGESTION OR EXTRACTION IN MULTIELEMENTAL DETERMINATION BY MIP OES

Christiane Duyck[a*], Edmilson Arruda dos Santos[a], João Victor Soares de Araújo[a], Thiago Silva Santos[a], Rodolfo Lorençatto[b], Ricardo Jorgensen Cassella[a], Rafaella Regina Alves Peixoto[a]

[a]Fluminense Federal University, Analytical Chemistry Department/Chemistry Institute, Niterói, RJ, Brazil, 24020-141
[b] Agilent Technologies - Brazil, Alameda Araguaia, 1142, Ground Floor, Barueri, SP, 06455-000
*e-mail: cbduyck@id.uff.br

Microwave induced nitrogen plasma optical emission spectrometry (N_2-MIP OES) with a Hammer cavity is a suitable technique for multielemental determination, with affordable maintenance, which is rapidly conquering space in Brazil[1]. The MIP OES limitation regarding the analysis of complex matrices is well known. However, studies involving concentrated acid digests or solutions, commonly employed in sample preparation for elemental determination, are scarcely documented. In this work, a systematic approach to the acid matrix effect based on a model solution of 0.2 % HNO_3 is performed with inorganic (nitric, hydrochloric, and sulfuric) and organic (formic and acetic) acid solutions, at four concentration levels (0.2 %, 1 %, 5 % and 1 mol L^{-1}). A 4210 (Agilent) N_2-MIP OES equipped with a OneNeb^{TM} nebulizer coupled to a cyclonic spray chamber is used to monitor atomic and ionic lines of 25 elements with wavelengths varying from 203.985 nm (Se) to 769.897 nm (K) and the emission of molecular species of nitrogen (N_2^+), oxygen (OH) and carbon (CO^+, CN, C_2). Standard solutions were diluted in each acidic matrix at concentrations varying from 0.5 mg L^{-1} to 25 mg L^{-1} (Ca, K, Na, P) and 0.01 mg L^{-1} to 10 mg L^{-1} for other elements. Scandium at 0.1 mg L^{-1} was used for internal standardization of signals. The plasma temperature and the electron number density were calculated for each matrix using the Saha-Boltzmann equation and were in agreement with other study[2], with no significant variations for the considered acid solutions. The plasma robustness was assessed with the Mg (II/I) and N_2^+/OH ratio, and formic, acetic, and hydrochloric acid solutions at 0.2 % and 1 % were the more robust conditions. The simple linear regression method was employed to compare the sensitivities for elements in each matrix, in biplots of the 8 points (blank + 7 standard solutions) calibration curve of the matrix to the 0.2 % HNO_3 one. The slopes were plotted against the wavelength value, and the trends were similar, except for formic acid. In this case, an increase in sensitivity for non-easily ionizable elements between 60 % (i.e., Cd, As) to more than 80 % (i.e., B, Pb) was observed for wavelengths ranging from 213 to 500 nm and for the 0.2 % and 1 % solutions. For organic acid solutions with higher carbon contents, the carbon effect, which is commonly observed in ICP plasmas, was not observed in MIP OES, suggesting another mechanism for signal enhancement in formic acid. Furthermore, the solutions of 1 mol L^{-1} acid concentrations showed similar slopes than the 0.2 % HNO_3 model solutions for most elements, whereas the 5 % acid solutions suffered from signal suppression. These results indicate that the acid matrix effect depends on acid concentration rather than the acid type, except for formic acid at low concentrations.

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068 - DETERMINATION OF TOTAL CONCENTRATION OF Ca, Fe, K, Mn AND Mg IN MUSHROOM SAMPLES BY MIP OES

Adryo N. Tavares[a*], Daisa H. Bonemann[a], Charlie G Gomes[a], Sabrina H. Scherdien[a], Anderson S. Ribeiro[a]

[a]Federal University of Pelotas, Chemical, Pharmaceutical and Food Science Center,
Capão do Leão, RS, Brazil, 96010-900.
*e-mail: adryo.nobre.tavares12@gmail.com.br

Varied species of mushrooms are consumed worldwide, among these, highlighted the *Agaricusbisporus, Pleurotusostreatus and Lentinula edodes*[1]. Considering that these foods are characterized by the bioaccumulation of different compounds, depending on the concentration present in the culture medium, it is essential to monitor its elemental composition, in order to assess the presence of essential elements that are potentially toxic to human health.[2] Thus, the objective of this work is to determine the total concentration of Ca, Fe, K, Mn and Mg in mushroom samples by Microwave-Induced Plasma Optical Emission Spectrometry (MIP OES). For this study, the acid decomposition conditions were optimized[3], through a multivariate design, evaluating the variables: sample mass, decomposition time and temperature of digester block, and volume of H_2O_2 35% m/v. For this experimental planning, the volume of HNO_3 65% m/v was fixed at 5 mL and the time of 1 h after addition of H_2O_2. In this way, an optimal condition for sample preparation was obtained: sample mass (500 mg), of sample, temperature of digester block (125 °C); decomposition time (120 min) and H_2O_2 volume (2 mL). The accuracy of the results was evaluate analyzing a mixture the two certified reference materials from the CRM-Agro Brazil with the samples: Sugar cane leaves CRM + mushroom sample and tomato pulp CRM + mushroom sample. For the calculation of the recovery percentage, the detected concentration value for the mixture of CRM plus mushroom and the reference value, for each analyte contained in the mixture was considered. After applying Student's t test with 95% confidence level, was no significant difference between the values found by the developed method and the certified values for each analyte. The method was applied to analyze 3 samples of three different species of mushroom: Agaricus Bisporus (which are found commercially as Paris), Portobello, and Pleutus ostreatus (marketed as Shimeji). The Portobello mushroom sample had the highest concentrations of Ca and K, while the Shimeji sample had the highest concentrations of Fe, Mg and Mn, as shown in Table 1. The concentrations in the different samples showed a great variation, demonstrating the importance of nutritional information of edible mushrooms. The recommended daily digestion limit for Ca, Fe, K, Mn, and Mg are: 1,000, 10, 4,700, 260 and 2 mg, respectively, considering the consumption of 100 g of mushroom, none of the elements exceeded the daily intake limits.

Table 1. Results for Ca, Fe, K, Mg and Mn in mushrooms samples by MIP OES. (n=3)

	Paris (mg/Kg)	Portubello (mg/Kg)	Shimeji (mg/Kg)
Ca	6.89 ± 0.17	10.8 ± 0.7	4.9 ± 0.4
Fe	2.29 ± 0.18	3.17 ± 0.01	8.1 ± 0.4
K	2958 ± 49	3808 ± 77	2149 ± 133
Mg	88 ± 5	89 ± 5	161 ± 5
Mn	0.51 ± 0.03	0.48 ± 0.02	1.07 ± 0.03

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[CNPq, CAPES, INCTAA]

069 - ELEMENTAL IMPURITIES DETERMINATION IN AUTHENTIC AND SEIZED SILFDENAFIL AND TADALAFIL TABLETS

Julia Facci Colangelo[a*], Laura Aguiar Santos[a], Fernanda Costa Pinheiro[b], Clésia Cristina Nascentes[b], Christian Fernandes[a].

[a]Federal University of Minas Gerais, Faculty of Pharmacy, Belo Horizonte, Minas Gerais, Brazil, 31270-901
[b]Federal University of Minas Gerais, Department of Chemistry, Belo Horizonte, Minas Gerais, Brazil, 31270-901
*e-mail: juliafacci@yahoo.com.br

Drug counterfeiting is an illegal activity in expansion worldwide, according to a research carried out by Wolrd Health Organization in 2017, one in ten medicines that circulates on the market of developing countries is counterfeit or has inferior quality.[1] In this regard, the main targets are those with the higher costs or the ones sought after by the population, among which stand out those intended for sexual impotence, particularly drugs containing sildenafil and tadalafil. Elemental impurities determination in pharmaceuticals has become an emerging topic due to the regulatory changes about the permissible limits and the analytical techniques applied for this determination.[4] The inductively coupled plasma mass spectrometry (ICP-MS) is the technique that presents the higher sensitivity for elemental impurities analysis, whose monitoring is crucial due to the toxicity of some elements even at trace levels.[2] Based on the above considerations, in this work six authentic samples and ten samples seized by the Federal Police and the Civil Police of the state of Minas Gerais of tablets containing sildenafil and tadalafil were analyzed in accordance with chapter <232> and <233> of the United States Pharmacopeia (USP).[3,4] The main goal of this work was to establish a comparison between the levels of elemental impurities determined in the authentic and seized samples. For this, a new method using ICP-MS was developed aiming at the simultaneous determination of the elements Ag, As, Au, Ba, Cd, Co, Cr, Cu, Hg, Ir, Li, Mo, Ni, Os, Pb, Pd, Pt, Rh, Ru, Sb, Se, Sn, Tl e V. The sample preparation procedure was proposed and optimized through a factorial design 2^2 with central point, in which 0.100 g of the samples were submitted to a acid microwave-assisted digestion using 5 mL of $3HNO_3$:1HCl 20% v v^{-1} and 2 mL de H_2O_2 30% v v^{-1}. The determinations were performed by ICP-MS in standard mode and with a collision cell using He 99,995%, and Y was used as internal standard to correct matrix effects. The precision and accuracy were evaluated by addition and recovery experiments at three levels (0.5; 1.0 e 5.0 µg L^{-1}) in two authentic samples. Recoveries ranged from 70 to 127% except for Ag, Cu and Ni. The limits of quantification were calculated from 10 authentic blanks and ranged from 0,005 (Tl) to 1.3 µg g^{-1} (Se). Considering all the analyzed samples, all analytes were below the respective limits of quantification except Ba, Cd, Cr, Co, Cu, Li, Mo, Ni, Pb, Sb, Sn e V. The levels determined ranged from 0.006 (Cd) to 6.0 µg g^{-1} (Ni) and the highest concentrations were determined in the seized samples. However, all the levels determined in authentic and seized samples are below their respective maximum allowable limits, as established in chapter <232> of USP. The proposed method entails a reduced amount of reagent required for sample digestion and explore the sensitivity of ICP-MS based methods to evaluate the inorganic contamination in seized and commercial samples of medicines.

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Sample Preparation

070 - REVERSED-PHASE DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR THE DETERMINATION OF Fe AND Cu IN ISOLATING VEGETABLE OIL

Oldair D. Leite[a*], Ian B. Tasistro[a], Eder L.M. Flores[b], Jessica F.B. Wendt[a], Rochele S. Picoloto[c]

[a]Federal Technological University of Paraná, Postgraduate Program Degree in Environmental Technologies, Medianeira, Paraná, Brazil, 85884-000
[b] Federal Technological University of Paraná, Department of Chemistry, Medianeira, Paraná, Brazil, 85884-000
[c] Federal University of Santa Maria, Department of Chemistry, Santa Maria Rio Grande do Sul,
*e-mail: oldairleite@utfpr.edu.br

In recent years, mineral oils used as insulators in electrical transformers are gradually being replaced by vegetable oils from soy or corn. Vegetable oils are modified in order to meet several qualities regulated by ASTM D6871 for their use as lubricants and insulators, such as: low volatility, little change in viscosity with temperature changes, and greater solubility for additives than mineral oils. Moreover, vegetable oils have advantages in terms of environmental impacts. The presence of metals such as Fe and Cu even at low concentrations (mg kg^{-1}) in insulating oils can reduce the breakdown voltage and accelerate the oxidation of insulating oils, so sensitive analytical methods for the quantification of these metals are required. In the present work, the reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) method was used as a sample preparation for extraction and preconcentration of Fe and Cu in vegetable insulating oil, as a green alternative to the methodology proposed by ASTM D7151-15. Flame atomic absorption spectrometry (FAAS) was used for the quantification of analytes, applying external standard calibration method. To optimize the method, some parameters were evaluated, such as: sample mass (2.5 g, 5 g and 10 g), type of extracting solvent (HNO_3 and HCl), type of dispersing solvent (isopropanol and n-propanol), solvent concentration extractant (0.2; 0.5; 1 and 1.5 mol L^{-1}), extractant/dispersant ratio (50:50, 60:40, 70:30 and 80:20 (v/v)), temperature (25, 40, 60 and 80 ºC) and centrifugation time (5, 10 and 15 min). For the experiments, assays were performed in triplicate for pure oil samples and spiked oil with 1 µg g^{-1} of Fe and Cu, using a standard solution in organic medium. The limits of quantification (LOD) obtained were 0.019 µg g^{-1} for Cu and 0.035 µg g^{-1} for Fe, with recoveries of 105% for Cu and 100% for Fe. The proposed methodology was applied to several samples of the insulating vegetable oil in 5 states of use and compared to the Emulsion Breaking Induced Extraction methodology. Finally, a study of the concordance of the proposed method with the 12 principles of green chemistry was performed using the AGREE software. The RP-DLLME proposed method is characterized by low cost, simplicity, high analytical frequency, and low limits of quantification, besides fitting in with the principles of Green Analytical Chemistry with low reagent consumption, less waste generation, and with the possibility of using 200 µL of diluted acid as extracting solvent.

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[UTFPR, CEANMED, Fundação Araucária, CAPES, CNPq]

071 - ECOFRIENDLY SOLID PHASE FOR THE PRECONCENTRATION OF LEAD PRIOR TO DETERMINATION BY ETAAS

Leticia B. Escudero[a*], Pamela Y. Quintas[b]

[a]Laboratory of Environmental Biotechnology (BioTA), Interdisciplinary Institute of Basic Sciences (ICB), UNCUYO–CONICET, Faculty of Natural and Exact Sciences, National University of Cuyo. Padre J. Contreras 1300, (5500) Mendoza, Argentina.
[a]Laboratory of Analytical Chemistry for Research and Development (QUIANID), Interdisciplinary Institute of Basic Sciences (ICB), UNCUYO–CONICET, Faculty of Natural and Exact Sciences, National University of Cuyo. Padre J. Contreras 1300, (5500) Mendoza, Argentina.
*e-mail: lescudero@mendoza-conicet.gob.ar

Lead is a highly toxic metal found naturally in the environment, although its greatest presence arises as result of human activities.[1] Its persistence in the environment facilitates transport of this element to rivers, lakes, streams, and may even contaminate water or food for human consumption. For this reason, the continuous monitoring of the metal in food is of fundamental interest. As lead concentrations in these matrices are generally very low (trace or ultratrace), very sensitive instrumental analytical techniques are required for its detection. However, even with techniques such as atomic absorption spectrometry with electrothermal atomization (ETAAS) or inductively coupled plasma mass spectrometry (ICP-MS), determination may not be feasible. In these cases, preconcentration based on the use of adsorbent materials is a very effective tool to increase the sensitivity of analytical methods, offering additional advantages such as simplicity and low consumption of organic solvents and other reagents.[2] In this context, the use of ecofriendly solid phases is welcome.

The objective of this work was to investigate the adsorption efficiency of a completely biodegradable hybrid material formed by bacteria and roots for the online preconcentration of lead. Initially, the biomaterial was prepared by mixing the components in an aqueous medium, under stirring for two hours at room temperature and finally drying in an oven. Then a lead solution was introduced using an online injection system to quantitatively retain the analyte on a microcolumn packed with the solid phase. The retained analyte was then desorbed with a flow of an acidic agent and finally it was determined by ETAAS. Under optimal experimental conditions, an analyte retention of 100% and an enrichment factor of 62 were achieved. The LOD for preconcentration of 5 mL of sample was 5.0 ng/L. The dynamic capacity of the hybrid adsorbent was 36 mg/g, which favoured the reuse of the column during more than five cycles cycles of adsorption-desorption. These results show that the proposed ecofriendly material is efficient for the preconcentration of lead from aqueous solutions and shows potential for its application in more complex matrices such as food.

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[PIBAA-1208 CONICET, M015-T1 UNCUYO]

072 - ASSESEMENT OF TRACE ELEMENTS CONTENT IN SEAWEED SAMPLES FROM BRAZILIAN NORTHEAST

Emanuelle E. V. Ribeiro[a*], **Iago G. M. Nobre**[a], **Débora R. O. Silva**[a], **William M. X. Silva**[a], **Samile K. O. Sousa**[a], **Gisele S. Lopes**[a], **Marjory L. H. Araújo**[b], **Francisco L. F. Silva**[c], **Wladiana O. Matos**[a*]

[a]Federal University of Ceara, Department of Analytical and Physical-Chemistry/ Laboratory of Studies in Applied Chemistry (LEQA), Fortaleza, Ceará, Brazil, 60440-900
[b]Federal University of Ceara, Department of Biochemistry and Molecular Biology/Laboratory of Biotechnology of Algae and Bioprocesses, Fortaleza, Ceará, Brazil, 60440-900
[c] State University of Ceara, Education and Integrated Science Faculty of Crateus (FAEC), Crateús, Ceara, Brazil, 63704-155
*e-mail: wladianamatos@ufc.br

Seaweed represents the base of the food chain in the oceans and is responsible for a good part of the global photosynthetic. In many countries, it has been widely used as a food source and feedstock for food, pharmaceutical and biotechnological industries. On the coast of Northeastern of Brazil, there are communities that cultivate and sell algae for these industries. However, there are no data about seaweed from Brazilian Northeast. In this work, seven species of macroalgae (red, green, and brown species) were collected in Flecheiras beach, Ceará, Brazil. The samples were digested in acid media (68% w $w^{-1}HNO_3$) using block digester and the elements Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Sb, Se, Sr, V e Zn were quantified by ICP OES. Mercury was determined using direct analysis by DMA-80 EVO. The European reference material CD-200 – Seaweed sample was analysed for accuracy tests obtained recovery higher than 90% for the certified elements. The results are summarized in radar-graph in figure 1 that shows the distribution of species in sample. The As content in the sample of brown alga (*Sargassum Vulgare*) stands out, which was more than 10 times higher than the other species, in addition to also having the highest concentrations of Hg. *Ulva Lactuca* is a green alga that also stands out for being that V was detected. Seaweed is commonly used as a marker of environmental pollution and the content of V may come from oil spills in the Brazilian Northeast in 2019. Studies on the effect of seasonality on the concentration of these elements and speciation analysis of As and Hg are ongoing.

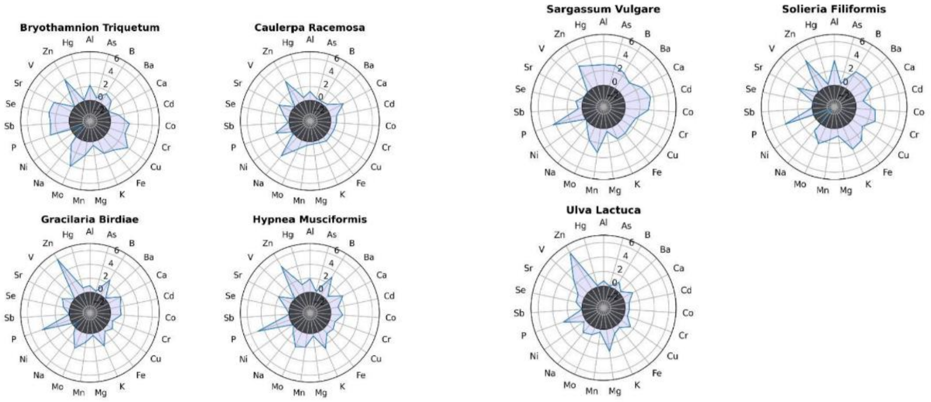

Figure 1. Profile of trace elements in seaweed

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[UFC, CAPES, FUNCAP, CNPq]

073 - DEVELOPMENT OF A SINGLE SAMPLE PREPARATION METHOD FOR MICROPLASTIC AND HALOGENS DETERMINATION IN FISH TISSUE

Débora P. de Almeida[a], Gustavo R. Bitencourt[a], Karen Giacobe[a], João Victor Jacobi[a], Cezar Augusto Bizzi[a*]

[a] Universidade Federal de Santa Maria, Departamento de Química, Santa Maria, Brazil, 97015-900
*e-mail: cezar.bizzi@ufsm.br

Plastic waste is the main component of marine debris due to overuse and inadequate disposal methods. When plastics are fragmented, damaging chemicals and microplastics (MPs) are released, which can lead to increased toxicity in the environment. As part of the problem, MPs raise particular concerns due to their unique characteristics that make them easy to transfer between oceans in the marine ecosystem, between different trophic levels in the food chain and even between various tissues of contaminated animals.[1] The purpose of this work is to develop a single sample preparation method for MPs and halogens determination in fish tissue, which is based on a selective digestion of fish tissue without damaging MPs. The proposed approach was developed using alkaline reagents for microwave assisted wet digestion, allowing quantitative recoveries of both MPs and F, Cl, Br, and I in the same digests. After sample digestion, MPs were gravimetrically determined, while halogens were determined by inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) and ion chromatography (IC). The determination of F was only possible with the use of high-resolution spectrometers operating with He plasma. Thus, this element tends to be determined using the ion chromatography technique, which requires an appropriate solution from sample preparation step.[2] Based on these conditions, optimization was carried out with up to 2 g of fish sample (shark species) added to 0.1 g of a mixture of MPs (polyethylene terephthalate, PET; polystyrene, PS; expanded polystyrene, EPS; polypropylene, PP; high-density polyethylene, HDPE; low-density polyethylene, LDPE; polycarbonate, PC; and, polyvinyl chloride, PVC). Suitable conditions were obtained using a solution of 0.1 mol L^{-1} NH_4OH, heated at 180 °C during 20 min. Optimized condition allowed the digestion of up to 1.5 g of *in natura* sample, with no suspended particles that would impair the filtering process (required for MPs determination). The proposed method allowed the gravimetric determination of seven types of plastics (PET, PS, EPS, PP, HDPE, LDPE, PC, and PVC) with a particle size greater than 0.5 mm, with recovery ranging from 93 to 98%. The same solution obtained after alkaline digestion was used for halogens determination. The results obtained by means of the proposed alkaline digestion protocol were compared with microwave assisted extraction (MAE) reference method, which used 1 mol L^{-1} of NH_4OH as extraction solution. The proposed alkaline digestion method was also applied for pink shrimp, yellow hake and tuna. The results obtained showed that it was possible to use the same digestion solution for the determination of MPs (gravimetric technique) and halogens using IC (F and Cl), ICP-OES (Cl) and ICP-MS (Cl, Br and I) techniques with no significant difference between the values. The accuracy was assessed by halogens determination in the CRM of fish protein (DORM-5) which presented agreement of 80% for Cl and Br, and 91% for I. As there are no values reported in the CRM for F, the IC was used for the accuracy assessment. The proposed method can be considered suitable for the determination of seven types of MPs and halogens using the same digestion protocol in different seafoods, providing a versatile and accurate method.

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074 - DETERMINATION OF METALS AND S IN LIGNOCELLULOSIC BIOMASS FOR STUDIES ON PYROLYSIS PROCESSES

Thalyta F. Silva[a], Eliana T. F. Larruscain[b], Ana Luísa S. Machado[c], Cezar A. Bizzi[c], Fábio A. Duarte[c], Paola A. Mello[c*]

[a]Post Graduation Program in Chemistry Engineering, [b]Post Graduation Program in Chemistry, [c]Chemistry Department,
Universidade Federal de Santa Maria, Santa Maria, RS, Brasil, 97105-900
*e-mail: paola.mello@ufsm.br

The dependence and high consumption of fossil fuels (non-renewable) has caused damage to the environment due to the emission of greenhouse gases, pollutants, such as NOx, SOx, chlorine species, and fine particulate matter, impairing air quality.[1] Sulfurous gases cause complications because they accumulate in the atmosphere and the condensation of sulfuric acid leads to the formation of acid rain.[2] The production of fuels with neutral or low carbon emissions through renewable resources, such as biomass, is an alternative to supply energy demand, minimize dependence on fossil fuels and reduce pollutant emissions.[3] It is possible to obtain biofuels through agricultural and forest residues, such as sugarcane straw, and pine by pyrolysis, for example. However, the contamination of the bio-oil will be dependent on the biomass composition and production process. As a consequence, it is necessary important to know the lignocellulosic biomass that is used to produce these biofuels. For this purpose, elemental analysis is necessary, since knowing the elemental chemical composition of the raw material is essential to understand the contamination in final products as well as to define the best processing routes.[1,3,4] The determination of metals and S in solid biomass has been carried out by different ways, such as following the digestion proposed by the EN ISO 16967 standard or combustion as in EN ISO 16994 standard for further determination by atomic spectrometry. The EN ISO 16967 standard proposes the digestion of 500 mg of sample in closed system, with the help of reagents, temperature, and pressure. Step 1 consists of using 3 mL 30% H_2O_2, 8 mL concentrated HNO_3, and 1 mL 40% HF and the irradiation program consists of a 15 min ramp to 190 ºC and a 20 min hold. In step 2, 10 mL of 4% H_3BO_3 is added with an irradiation program of fast heating to 150 ºC and holding for 15 min. The present study aims to establish an alternative analytical protocol for the elemental chemical characterization of lignocellulosic biomass. The elementary determination of Al, Ca, Fe, Mg, P, K, Si, Na, Ti, and S in the biomass of sugarcane straw and pine residue by inductively coupled-plasma optical emission spectrometry (ICP-OES, Spectro Ciros model, CCD Spectro Analytical Instruments, Germany) was investigated through the decomposition of the samples, adapting method A of the EN ISO 16967 standard in a microwave digestion system (Ethos Easy model, Milestone Systems, Denmark). The sample mass required for the analysis was investigated (100 to 500 mg) and the influence of the use of boric acid was investigated. The accuracy of the proposed method was evaluated using certified reference material (CRM) of Spruce needles (BCR 101) and spike recovery experiments. For sulfur, a comparative study was carried out using an elemental analyzer (Multi EA® 5000 model, Analytik Jena, Germany).

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[PRH ANP 52.1, UFSM and CAPES]

075 - DETERMINATION OF Fe, Ni, V, AND S IN CRUDE OIL BY ICP-OES AFTER MICROWAVE-ASSISTED ULTRAVIOLET DIGESTION

Ariadne Gabriela L. P. Gonçalves, Bruna C. Padoin, Alice P. Holkem, Jussiane S. Silva, Erico M. M. Flores, Rochele S. Picoloto, and Paola A. Mello *

Federal University of Santa Maria, Chemistry Department, Santa Maria, RS, Brazil, 97105-900
*e-mail: paola.mello@ufsm.br

Crude oil is a mixture of hydrocarbons and contains water, sediments, and some metals (Fe, Ni, and V), and non-metals (S).[1] The presence of Fe, Ni, V, and S can cause catalyst poisoning, corrosion in furnaces and boilers, as well as environmental pollution.[2] Therefore, the determination of these contaminants in crude oil is required. For this purpose, the American Society for Testing and Materials (ASTM) proposed methods D7876[3] and D4294[4] for the determination of Fe, Ni, and V by flame atomic absorption spectrometry (FAAS) or inductively coupled plasma optical emission spectrometry and X-ray fluorescence spectrometry (XRF) for S. Additionally, the method D7876[3] recommends using a microwave equipped with PTFE flasks to decompose up to 1 g of sample with 4 mL of concentrated acid. However, the ASTM methods present several disadvantages, such as the use of high amounts of concentrated reagents and consequently high waste generation. In addition, interferences during the determination can be observed due to the high carbon concentration in the final solutions, because matrix complexity makes digestion commonly ineffective. In the present study, a microwave-assisted ultraviolet wet digestion (MAWD-UV) method was proposed for the digestion of crude oil for further Fe, Ni, V, and S determination by inductively coupled plasma optical emission spectrometry (ICP-OES). Reference values were obtained by ICP-OES after microwave-assisted wet digestion (MAWD) using 100 mg of crude oil and 6 mL of concentrated HNO_3. A microwave oven (Multiwave 5000, Anton Paar, Austria) equipped with 8 quartz vessels (internal volume of 80 mL) and maximum temperature and pressure of 280 °C and 80 bar, respectively, was used for the experiments for the proposed and the reference methods. For the proposed method, UV radiation was generated *in situ* by an immersed electrodeless Cd discharge lamp (main emission line of 228 nm). Diluted HNO_3 solutions (0.5 to 7.0 mol L^{-1}), sample mass (100, 250, and 500 g), and H_2O_2 volume (1, 2, and 3 mL) were evaluated trying to find a condition allowing suitable digestion efficiency. All the determinations were carried out using an ICP-OES spectrometer with axial view (Ciros CCD, Spectro Analytical Instruments, Germany). The digestion efficiency for both methods was evaluated by measuring carbon and acid content in digests and results for these parameters as well as the results for metals and S were compared with those obtained using wet acid digestion without the UV lamp (using 6 mL of concentrated HNO_3 and the same heating program). The determination of dissolved carbon in digests was also performed by ICP-OES. The residual acidity was determined using an automatic titration system (836, Metrohm, Switzerland) equipped with a combined pH electrode (6.0262.100, Metrohm). For the proposed method, the heating program was adapted from ASTM D7876[3] as follows: *i*) hold at 400 W for 20 min, *ii*) ramp up to 700 W for 10 min, *iii*) hold at 700 W for 25 min, and *iv*) hold at 0 W for 20 min, for cooling. No statistical difference was observed for Fe, Ni, V, and S (*t-test*, confidence level 95%), using 500 mg of crude oil with 15 mL of 1.0 mol L^{-1} HNO_3 plus 2 mL of H_2O_2 for MAWD-UV in comparison with reference values (MAWD using concentrated HNO_3). Finally, the proposed MAWD-UV method was suitable for the digestion of crude oil and further simultaneous Fe, Ni, V, and S determination by ICP-OES. Advantages of using MAWD-UV for sample preparation can be highligjted such as high efficiency of crude oil digestion even using diluted acids, low waste generation, low dissolved carbon (4,4 g L^{-1}) and low acidity (20%) of digests and low detection limits (ranging from 0.12 to 1.3 µg g^{-1}).

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[CNPq, CAPES, and UFSM]

076 - SAMPLE PREPARATION METHODS WITH DILUTE ACID FOR DETERMINATION OF SELENIUM IN PROBIOTICS BY GFAAS

Larissa M. A. Oliveira[a*], Nicole Pereira Bins[a], Diogo Pompéu de Moraes[a],
Juliana S. F. Pereira [a]

[a] Universidade Federal do Rio Grande do Sul, Departament of Chemistry, Porto Alegre, RS, Brazil, 91501-900
*e-mail: lary.mayar@gmail.com

Selenium (Se) is an essential micronutrient for humans, as it plays a critical role in biological activities such as reproduction, DNA synthesis, thyroid hormone metabolism, and protection against oxidative stress. However, it's an element that presents a narrow concentration range between essential and potentially toxic levels. Se deficiency is associated with Keshan disease, an increase and weakening of cardiac muscle. On the other hand, excess selenium can lead to hair loss, gastrointestinal and hormonal disorders, and skin rashes, among others [1]. Among the options for supplementing this micronutrient, the use of dietary supplements is the only form in which it can be prescribed or self-administered, and they are commercially available in multivitamin and/or multimineral or probiotic supplements. A probiotic is a beneficial microorganism that helps maintain intestinal microbial balance, synthesis bioactive compounds and essential amino acids, among other functions [2]. Randomized clinical trials reveal that adequate selenium intake is associated with a lower incidence and lower mortality from cardiovascular diseases and a reduction in the risk of prostate, lung, and colorectal cancer [3]. In this study, two decomposition methods using diluted acid in a closed system were evaluated for the subsequent determination of total selenium in probiotics. In microwave-assisted decomposition (MWAD), parameters such as diluted HNO_3 concentration, volume of H_2O_2 addition, and sample mass were analyzed. In microwave-induced combustion (MIC), sample mass and diluted HNO_3 concentration were evaluated. A sample containing the bacterium *Lactobacillus acidophilus* and two samples containing *Saccharomyces cerevisiae* yeast, both acquired locally, were selected. The evaluation of the decomposition methods was conducted through residual carbon content (RCC) and residual acidity (RA). The analytical frequency for the decomposition methods was 60 minutes for MWAD, while for MIC, it was 25 minutes. The quantification of total selenium by graphite furnace atomic absorption spectrometry was optimized using MWAD digests. The optimized pyrolysis and atomization temperatures for analyte quantification were 1200 and 2000 °C, respectively, using Pd as a chemical modifier. Accuracy was evaluated using the certified reference material (SELM-1). The selenium concentration in the three analyzed samples ranged from 32.6 to 211.26 $\mu g\ mg^{-1}$, in agreement with the values described on the probiotics' packaging. The limits of quantification (LQ) of the methods were lower than 1.0 $\mu g\ mg^{-1}$. Results obtained by the digestion methods were in agreement with the certified value for total Se.

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[UFRGS, CAPES and CNPq]

077 - A NEW MAGNETIC NANOMATERIAL AS SOLID PHASE FOR TRACE ELEMENTS ANALYSIS IN BRAZILIAN PRE-SALT PRODUCED WATER BY ICP OES

Maradona C. da Silva[a], Tiago M. Freire[b], Pierre B. A. Fechine[b], Gisele S. Lopes[a], Francisco L. F. Silva[c], Wladiana O. Matos[a*]

[a]Federal University of Ceara, Department of Analytical and Physical-Chemistry/ Laboratory of Studies in Applied Chemistry (LEQA), Fortaleza, Ceará, Brazil, 60440-900
[b]Federal University of Ceara, Department of Analytical and Physical-Chemistry/Advanced Material Chemistry Group (GQMAT), Fortaleza, Ceará, Brazil, 60440-900
[c] State University of Ceara, Education and Integrated Science Faculty of Crateus (FAEC), Crateús, Ceara, Brazil, 63704-155
*e-mail: wladianamatos@ufc.br

In general, Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) is applied for the quantification of most inorganic elements in petroleum-produced water (PW). However, the analysis of this type of matrix by ICP OES is not so trivial due to its high salinity, which can cause problems in the transport of the sample to the plasma, light scattering, ionic suppression of the analyte, moreover salt deposition on the torch and injection tube[1]. Matrix effects can be minimized by diluting the sample, but this strategy also causes loss of sensitivity, impairing the detection of analytes at lower concentrations. Thus, to avoid the need to use more expensive and sensitivity analysis techniques, an extraction/pre-concentration procedure can be a strategy to make ICP OES analysis of inorganic elements at trace levels in PW possible. In this work, a new magnetic nanomaterial functionalized with carboxymethylcellulose (Fe_3O_4@CMC) was synthesized and characterized to be used as a solid phase in an extraction/pre-concentration procedure for Co, Cu, Mn, Pb and Zn in PW samples from the pre-salt layer. For the synthesis of nanoparticles, it was dissolved 1.85 g of $FeCl_3.6H_2O$ (7 mmol) and 1.16 g of $FeSO_4.7H_2O$ (4 mmol) in 15 mL of distilled water. After that, 1 g of CMC dissolved in 10 mL of distilled water was added. This mixture was taken to the ultrasonic probe with a pulse regime of 2s/1s (on/off) for 6 min, and 7 mL of 27% w v^{-1} NH_4OH was slowly added during the sonication step. Then, the nanomaterial was dried using lyophilization. For the crystalline structure studies and its characteristics, the techniques X-Ray Diffraction and FTIR were employed (Figure 1). The optimization of extraction method was performed using a Doehlert design. The pH was tested at 6 levels, the pre-concentration time at 4 levels and the nanomaterial mass at 2 levels. The desirability function was used in response to analyte recovery. The desirable conditions were for 40 mL of sample: pH 5.7, 46 mg of Fe_3O_4@CMC mass and 20 min of pre-concentration time. For desorption, 3 mL of HNO_3 10 % v v^{-1} was added and mixed for 3 min reaching a preconcentration factor around 13 times. The solution was magnetically separated, and the supernatant was carried out to ICP OES. The proposed method was applied for the analysis of PW samples. The content of trace elements found was: Co (0.02 ± 0.01 mg L^{-1}), Cu (0.04 ± 0.01 mg L^{-1}), Mn (0.10 ± 0.03 mg L^{-1}), Pb (0.06 ± 0.01 mg L^{-1}) and Zn (0.13 ± 0.02 mg L^{-1}). All analytes presented levels of concentration within the acceptable limits of CONAMA legislation 430/11. Robustness tests of the method with different salinities are being carried out.

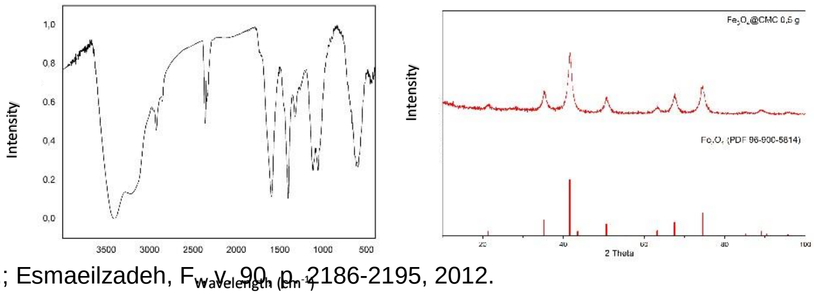

Figure 1: FT-IR and DRX

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[UFC, CAPES, CNPq, FUNCAP, NUTEC, LEA-UFES]

078 - RARE EARTH ELEMENTS IN CRICKETS: CAN DILUTED ACIDS BE USED FOR SUITABLE SAMPLE PREPARATION?

Gustavo Gohlke[a], João L. K. Rocha[a], Thiago C. Pereira[a], Alessandra S. Henn[a], Jussiane S. Silva[a], Fábio A. Duarte[a], Érico M. M. Flores[a*]

[a] Federal University of Santa Maria, Department of Chemistry, Santa Maria, RS, Brazil, 97105-900
*e-mail: ericommf@gmail.com

Crickets have recently become an alternative source of protein due to many nutritional and breeding advantages over conventional protein sources.[1] However, contamination by rare earth elements (REE, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) can occur during their breeding. REE are emerging contaminants in food due to their release into the environment from mining, electronic, and industrial waste, leading to bioaccumulation in organisms. These elements may be potentially toxic to humans, with a probable risk of cardiovascular and neurologic diseases.[2] In this sense, the determination of REE in crickets is necessary to ensure consumers health. REE are usually determined by inductively coupled plasma mass spectrometry (ICP-MS) with desolvation systems (e.g., ultrasonic nebulization, USN). However, this technique requires the sample in a solution form, demanding a previous sample preparation step. Due to the high content of proteins, carbohydrates, lipids, and inorganic fraction, crickets are difficult to digest by conventional acid wet digestion. Therefore, alternative energies, such as microwave (MW) and ultraviolet (UV) radiation, have been proposed for suitable sample preparation of several matrices, resulting in low carbon and acid in solution, avoiding interferences in the determination step. Furthermore, the combination of MW and UV allows the digestion of high sample mass, reducing the limits of quantification (LOQ) to ng g^{-1} order.[3] Thus, the goal of this study is to evaluate the microwave-assisted ultraviolet digestion (MAWD-UV) method for sample preparation of crickets for further REE determination by USN-ICP-MS. For this, three cricket samples of different origins (China, Brazil, and Thailand) were used. All samples were dried and then ground in an impact grinding mill. Different digestion solutions were evaluated in the proposed MAWD-UV method (using 500 mg of sample): 0.5 mol L^{-1} HNO_3 + 1.3 mol L^{-1} H_2O_2; 1 mol L^{-1} HNO_3 + 1.3 mol L^{-1} H_2O_2; 1 mol L^{-1} HNO_3 + 1.3 mol L^{-1} H_2O_2 + 0.8 mol L^{-1} HCl; 2 mol L^{-1} HNO_3 + 1.3 mol L^{-1} H_2O_2; 2 mol L^{-1} HNO_3 + 0.65 mol L^{-1} H_2O_2; 3 mol L^{-1} HNO_3; and 3 mol L^{-1} HNO_3 + 0.8 mol L^{-1} HCl. The efficiency of the proposed method was evaluated based on the agreement of the results for REE with the reference method (microwave-assisted wet digestion with concentrated HNO_3, MAWD), the carbon content in the solution, and the residual acidity of digests. The accuracy evaluation of the proposed MAWD-UV method was performed by the analysis of certified reference material of mussel tissue (BCR-668), recovery experiments (at two concentration levels, 50 and 250 ng g^{-1}), and by comparison with results obtained after MAWD. Complete digestion of cricket samples was observed when solutions with up to 1 mol L^{-1} HNO_3 were used. However, agreement higher than 90% with MAWD results was obtained only using 3 mol L^{-1} HNO_3 + 0.8 mol L^{-1} HCl as a digestion solution. Furthermore, when 3 mol L^{-1} HNO_3 was used as a digestion solution, agreement with the reference method was below 90% for Eu (80%), Ho (22%), and Tb (81%), demonstrating that the use of HCl is necessary. Under optimized conditions, no significant difference (t-test, 95% confidence level) was observed between results obtained by MAWD-UV and MAWD for all REE in cricket samples from China, Brazil, and Thailand. Moreover, no significant difference (t-test) was observed between certified and obtained values after CRM BCR-668 analysis. Additionally, recoveries ranging from 92 to 110% were obtained, indicating a good accuracy of the proposed method. In this sense, MAWD-UV was demonstrated to be suitable for crickets digestion for further REE determination, allowing solutions with low C concentration (1370 mg L^{-1}) and acidity (1.1 mol L^{-1}), in addition to very low LOQs (0.15 ng g^{-1} (Eu) to 37 ng g^{-1} (Ce)).

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[CNPq, FAPERGS and CAPES]

079 - A SIMPLE MICROWAVE-ASSISTED DIGESTION FOR FURTHER Os AND OTHER PLATINUM GROUP ELEMENTS DETERMINATION IN DRUGS

Vitoria H. Cauduro[a], Alessandra S. Henn[a], Erico M. M. Flores[a*]

[a]Federal University of Santa Maria, Chemistry Department, Santa Maria, RS, Brazil, 97105-900
*e-mail: ericommf@gmail.com

The presence of elemental impurities in pharmaceutical products is an ever-present concern regarding consumer safety. In this sense, the ICH Q3D guideline establishes permitted daily exposure (PDE) values for these impurities[1]. Among them, it is important to mention the need for quality control regarding the presence of platinum-group elements (PGEs), generally used as catalysts in drug synthesis[1]. This is because determination of these elements is a challenge when using techniques such as inductively coupled plasma mass spectrometry (ICP-MS), due to the difficulty in obtaining sample solutions in which these analytes are stable. This is especially relevant in the case of Os, for which only a few studies have managed to obtain results in accordance to the accuracy range established by the United States Pharmacopeia (75 to 150%).[2,3] In this sense, this study aimed to develop a simple sample preparation method based on microwave-assisted wet digestion (MAWD) for further determination of PGEs, including Os, in active pharmaceutical ingredients (APIs) by ICP-MS. For this, the API sulfamethoxazole was used for method optimization. For the MAWD procedures, samples were weighed into polytetrafluoroethylene vessels, to which 6 mL of digesting solution were added. The vessels were then closed and placed in a rotor, which was positioned in a microwave oven. The irradiation program used consisted of three steps: *i)* 10 min ramp to 1400 W; *ii)* 30 min at 1400 W; and *iii)* 20 min at 0 W (cooling step). Afterwards, the digests were collected into polyethylene (PE) vessels and the volume was made up to 20 mL with ultrapure water. For Os determination, 1 mL of the final sample solution was transferred into a PE vessel containing 20 mL of stabilizing solution (83.8 mmol L^{-1} acetic acid, 10 mmol L^{-1} thiourea and 0.568 mmol L^{-1} ascorbic acid),[4] prior to the determination step. Sample mass (100 to 500 mg), digesting solution (14.4 mol L^{-1} HNO_3, and mixtures of 14.4 mol L^{-1} HNO_3 and 12 mol L^{-1} HCl in the ratios of 1:1, 1:3 or 3:1, v v^{-1}) were evaluated. The best conditions were selected based on analyte recovery tests (at the *J* level),[3] residual carbon content and residual acidity in digests. For the determination step, the composition of the calibration solution (5% HCl or stabilizing solution) was evaluated, and the possibility of carbon interference (up to 2000 mg L^{-1} of C) was investigated for all analytes. Accuracy of the proposed method was evaluated by analyte recovery tests at 50, 100 and 150% of the *J* level.[3] The optimized conditions for the proposed MAWD method were 500 mg of sample and 6 mL of 1:1 HNO_3:HCl (v v^{-1}) as digesting solution. It was observed that C concentrations higher than 800 mg L^{-1} caused interferences for PGEs determination, with the exception of Os. Furthermore, 5% HCl was an adequate calibration solution for all PGEs except for Os, for which the calibration solutions for ICP-MS determination had to be prepared in stabilizing solution. Overall, analyte recoveries were quantitative for all samples, and determination of all PGEs, including Os, could be achieved using a relatively simple sample preparation method based on MAWD. Furthermore, limits of quantification were adequate for PGEs determination according to the ICH Q3D guidelines. Finally, this method has the potential to be applied for routine quality control procedures of active pharmaceutical ingredients.

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[The authors are thankful to CNPq, CAPES and FAPERGS]

080 - ANALYTICAL METHODS FOR ELEMENTAL DETERMINATION IN BIODIESEL: COMPLIANCE WITH REGULATORY STANDARDS

Leticia M. Rodrigues[a*], Luís Eduardo Bernardes[a], Marcia A.M.S Veiga[a].

[a]University of Sao Paulo, Department of Chemistry, Ribeirão Preto, São Paulo, Brazil, 14040900
*e-mail: lmrodrigues@usp.br

In response to increasing energy demands and environmental concerns about finite fossil fuel reserves, biodiesel has emerged as a renewable energy source produced through a chemical process called transesterification, which involves converting triglycerides found in vegetable oils or animal fat into biodiesel using short-chain alcohols. Like conventional oil-based fuels, biodiesel must adhere to specific quality standards the Brazilian National Agency for Petroleum, Natural Gas and Biofuels (ANP) sets. The stability and quality of biodiesels are influenced by their concentration of magnesium (Mg), calcium (Ca), sodium (Na), potassium (K), sulfur (S), and phosphorus (P). This study aimed to develop unified methods for measuring these elements using flame atomic absorption spectrometry (F AAS) and high-resolution continuum source molecular absorption spectrometry (HR-CS MAS). Three acid digestion conditions and photodegradation procedures, such as photo-Fenton (190 to 378 nm by UV-Vis) and TiO_2 (as anatase mineral), were evaluated on biodiesel samples to determine Mg, Ca, Na, and K by FAAS. The biodiesel samples were within the specifications legally required. To assess the accuracy of the proposed methods, recovery tests were conducted. The combination of acid digestion and photodegradation through photo-Fenton reaction yielded the best recoveries for all four analytes, ranging from 88% to 108 %. Sulfur was determined using the diatomic molecule CS by HR-CS MAS. Using 2-mercaptoethanol as a standard was more effective than a mineral oil-based standard. Iridium, as a permanent chemical modifier and a solution of Pd/Mg, provides good stabilization of CS molecules for sulfur quantification. The obtained value was 6.2 µg g^{-1}, below the legally established limit. The phosphorus concentration in biodiesel was measured at the analytical signal obtained at 246.40 nm, corresponding to a rotational transition of the PO molecule. The estimated concentration for P in the pure sample fell between the LOD and LOQ, also attending the legally established limit. In both determinations of S and P, a standard addition technique was necessary to circumvent matrix effects. Table 1 presents the analytical parameters for all evaluated analytes obtained in this work. The procedures developed demonstrated the accuracy and precision required for determining the proposed analytes set in biodiesel samples using atomic and molecular absorption spectrometry techniques in compliance with current legislation.

Table 4: Analytical parameters for determining Na, K, Ca, and Mg by FAAS and S and P by direct analysis in GF MAS in biodiesel samples.

Analyte	Wavelength (nm)	Sample Preparation	R^2	RSD (%)	LOD (µg g^{-1})	LOQ (µg g^{-1})
Na	589.0	Acid digestion	0.9961	2.7	0.6	2.0
K	766.5	Acid digestion	0.9956	2.3	0.2	0.6
Ca	422.7	Acid digestion	0.9994	2.3	1.5	5.2
Mg	285.2	Photo-Fenton degradation	0.9992	1.4	0.32	1.1
P (PO)	246.40	Direct analysis	0.9995	6.5	1.8	5.8
S (CS)	258.056	Direct analysis	0.9997	6.6	2.2	7.4

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[CAPES. FAPESP. CNPq]

081 - MIC-DV AS AN EFFICIENT AND FEASIBLE METHOD FOR SULFUR DETERMINATION IN COAL

Diego T. Gomes[a], Eliana T. F. Larruscain[a], Letícia C. Brudi[a], Paola A. Mello[a],
Fábio A. Duarte[a*]

[a]Universidade Federal de Santa Maria, Department of Chemistry, Santa Maria, Rio Grande do Sul, Brazil, 97105-900
*e-mail: fabio.duarte@ufsm.br

Coal is considered one of the main energy sources in the world for industrial purposes, exceeding 8 billion tons in 2022, according to the International Energy Agency.[1] Its high utilization is associated with the low extraction cost when compared to other available fuels.[2] Its composition consists majority of carbon, hydrogen, oxygen and relatively low amounts of sulfur and nitrogen. On the other hand, approximately 50% of coal is composed of minerals, such as pyrite (FeS_2), which is the main source of sulfur in coal, that can also be found as inorganic sulfates and organic compounds.[3] The determination and removal of sulfur from coal has become important to the industry and the environment for the pollution control. The sulfur content is directly related to the corrosion of industrial equipment and the production of SOx, that when combined with water in the atmosphere produce acids that cause acid rain and contribute directly to the greenhouse effect.[4] Since coal present a complex matrix, the development of suitable sample preparation methods for sulfur determination is still a challenge. Numerous sample preparation protocols have been described in the literature, but most of methods require the use of high amounts of acids, or mixtures of them, depending on the inorganic fraction of the matrix, generating high amounts of waste. Therefore, the microwave-induced combustion in disposable vessels (MIC-DV)[5] for sulfur determination in coal by inductively coupled plasma optical emission spectrometry (ICP-OES) was proposed. MIC-DV is an alternative to the conventional digestion methods that presents benefits such as low energy consumption (combustion being achieved in a few seconds) and low reagent consumption, due to the small volume of the polypropylene vessel used in the procedure. The parameters that could influence in the combustion, such as sample mass (5 to 30 mg), influence of pressurization (1.0 to 1.8 bar), and type (H_2O and HNO_3), concentration (1.0 to 14.4 mol L^{-1}) and volume (2.5 to 12.5 mL) of absorbing solution were evaluated. The proposed MIC-DV method was compared with microwave-assisted digestion (MAD), microwave-induced combustion (MIC) and direct solid sampling elemental analysis (DSS-EA) and the accuracy achieved ranged from 91 to 97%, 82 to 102% and 91 to 94%, respectively. The limits of detection and quantification for sulfur in coal after MIC-DV/ICP-OES optimization were 11 and 37 µg g^{-1}. It is important to mention, that the MIC-DV employs low cost and environmentally friendly materials and instrumentation. Moreover, the sample preparation time was reduced comparing to MAD, MIC and DSS-EA, since sample combustion was achieved in less than 30 s in a rotor containing 5 vessels. Finally, the proposed method is based on the single vessel principle, using the same vessel from sample preparation up to the quantification, minimizing the use of additional vessels for dilution, which reduces the risk of contamination by excessive handling.

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[UFSM, CAPES, CNPq and FAPERGS]

082 - MICROWAVE-INDUCED COMBUSTION FOR ELEMENTAL IMPURITIES DETERMINATION IN MEDICATION WITH HIGH INORGANIC CONTENT

Vinícius P. Souza[a], Vitoria H. Cauduro[a], Alessandra S. Henn[a], Rochele S. Picoloto[a], Erico M. M. Flores[a*]

[a]Federal University of Santa Maria, Chemistry Department, Santa Maria, Rio Grande do Sul, Brazil, 97105-360
*e-mail: ericommf@gmail.com

The ICH Guideline for Elemental Impurities (Q3D) established limits for potentially toxic elements in oral medication[1]. The elements classified as Class 1, such as As, Cd, and Pb, are the most dangerous to human health, and their presence must always be monitored[1]. Therefore, it is necessary to develop analytical methods for the determination of those elements to ensure consumer safety. In this sense, inductively coupled plasma mass spectrometry (ICP-MS) is an analytical technique that allows multielement determination and highly sensitive analysis. However, samples must be in the form of a solution for introduction in the equipment in its conventional assembly, hence, it is often necessary to perform a sample preparation step. Microwave-induced combustion (MIC) is a promising sample preparation method, allowing the use of diluted solutions and presenting low carbon content in digests when compared to conventional digestion methods[2]. However, samples with high inorganic content may be a challenge for combustion-based methods, once the necessary energy for analyte volatilization might not be achieved, due to insufficient organic matter acting as the fuel for the combustion reaction[3]. Therefore, the present study aimed for the development of a sample preparation method based on MIC for As, Cd, and Pb determination in oral pharmaceutical tablets with high inorganic content, used in the treatment of type 2 diabetes. Five generic commercial pharmaceutical tablets employed in the treatment of type 2 diabetes (all containing inorganic excipients) were used in this study, namely sitagliptin phosphate, metformin hydrochloride, saxagliptin, dapagliflozin and glimepiride. The samples were ground and pressed as pellets (5000 ton for 2 min) prior to decomposition. For method optimization, the sitagliptin phosphate sample was used, due to the higher inorganic content. The MIC procedures were performed in closed quartz vessels pressurized at 20 bar with O_2. Sample pellets were placed in quartz holders on filter paper moistened with 50 µL of igniter (6 mol L^{-1} NH_4NO_3), and then transferred to quartz vessels containing 6 mL of absorbing solution, which were then closed and pressurized. The microwave irradiation program was set to 5 min at 1400 W (combustion and reflux steps) and 20 min at 0 W (cooling step). The accuracy of the proposed MIC method was evaluated by decomposition of certified reference material (CRM) of fish protein (DORM-3) mixed with sitagliptin phosphate sample matrix at a 1:1 (m m^{-1}) ratio, as well as by standard addition of the analytes at 50, 100 and 150% of the permitted daily exposure level for all MIC procedures. The sample mass (150 to 400 mg), use of combustion aids (microcrystalline cellulose, 300 or 400 mg) and concentration of absorbing solution (1 to 14.4 mol L^{-1} HNO_3) were evaluated. The conditions were evaluated based on analyte recovery and visual aspect of digests. The optimized conditions were defined as 250 mg of sample, 400 mg of microcrystalline cellulose as combustion aid, and 7 mol L^{-1} HNO_3 as absorbing solution. Analyte recovery ranged between 97 and 105% for all evaluated samples and no significant differences were observed between obtained and certified values for CRM analysis (Student's t test, 95% of confidence). The limits of quantification obtained for As, Cd, and Pb were 0.061, 0.067, and 0.076 µg g^{-1}, respectively, which are adequate for determination according to ICH Q3D limits.

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083 - IDENTIFICATION OF TITANIUM DIOXIDE NANOPARTICLES IN FOOD SAMPLES BY ICP-OES AND SCANNING ELECTRON MICROSCOPY

Cristian K. Pereira[a], Caroline M. Senger[a], Aline L. H. Muller[a], Edson I. Muller[a*].

[a]Federal University of Santa Maria, Department of Chemistry, Santa Maria, Rio Grande do Sul, Brazil, 97105-900
*e-mail: cristian.pereira@acad.ufsm.br

Titanium dioxide (TiO_2) is a white powder widely used as pigment in various industries, such as foods, paints, plastics and cosmetics. Although not intended, TiO_2 nanoparticles (TiO_2-NPs) could be a by-product of the production of TiO_2[1]. Nanoparticles (NPs) are any object with at least one dimension comprising 1 to a 100 nm.[1,2] The electron microscopy is a very well recognized technique for the characterization of NPs, being mainly used to determine its size distribution. The main challenge for NPs determination is that the sample preparation must isolate and keep the integrity of the NPs[2]. In this work, sample preparation using microwave-assisted wet digestion (MAWD) of three food samples was applied for the identification of TiO_2-NPs by scanning electron microscopy (SEM) and determination of total Ti by ICP-OES (Optima 4300 DV spectrometer, Perkin Elmer, USA). A sample of chewing gum, powder soup and powder juice containing TiO_2 as pigment in its composition were used. For the determination of total Ti by ICP-OES, MAWD was carried out with the digestion of 250 mg of sample into a PTFE vessel with 6 mL of concentrated nitric acid and 1 mL of hydrofluoric acid in Ultrawave system (Milestone, Italy). For the analysis using SEM (Sigma 300 VP microscope, Carl Zeiss, Germany) sample masses were digested in quartz tube using only concentrated HNO_3. These final HNO_3-digests were filtered through a 0.015 µm polycarbonate membrane for the isolation of TiO_2-NPs and subsequent characterization by SEM and energy dispersive X-ray spectrometry (EDS).

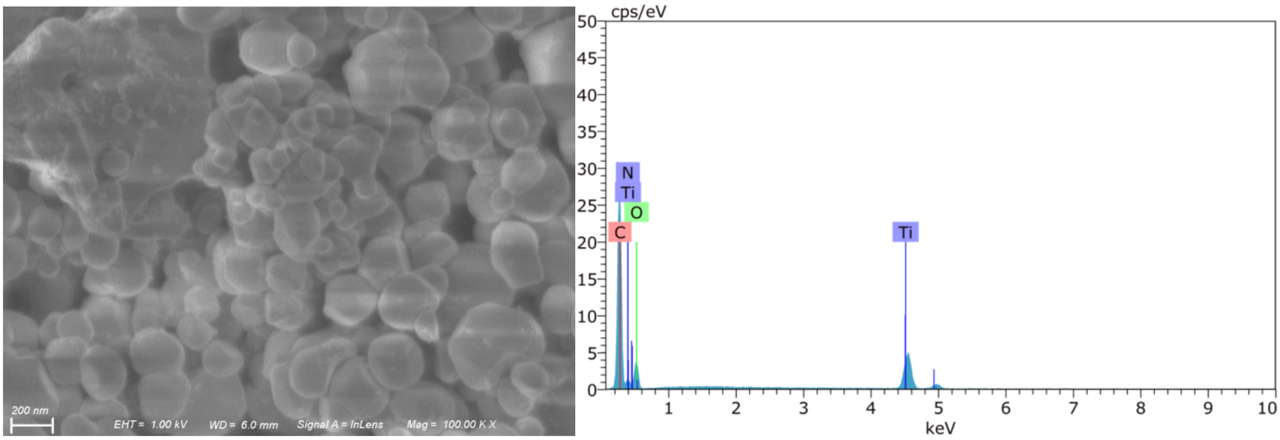

Figure 1. SEM image and X-ray spectrum obtained by EDS of TiO_2-NPs in powder juice sample.

Total Ti determination by ICP-OES of HNO_3+HF sample digests showed that powder soup presented the highest concentration of Ti followed by the powder juice and chewing gum samples (2976, 748 and 545 µg g^{-1} of Ti, respectively). Membranes containing TiO_2-NPs isolated from powder juice sample were observed by SEM and the most particles had a diameter greater than 100 nm, but it also was possible to detect smaller particles (Figure 1). The composition of the NPs was confirmed with EDS spectrum (Figure 1). Further studies are necessary for the quantification of NPs by ICP-MS using single-particle mode.

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[CAPES, CNPq, FAPERGS and UFSM]

084 - A GREENER METHOD FOR DETERMINATION OF ARSENIC AND CADMIUM IN SOIL BY ICP-MS EMPLOYING DEEP EUTECTIC SOLVENTS

Sabrina S. Ferreira[a*], Floriatan S. Costa[b], Taciana G.S. Guimarães [c], Clarice D.B. Amaral[b], Mario H. Gonzalez[a]

[a] São Paulo State University (UNESP), Department of Chemistry and Environmental Sciences, São José do Rio Preto, SP, Brazil, 15.054-000
[b] Federal University of Paraná, Department of Chemistry, Curitiba, PR, Brazil, 81.531-980
[c] Federal University of São Paulo, Laboratory of Integrated Sciences, Diadema, SP, Brazil, 09972-270
* e-mail: sabrina.s.ferreira@unesp.br

Green Analytical Chemistry (GAC) is making increasing progress in the quest for more sustainable methods, promoting the substitution or reduction of toxic reagents, lower energy consumption, waste generation minimization, and avoidance of toxicity[1,2]. The development of green solvents is an example of the production of new sustainable materials based on the principles of GAC. Natural deep eutectic solvents (NADES), classified as green solvents, have demonstrated commendable outcomes in extracting inorganic analytes from environmental samples[3]. When precursors based on amino acids are used in their formation, they are called amino acids-based deep eutectic solvents (AADES). These solvents are characterized by low toxicity, high biodegradability, negligible volatility, simplicity of preparation, and low cost[4]. In this work, NADES based on carbohydrates and amino acids were prepared, characterized, and evaluated in terms of their capacity to extract arsenic and cadmium from soil samples, prior to subsequent analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). NADES based on citric acid/xylitol/water (CA-Xyl) and AADES based on citric acid/β-alanine/water (CA-Ala) were prepared using ratios of 42:13:45 (% w w^{-1}) and 43.75:12.5:43.75 (% w w^{-1}), respectively, under stirring and heating[5], followed by characterization using viscosity and density measurements. These solvents were employed using Doehlert Design for optimization of a procedure based on microwave-assisted extraction of As and Cd from soil, followed by detection using ICP-MS. The density and viscosity values obtained for the CA-Xyl NADES were 1.25 ± 0.01 g mL^{-1} and 6.75 ± 0.048 mPa.s, respectively, while the values for the CA-Ala AADES were 1.26 ± 0.01 g mL^{-1} and 10.13 ± 0.03 mPa.s, respectively. Optimization of the extraction conditions considered the effects of temperature, extraction time, and sample mass/solvent volume ratio. Recoveries of As and Cd in the range from 80 to 110% were obtained when the CA-Xyl NADES and the CA-Ala AADES were used for the analyte extraction in reference material of soil (EMBRAPA, Agro E2002a). The solvents were shown to be promising as extractors for the matrix evaluated. The best condition indicated by the experimental design model results (extraction time of 50 min, heating at 140 ºC, and sample-solvent ratio of 60:1 mg mL^{-1} will be used for the validation of the proposed method.

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[CAPES (88887.485183/2020-00), FAPESP (2021/14759-5 and 2021/14581-1), CNPq (465571/2014-0), and INCT-DATREM (FAPESP, 14/50945-4; CNPq, 465571/2014-0)]

085 - AUTOMATION OF A DISPERSIVE LIQUID-LIQUID MICRO-EXTRACTION USING A FLOW BATCH-SEQUENTIAL INJECTION APPROACH FOR MO DETERMINATION BY ET AAS

Florencia Tissot[a*], Juan Carlos Rodríguez[a], Lucía Gutiérrez

Analytical Chemistry, DEC, Faculty of Chemistry, Universidad de la República, Gral. Flores 2124, Montevideo, Uruguay.
*e-mail: ftissot@fq.edu.uy

Molybdenum is an essential trace element of biological and environmental relevance. Since the concentration levels found in natural waters, plant material and animal tissue are very low, sensitive, selective, and accurate methods are required for its determination in these types of matrices. Sensitive techniques like ICP MS are not always available, so an alternative is to increase the sensitivity of more accessible spectrometric techniques such as electrothermal atomic absorption spectroscopy (ET AAS), through a previous preconcentration process.

Dispersive liquid-liquid microextraction (DLLME) was proposed as a useful pre-concentration strategy[1,2]. It uses very small amounts of organic solvents, thus generating less waste, in line with the principles of Green Chemistry. In a typical DLLME procedure an appropriate mixture of solvents (extraction and dispersive) is rapidly injected into an aqueous sample solution containing the analyte. In the case of Mo, a ligand in excess should be added to form a neutral complex that is more soluble in the extraction solvent. After injection of the solvent mixture, opalescence immediately appears due to the dispersion of the extraction solvent in the form of small droplets. Thus, the extraction of the metal complex is usually very efficient due to a higher contact surface area, and thus high mass transfer efficiency. After separation, the remaining organic phase is analyzed.

Automation of DLLME technique is a great challenge and it has as purpose to improve the repeatability, reproducibility, analytical frequency, minimize sample cross-contamination and exposure to organic solvents. To carry out this process it is necessary to consider the appropriate automation approach, the specific limitations and further optimization steps. Different approaches have been developed for the automation of the DLLME by exploiting flow analysis techniques, like flow injection analysis (FIA) and sequential injection analysis (SIA)[3].

This work presents a novel on-line flow batch - sequential injection - dispersive liquid-liquid microextraction system, for the determination of Mo concentration in waters, meat, and pastures with ET AAS as a detection technique. The developed system combines the benefits of flow and batch analysis.

After optimizing the experimental conditions of the system, the new methodology was validated. A limit of detection of 0.03 µg L^{-1} for water and 0.02 µg kg^{-1} for the other matrices, respectively, as well as an enrichment factor of 130 were obtained employing this methodology. During the validation, standard reference materials were used for trueness and precision evaluation. No significant differences were found at the 95% confidence level between the certified and obtained values, and precision expressed as repeatability (sr %) was better than 5% in all cases. The developed automated methodology offers great advantages when compared to manual dispersive liquid-liquid microextraction, such as low risk of contamination while working in closed systems, minimal handling, reduced exposure of the analyst to the chemical products, greater security, relatively short extraction time, improvement in repeatability and the elimination of the laborious and time-consuming procedure of phase separation by centrifugation. The method was successfully applied for the determination of Mo in natural groundwaters, bovine and sheep meat, and pasture samples.

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086 - METALS DETERMINATION IN WOOD WASTE USED FOR BIOFUEL PRODUCTION: SAMPLE PREPARATION USING DILUTED REAGENTS

Vanessa Ramos do Nascimento [a], Luana Farias da Rocha[a], Karen Giacobe [a], Cezar A. Bizzi[a]*

[a] Federal University of Santa Maria, Departament of Chemistry, Santa Maria, Rio Grande do Sul, Brazil, 97105-900
*e-mail: cezar.bizzi@ufsm.br

Lignocellulosic biomass is frequently used to produce second-generation of renewable fuels, with the main advantage of not being competitive with the food matrix. Biomass can be sourced from vegetal origin or wood waste, mainly from agriculture or forestry activities. The main composition of these raw materials is cellulose (30 at 50%), hemicellulose (15 at 35%) and lignin (10 at 20%). Beside this, the biomass may present a small fraction of extractives, proteins, and ash[1]. To understand the composition of the inorganic fraction is important for predicting the environmental and technological risks associated with the processing and their use as fuels. The elements composing the inorganic fraction are essential to plant growth, like macronutrients (Ca, K, Mg, P and S) and micronutrients (Cl, Fe and Mn). To determine the inorganic fraction methods using concentrate acids and closed system are conventionally employed, which results in a good digestion efficiency and low dissolved carbon content.[2] Thus, this work aims to evaluate the use of diluted HNO_3 and H_2O_2 for digestion of wood waste, used as biomass source, employing a microwave-assisted single reaction chamber (MAD-SRC, Ultrawave™, Milestone Srl) to further metals determination (Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr, Ti and Zn) with an induced coupled plasma optical emission spectrometry (ICP-OES) technique. The proposed sample preparation protocol was developed for two kinds of samples, pinus wood, and eucalyptus wood waste. The samples were grounded in a knife mill and sieved in 0.84 mm (20 mesh). Samples (250 mg) were digested in a MAD-SRC equipment equipped with 15 quartz vessels (15 mL). The heating program used was: 15 min up to 270 ºC, followed by 10 min at 270ºC. The digestion protocol was performed using pinus wood under several HNO_3 concentrations (14, 7, 2, 1 e 0.1 mol L^{-1}). The use of auxiliary reagent (1 or 2 mL of H_2O_2 35%) was evaluated with diluted HNO_3 (1 and 2 mol L^{-1}). The efficiency of sample digestion was evaluated by dissolved carbon (DC, mg L^{-1}) determination. When digestion was performed using only HNO_3 (without auxiliary reagent), DC values of 10.3, 16.2 and 18.0 µg g^{-1} were found for 14, 7, 2, and mol L^{-1} HNO_3, respectively. When more diluted HNO_3 was evaluated (1 or 0.1 mol L^{-1}), the presence of suspended solids impaired DC determination. The use of the auxiliary reagent (1 or 2 mL of H_2O_2 35%) resulted in an efficient sample digestion even using HNO_3 as diluted as 1 or 2 mol L^{-1}. The use of 2 mol L^{-1} HNO_3 resulted in DC values of 12.6 and 13.6 µg g^{-1}, while the use of 1 mol L^{-1} HNO_3 resulted in DC values of 22.0 and 16.0 µg g^{-1} (for 1 and 2 mL of H_2O_2 35%, respectively). Based on the digestion efficiency, 2 mol L^{-1} HNO_3 with the aid of 1 mL H_2O_2 was selected as the best condition, being applied for digesting pinus wood, and eucalyptus wood residues for further metals determination by ICP-OES. The proposed sample preparation method was compared with EN ISO 16967[3] for biomass digestion, which used 250 mg of sample in PTFE flasks, using 1,5 mL H_2O_2 35%, 4 mL of HNO_3 14 mol L^{-1}, 0,5 mL HF 23 mol L^{-1} (heating program: 15 min up to 190 °C; 20 min at 190 °C). After, 5 mL H_3BO_3 4% (m/m) was added to the protocol described in EN ISO 16967[3], which was followed by an additional heating step (5 min up to 150 °C; 15 min at 150 °C). Quantitative recoveries for metals determination were observed, even using diluted reagents. Recoveries lower than 50% were observed for Ti, Al and Fe, due to the absence of HF in the proposed method. Considering the results, the proposed sample preparation method based on the use of diluted reagents proved to be efficient for digesting samples with complex matrices, like pinus and eucalyptus wood, saving reagents and generating less residues.

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[CAPES and CNPq]

087 - DETERMINATION OF COPPER IN TEA BY GF AAS AFTER EXTRACTION WITH DEEP EUTECTIC SOLVENT

Eduardo da Silva Macedo[a], Morgana Lurdes da Rocha* Eduardo Sidinei Chaves[a]

[a]Federal University of Santa Catarina, Chemistry Department, Florianópolis, Santa Catarina, Brazil, 88040-900
*e-mail: moraganalrocha@gmail.com

Tea is a traditional drink made from *Camellia sinesis* leaves consumed in many countries. Variations of traditional tea, called infusions, can be produced from different mixtures of plants. As well as containing organic compounds, infusions can also have metals such as copper (Cu). Cooper is widely used in agriculture and can result from the plant's contact with the soil, irrigation water, and other additives used during cultivation.[1, 2] Therefore, monitoring the element composition of infusions to avoid consuming high concentrations of metals is essential.[3] According to Resolution-RDC No. 269 of September 22, 2005, issued by the Ministry of Health of the Brazilian Federal Government, the Cu recommended intake for an adult is 900 µg per day; intakes higher than this can be toxic. Atomic absorption spectrometry (AAS) is one of the most used analytical techniques for metal determination. [1, 2, 4] However, an appropriate sample preparation procedure is generally required before the analysis. In this way, the use of deep eutectic solvents (DES) in sample preparation, prior to AAS techniques analysis, has increased. DES is an alternative, low-cost, and environmentally friendly extracting solvent.[5] Thus, the determination of the total Cu concentration in herbal was performed by graphite furnace atomic absorption spectrometry (GF AAS) using ultrasound-assisted extraction with DES (UAE-DES) as sample preparation. The temperature program of GF AAS was optimized, and the atomization and pyrolysis temperatures were 900 and 2100 ºC, respectively. Besides the total concentration, the bioavailability of Cu in the infusions was investigated by determining the extractable Cu in the aqueous phase. Among the evaluated solvents, the DES composed of choline chloride and oxalic acid (ChCl:Ox) in the ratio 1:1, showed the best extraction efficiency of Cu, and it was characterized by infrared spectroscopy with Fourier transform (FTIR). The optimization of the UAE-DES was performed by a Box-Behnken design; the evaluated parameters were: extraction time (5; 30; 55 min), temperature (25; 50; 75 ºC), and water content in DES (10; 30; 50 % w/v). The optimized conditions were 45 min of extraction time, 60 ºC, and using DES with 20% of water. Three different calibration strategies were evaluated for the determination of Cu: external calibration with aqueous standards, matrix-matching calibration using standard solutions with DES, and analyte addition calibration. No significant difference was observed between the evaluated calibration techniques ($p\text{-value} > 0.05$, according to ANOVA one-way at 95% confidence level). Thus, the simplest external calibration was selected for Cu determination. The accuracy of the proposed method was assessed by analysis of two certified reference materials (CRMs). The obtained Cu concentration in CRMs samples showed a good agreement (81 to 91%) and had no significant differences compared to those found in the certificate (t-student test with 95% confidence level). The relative standard deviation (RDS) evaluated the precision, which was better than 8,00% for most samples. The limits of detection (LOD) and quantification (LOQ) were 0.24 and 0.83 $\mu g\ g^{-1}$, respectively. The proposed method was applied to determine the total Cu concentration in five tea samples (black, boldo, green, citrus, and chamomile), and the obtained concentrations ranged from 2.34 to 35.97 $\mu g\ g^{-1}$. Considering the Cu bioavailability, the concentration of extractable Cu in the analyzed infusions was from 22.1 to 85.7 $\mu g\ L^{-1}$, corresponding to 12- 90% of the total concentration of Cu. Though the concentration of Cu released in the infusion samples was low, the combination of a diet involving different sources of this element should be monitored not to exceed the daily intake limit for this metal.

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[CNPq, CAPES and UFSC]

088 - SAMPLE PREPARATION FOR SUBSEQUENT METALS DETERMINATION BY ICP-OES IN BIODIESEL

Ana Caroline V. Rubin[a], Alice P. Holkem[a], Ana Luiza B. Nunes[b], Fernanda Castilhos[b], Paola A. Mello[a*]

Universidade Federal de Santa Maria, [a]Chemistry Department, [b]Chemistry Engineering Department, Santa Maria, Rio Grande do Sul, Brazil, 97105-900
*e-mail: paola.mello@ufsm.br

Biodiesel has been chosen as an alternative for replacing diesel oil from fossil fuels, as it has significant advantages, such as reducing polluting gases and providing renewable resources.[1] It is produced through the process of transesterification of vegetable oil or animal fat with short-chain alcohol, preferably methanol, through alkaline catalysis.[1] The diversified constitution of the sources of raw materials for biodiesel production and the process itself can contaminate the final product by chemical elements.[2] The determination of contaminants in biodiesel is of great importance, as their presence can change some characteristics, such as, reduce the oxidation stability, even in concentrations of parts per billion.[1,3] In Brazil, the Resolution 07/2008 of the National Agency of Petroleum, Natural Gas and Biofuels (ANP) stipulates the minimum and maximum limits of Ca, K, Mg, and Na in 5 mg kg^{-1}.[1] According to the NBR 15553:2019, samples can be diluted five times with xylene or kerosene for further direct determination of Na, Ca, Mg, P, and K by inductively coupled plasma optical emission spectrometry (ICP-OES). In spite of its simplicity, this approach can impair some problems in the measurement step, due to the formation of carbon deposits in the equipment spare parts, as well as interferences, poor precision, among other problems. On the other hand, the acid digestion can be an easy approach in laboratory routines for most samples to convert them into aqueous solutions compatible with spectrometric techniques. However, the decomposition of biodiesel is not a simple task. In this context, the objective of this work was to evaluate a sample preparation method for subsequent determination of Al, Ca, K, Mg, and Na by ICP OES in biodiesel. The challenge was to obtain a suitable condition for the digestion of sample mass (about 0.5 g) to allow the achievement of the limit of quantification (LOQ) required by RANP 007/2008 using ICP-OES. An acid digestion method was investigated using a microwave oven with single reaction chamber technology (model UltraWave®, Milestone, Italy), equipped with five quartz vessels with maximum capacity of 40 mL. The system operates with maximum temperature, pressure and power of 300 °C, 199 bar and 1500 W, respectively. For the digestion, 500 mg of sample was transferred to a digestion vessel and 6 mL of concentrated HNO_3 were added. Then, the samples were heated at 80 °C in a hot plate for 60 min and 100 °C for 15 min, for a previous step of matrix oxidation. Afterwards, the vessels were inserted into the microwave oven cavity, previously pressurized with 40 bar of argon (99.5%, White Martins, Brazil) and the following irradiation program was used: *i*) 5 min ramp at 90 °C; *ii*) 10 min ramp at 110 °C with 5 min hold; *iii*) 10 min ramp at 120 °C; *iv*) 10 min ramp at 130 °C; *v*) 20 min ramp at 250 °C and 15 min at 0 W for cooling. Finally, the digests were made up to 10 mL with ultrapure water. Using this method, LOQs were in agreement with RANP 007/2008 and suitable digests were obtained for plasma-based OES detection.

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[CNPq, CAPES, and FAPERGS]

089 - A MINIATURIZED ULTRASOUND-ASSISTED LIQUID-LIQUID EXTRACTION FOR REE DETERMINATION BY USN-ICP-MS IN CRUDE OIL

Bruna C. Padoin[a], **Cristian R. Andriolli**[a], **Ariadne G. L. P. Gonçalves**[a], **Erico M. M. Flores**[a]
Rochele S. Picoloto[a] **and Jussiane S. Silva**[a]*

[a]Federal University of Santa Maria, Chemistry Department, Santa Maria, RS, Brazil, 97105-900
*e-mail: jussiane.silva@ufsm.br

Concentration information of rare earth elements (REE) in crude oil is important because it enables prediction of origin, maturity, and correlation of oil to source rock, among other geological aspects, and is used to trace geological fluids.[1, 2] However, these elements (lanthanides, Y and Sc) are present in low concentrations (ng g^{-1}), demanding analytical techniques with high sensitivity. Some analytical techniques have been used for the determination of REE in crude oils, such as neutron activation analysis (NAA), inductively coupled plasma optical emission spectrometry (ICP OES), and inductively coupled plasma mass spectrometry (ICP-MS). These techniques present a series of limitations, such as the long time for analysis, the necessity to use a nuclear reactor (NAA), and several spectral interferences common for ICP OES and ICP-MS. Additionally, ICP-OES presents lower sensitivity and inadequate limits of quantification (LOQs) compared to ICP-MS. This way, a sample preparation method was proposed to use high sample masses and diluted acids to determine REE in crude oil. The miniaturized ultrasound-assisted liquid-liquid extraction (US-LLE) method is based on the extraction and pre-concentration of analytes using a dilute extraction solution and sonication. For this method, samples were directly weighed into vessels and subjected to a heating bath, followed by adding a low volume (2 mL) of an organic solvent and extracting solution. The samples were then manually shaken for one minute and subjected to an ultrasonic bath at 80 °C. The aqueous phase with the analytes was collected after extraction for determination by an ICP-MS coupled to the ultrasonic nebulizer (USN). For the procedure, ultrasonic water baths (Elmasonic, Germany) with an operating frequency of 25 or 45 kHz, capacity of 3.5 L, effective power of 100 W, and temperature control of up to 80 °C were used. Reference values were obtained using microwave-assisted wet digestion in a single reaction chamber (MAWD-SRC) with concentrated nitric acid, followed by REE determination by USN-ICP-MS. A crude oil sample from the Brazilian pre-salt reservoir was used in this study. This oil sample was characterized and showed a relative density of 27.9 °API and water content of 5.2%. For the optimization of the US-LLE method, an evaluation of several parameters was conducted using a 2.0 g sample mass, 2.0 g of toluene, and 2.0 g of extraction solvent. The parameters assessed included different extracting solvents (solutions of HNO_3 and HCl) in concentrations ranging from 3 to 10 mol L^{-1}, demulsifier volumes of 1 and 2 mL, US frequencies between 25 and 130 kHz, and sonication times from 10 to 30 minutes. Suitable results were obtained using a 2.0 g sample mass, 2.0 g of toluene, and a heating time of 10 minutes at 80 °C. Additionally, a 2.0 mL volume of a 50 g L^{-1} demulsifier, a 2.0 mL extraction solution of 7 mol L^{-1} HNO_3, and a US frequency of 25 kHz for 10 minutes at 80 °C were used. The method also used a step of manual agitation for one minute and another of centrifugation for 10 minutes. From the optimized method, approximate agreements of 80% were obtained for Ce, La and Y compared to the reference method (MAWD-SRC). The miniaturized US-LLE method offers a simple approach to the use of materials and equipment, in addition to minimizing the use of reagents and residue generation. Furthermore, the US-LLE method allowed the use of a high sample mass (2 g), contributing to obtaining low LOQs (0.5, 0.6, and 0.4 ng g^{-1} for Ce, La, and Y, respectively), being suitable for the determination of REE in oil.

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[PRH-ANP 52.1, FAPERGS and UFSM]

090 - METALS DETERMINATION IN CERAMIC MATERIALS: CHALLENGES AND POSSIBILITIES

Alice P. Holkem[a*], Maria Eduarda L. Santos[a], Luiza F. B. Souza[b], Gabriel K. R. Pereira[b], Paola A. Mello[a,*]

[a]Universidade Federal de Santa Maria, Chemistry Department, [b]Odontology Department, Santa Maria,
Rio Grande do Sul, Brazil, 97105-900
*e-mail: paola.mello@ufsm.br

Ceramic materials are commonly used in odontology, especially due to their stability and biocompatibility. The main uses of ceramic materials include the production of dental crowns and bridges, veneers, restorations (inlays and onlays), implants, prostheses, orthodontic components, dental instruments, among others[1]. Yttrium oxide is frequently employed in the production of these materials as stabilizing agent to increase mechanical and chemical resistance, as well as to adjust optical properties, such as translucency and color (making ceramics aesthetically similar to natural teeth)[2]. Furthermore, the correct dosage of yttrium ensures its biocompatibility with tissues. Therefore, it is extremely important to know the concentration of yttrium, as well as other potentially toxic metals, in ceramic materials. However, the determination of Y and other elements it this type of material can be considered an analytical challenge due to the chemical stability of the ceramic matrix. In this context, different sample preparation protocols were evaluated to enable accurate quantification of Y and metals in ceramic materials. Among these, six sample of ceramic materials were digested by microwave-assisted wet digestion (MAWD) using two microwave systems and by microwave-induced combustion (MIC). For the MAWD, the system 1 (model Ethos Easy, Milestone, Italy) was used operating with 32 PTFE vessels with maximal internal capacity of 100 mL, 200 °C and 35 bar of maximum temperature and pressure, respectively. The digestion program was 25 min of ramp to reach 200 °C at 1800 W (fan level 1), maintaining for 15 min at 200 °C and 1800 W (fan level 1) and 20 min for cooling (0 W down to 60 °C). Additionally, the system 2 (model Ultrawave, Milestone, Italy) was used operating with 15 PTFE vessels with maximal internal capacity of 15 mL, 220 °C and 199 bar of maximum temperature and pressure, respectively. The digestion program was 25 min of ramp to reach 220 °C at 1500 W (fan level 1), maintaining for 15 min at 200 °C and 1500 W (fan level 1) and 20 min for cooling (0 W down to 40 °C). Using these systems, two digestion mixtures were evaluated using 150 mg of sample: *i*) 3.5 mL HCl (12 mol L^{-1}) + 1.5 mL HF (23 mol L^{-1}) + 1.0 mL HNO_3 (14 mol L^{-1}) or *ii*) 3.5 mL HF (23 mol L^{-1}) + 1.5 mL HCl (12 mol L^{-1}) + 1.0 mL HNO_3 (14 mol L^{-1}). For the MIC procedure a microwave oven (model Multiwave PRO, Anton Paar, Austria) was used operating with four quartz vessels with maximal internal capacity of 80 mL, 280 °C and 80 bar of maximum temperature and pressure, respectively. For this procedure, 25 mg of sample was mixed with 250 mg of cellulose, pressed as a pellet, and positioned in the quartz holder with the filter paper containing the combustion aid (50 µL of 6 mol L^{-1} NH_4NO_3). The quartz vessels were previously filled with 3 mL H_2O + 1.5 mL HCl (12 mol L^{-1}) + 1.0 mL HNO_3 (14 mol L^{-1}) as absorbing solution. The vessels were closed, pressurized with 20 bar of O_2 and placed inside the microwave oven. The digestion program was 5 min at 900 W (fan level 1) with 20 min for cooling (fan level 2). The determination of Al, Ba, Fe, K, Mn, and Y in all digests was carried out using an inductively coupled plasma optical emission spectrometer with axial view configuration (ICP-OES, model Spectro Ciros CCD, Spectro Analytical Instruments, Germany) equipped with a cross flow nebulizer coupled to a double pass-Scott type spray chamber. Under all conditions (using MAWD or MIC digestion) changing the sample mass and the acid mixture, and for all samples, a solid residue was observed. These residues were characterized using a scanning electron microscope (model Sigma 300 VP, Carl Zeiss, Germany) equipped with an energy-dispersive detector for X-ray spectrometry (model Quantax EDS, Bruker, Germany) with an excitation voltage of up to 28 kV and signals for Y were observed.

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[CNPq, CAPES, and UFSM]

091 - DETERMINATION OF Pb IN BIOLOGICAL SAMPLES BY GF AAS AFTER EXTRACTION WITH DEEP EUTECTIC SOLVENT

Fabiana Luvizon Germer[a*], Elenice Hass Caetano Lacerda[a], Eduardo da Silva Macedo[a] and Eduardo S. Chaves[a]

[a] Federal University of Santa Catarina, Chemistry Department, Florianópolis, SC, Brazil, 88040-900
*e-mail: f.luvizon@posgrad.ufsc.br

The use of conventional organic solvents in sample preparation is of environmental concern. Thus, deep eutectic solvents (DES) emerge as an environmentally friendly alternative, aligned with the principles of green chemistry (GC). DES can be obtained by combining two or more components, one being a hydrogen bond receptor species (HBA) and one or more hydrogen bond donor compounds (HBD). The HBAs are usually salts of quaternary amines, and HBDs can be of different chemical species, such as alcohols, carboxylic acids, amides, and carbohydrates.[1,2] Thus, the feasibility of DES as an extractor solvent for biological sample preparation for further determination of Pb by graphite furnace atomic absorption spectrometry (GF AAS) was evaluated.

Additionally, the greenness of the proposed methodology was evaluated by Green Star (GS) and Eco-scale metrics. For Pb extraction, different DES were assessed. The DES composed of choline chloride and oxalic acid (ChCl: Ox) in the ratio 1:1 promoted the best extraction efficiency of Pb. This solvent was characterized by infrared spectroscopy with Fourier transform (FTIR). The optimized conditions for Pb extraction were found using 40 mg of sample combined with 400 µL of DES (ChCl: Ox). This mixture was homogenized and heated at 95 ± 5 °C for 30 min. The obtained solutions were diluted up to 10 mL with ultra-pure water, and GF AAS determined Pb concentration. The temperature program for GF AAS analysis was optimized, and Pd was used as a chemical modifier. The optimized pyrolysis and atomization temperatures were 900 °C and 2100 °C, respectively. For Pb determination, different calibration techniques were evaluated: external, obtained through diluting aqueous standards; matrix-matching, containing aqueous standards added of DES in the same proportion found in the solution of the samples and the analyte addition calibration. The results showed that the evaluated calibration curves showed good linearity and similar sensitivity. According to the t-test applied with a confidence level of 95%, there is no evidence of a significant difference between the sensitivity of the evaluated calibration. Thus, the external calibration was selected to determine Pb in biological samples. The limits of detection and quantification obtained were 0.04 µg g^{-1} and 0.12 µg g^{-1}, respectively. The method precision was evaluated by the relative standard deviation (<15%), and the accuracy of the proposed method was assessed by analyzing four certified reference materials (CRM). Considering the certified concentration values, the obtained recoveries ranged from 91 to 110 %, and according to the Student's t-test, with a confidence level of 95%, there is no significant difference between the concentration determined by the proposed method and those expressed in the CRMs certificate. The Student's t-test was conducted to confirm the absence of a significant difference between the values obtained through the developed method using DES as the extracting solvent and the concentrations expressed in the certificate. The greenness of the proposed method was also evaluated from the perspective of Green Chemistry by using the Green Star metrics and the Eco-scale. Considering the Green Star, the DES synthesis reached the star-filling index 75 out of a maximum of 100. Moreover, the evaluation of the analytical procedure utilizing the Eco scale indicated an excellent score of 95 points, proving the excellent chemical greenness of the proposed methodology.

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[UFSC, CAPES and CNPq]

092 - CLOSED-VESSEL CONDUCTIVELY HEATED DIGESTION OF DOG FOOD FOR SPECTROMETRIC DETERMINATION OF ESSENTIAL NUTRIENTS

Rayane C. Vieira Costa[a*], **João V. Biagi Santiago**[a], **Edilene C. Ferreira**[a],
José A. Gomes Neto[a] **and Alex Virgilio**[b]

[a]São Paulo State University (UNESP), Institute of Chemistry, Araraquara, São Paulo, Brazil, 14800-060.
[b] Center for Nuclear Energy in Agriculture, University of São Paulo, Piracicaba, São Paulo, Brazil, 13400-970.
*e-mail: rayane.cristina@unesp.br

Currently, with the increase in pet population and growth of market, the development of this food sector has aroused great interest. One of the most consumed products is dry pet food[1]. Food is directly linked to the nutrition and health of these animals, so chemical analysis of feed is essential[2]. Considering the simplicity and low cost of maintenance and instrumentation, the recent proposed closed vessel conductive heating digestion system (CHDS) was evaluated for the digestion of dog food samples for the determination of macronutrients (Na and K) and micronutrients (Fe, Cu, Zn and Mn) by HR-CS FAAS (high resolution continuum source flame atomic absorption spectrometry).

The method optimization was carried out using a factorial design with five variables (HNO_3 concentration, H_2O_2 volume, temperature, pre-digestion and digestion times) at two levels. Dog food samples were digested in CHDS under these factorial design conditions and then residual carbon content (RCC) measurements were performed on all digests. RCC values were the main response considered to identify the significant variables. Considering the results of the factorial design, the effect of sample mass and HNO_3 concentration on accuracy were evaluated using certified reference materials. With the optimized method, dog food samples with different matrices were digested by CHDS and by microwave-assisted digestion (MW-AD) for comparison purposes.

The results for Na, K, Cu, Fe, Mn and Zn determined in digestions of samples obtained by CHDS and MW were statistically concordant at a 95% confidence level. Analysis of CRMs showed recoveries in the 77 - 103% range. The limits of detection and quantification obtained by the CHDS (LOD 0.2 – 28.8 mg Kg^{-1}; LOQ 0.7 – 95.9 mg Kg^{-1}) were similar to those obtained by MW (LOD 0.2 – 38.3 mg Kg^{-1}; LOQ 0.5 -127.6 mg Kg^{-1}). Low RCC values (6.0 – 9.7 mg C/ 100 mg sample) showed efficacy of the CHDS digestion. It should be mentioned that all samples digested in the closed-vessel conductively heated digestion system may also be analyzed by other techniques (e.g., ICP OES, ICP-MS, and MIP OES) with pneumatic sample introduction systems that require solutions. The CHDS is a promise tool for sample preparation of dog food for the effective determination of macronutrients and micronutrients.

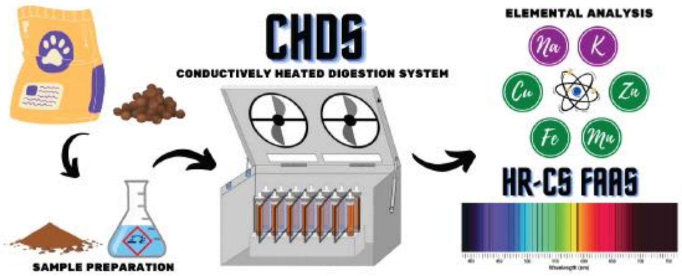

Figura 1. Simplified CHDS digestion scheme for elemental determination by HR-CS FAAS.

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093 - A SIMPLE, LOW COST AND FAST SAMPLE PREPARATION FOR FLUORIDE DETERMINATION IN LEGUMINOUS SEEDS AND OILSEEDS

**Paola C. Crestani[a], Eliana T. F. Larruscain[a], Conrado R. Laureano[a],
Bernardo P. Kaminski[a], Érico M. M. Flores[a], Fábio A. Duarte[a*]**

[a] Universidade Federal de Santa Maria, Departament of Chemistry, Santa Maria, Rio Grande do Sul, Brazil, 97105-900
*e-mail: fabio.duarte@ufsm.br

Leguminous seeds and oilseeds are an important source of protein, peptides and nutrients for human nutrition.[1] The increase of the consumption of alternative protein sources and the health awareness for preventing diseases has required the quality control of foods, mainly for halogens determination.[2,3] Fluoride is an ubiquitous element in the environment due to its wide use in water treatment to prevent dental caries.[4] However, its excessive intake can lead to health issues such as fluorosis, enzymatic poisoning and hormonal disruptions.[5] In this work, the use of microwave-induced combustion in disposable vessels (MIC-DV) for fluoride determination in leguminous seeds and oilseeds (almond, peanut, hazelnut, Brazil nut, pecan nut, pea, pinto bean, chickpea, and lentil) was evaluated.[6] The microwave-induced combustion (MIC) was used to obtain the reference values. The fluoride determination was performed by ion chromatography (IC) and by ion selective electrode (ISE) for fluorine. The analyte was detected only in Brazil nut and pinto bean samples, and the quantification was feasible only by IC. In order to improve the limit of quantification (LOQ) and to allow the determination by ISE, successive sample combustions were carried out in MIC and the results were in agreement with those previously obtained. Since in the literature, there are no works about the determination of fluoride after MIC-DV in food, some parameters as sample mass (10, 20, 30 and 40 mg for samples that make pellets, and 5, 10, 15 and 20 mg for the pasty samples), the type and concentration of the absorbing solution (water, 25, 50, 100 and 200 mmol L^{-1} NH_4OH solution and TISAB solution), volume of combustion igniter (10, 20, 30, 40 and 50 µL of 10 mol L^{-1} NH_4NO_3 solution) and purging time with O_2 (10, 20, 30, 40, 50 and 60 s), were evaluated. The use of successive combustion cycles for analyte preconcentration was also evaluated. Therefore, it was possible to determine fluorine concentration in the MIC-DV digests from samples of leguminous seeds and oilseeds and only pinto bean and Brazil nut samples presented detectable fluorine amounts, corresponding to 11.1 ± 0.7 and 17.1 ± 0.5 µg g^{-1}, respectively. The LOQ values for fluorine by using MIC-DV/ISE were 8.3 for samples that make pellets and 16 µg g^{-1} for the pasty samples, respectively. The accuracy of the MIC-DV/ISE method was evaluated by results comparison with those from MIC/IC, which were in agreement (from 94 to 106%). The White Analytical Chemistry (WAC)[7] approach was applied for performance comparison among the methods used throughout this study. This metric allows a quantitative comparison related to the method's "greenness" with its applicability and other analytical chemistry criteria.[7] Considering the three pillars of WAC, the proposed method is the best among the others methods that were used throughout this work. The proposed MIC-DV method allowed carrying out a fast sample preparation and with the possibility of determining the fluorine concentration using an ISE, a relatively low-cost and simple handling technique.

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[UFSM, CNPq, FAPERGS and CAPES]

094 - ANALYTICAL CHARACTERIZATION OF PHOSPHORUS ALLOCATION IN EUCALYPTUS AND MACAÚBA PLANTS: A COMPARATIVE STUDY.

Larissa G. R. Mourão[a], Vitor L. Ribeiro[a], Maycon L. de Oliveira[a], Luiza C. Pomarolli[a], Márcia A. M. S. da Veiga[a*]

[a] Department of Chemistry, Faculty of Philosophy, Science and Letters at Ribeirão Preto, University of São Paulo, Ribeirão Preto, São Paulo, Brazil, 14040-901
*e-mail: larissamourao2017@usp.br

Physiological processes and organic compound degradation in aging tissues affect plant nutrient reabsorption efficiency. Due to fixation and mineralization processes, low phosphorus (P) availability in tropical soils is expected. This prompts plants to use strategic mechanisms to shift P from biomass to meet their requirements. Understanding P accumulation in plant tissues and its release into the soil solution is crucial for sustainable agricultural production with reduced reliance on soluble fertilizers. The fractionation of P species in samples of Eucalyptus (*Eucalyptus myrtacea*) and Macaúba (*Anadenanthera columbrina*) leaves was evaluated in this study. Initially, the samples were oven-dried at 100°C for 24 h and subsequently subjected to additional treatment in the cryogenic mill, using 3 cycles of 2 minutes at 10 Hz. Then, 200 mg of each weighed replicate was subjected to the fractionation process, as shown in Figure 1 and divided into 4 supernatant aliquots. These aliquots were then digested in a block digester with 4 mL aqua regia, initially heated at 80°C for about 30 minutes and subsequently heated to 120°C until all the liquid in the tubes had evaporated. The digestion residues containing P were recovered through five successive additions of 1 mL of ultrapure water. Phosphorus content was measured using UV-Vis spectrophotometry (molybdenum blue method) and inductively coupled plasma optical emission spectrometry (ICP OES) in four fractions: total soluble (P_{TS}), lipid (P_{LIP}), RNA/DNA (P_{NA}), and residual (P_{RES}). The phosphorus content for Eucalyptus was 412 (± 40) mg P Kg^{-1}, while Macaúba's was 712 (± 43) mg P Kg^{-1}. Eucalyptus has the highest P concentration in the soluble fraction, especially in the P_{INO} (68 ± 11 mg P Kg^{-1}). There is no P in the residual and lipid fraction (lower than the LoQ). Otherwise, Macaúba contains evenly distributed contents among all the fractions, with the highest concentrations in the total soluble fractions (48 ± 3 mg P Kg^{-1}) and nucleic acids (31 ± 2 mg P Kg^{-1}). The comparison of concentrations observed between ICP OES and UV-Vis quantifications showed non-significance differences in the contents of phosphorus obtained. Therefore, even though the modified method requires many sample preparations to quantify the steps and there is a high probability of contamination, it still allows for understanding the dynamics of phosphorus reallocation in the leaves.

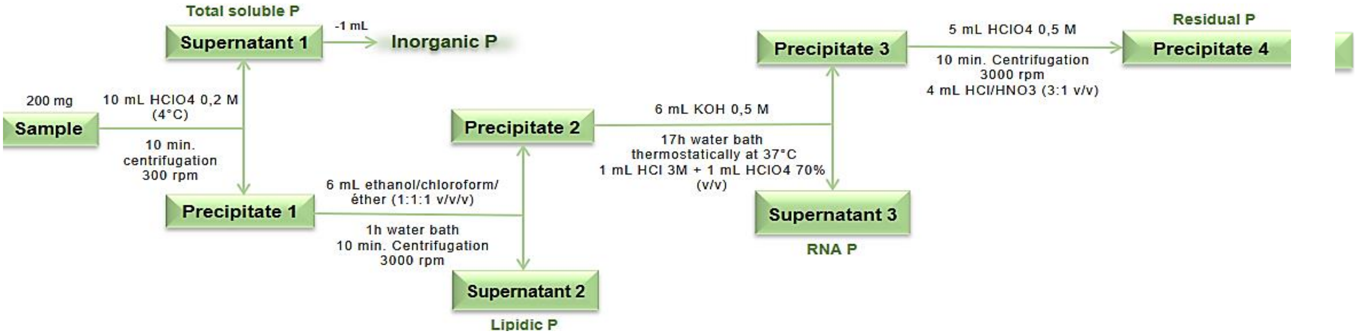

Figure 1. Phosphorus fractionation method flowchart.

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095 - CHLORINE DETERMINATION IN ANTIDEPRESSANT AND ANTIHYPERTENSIVE DRUGS AFTER PYROHYDROLYSIS

Daiana K. Oliveira[a], Cristian R. Andriolli[a], Thamires R. Silva[a], Vitoria H. Cauduro[a], Alessandra S. Henn[a] Érico M. M. Flores[a]*.

[a] Federal University of Santa Maria, Department of Chemistry, Santa Maria, Rio Grande do Sul, Brazil, 97105-900
*e-mail: ericommf@gmail.com

The increase in cases of depression and hypertension in the last years has also lead to the increase in the prescription of drugs for its treatment.[1,2] Generally, antidepressant and antihypertensive drugs contain active ingredients that present chlorine atoms on their structure or as hydrochlorides. In this sense, chlorine is considered an indispensable element for pharmaceutical industries.[3] Thus, monitoring the concentration of chlorine in this type of sample is required, to assure consumers health and drug efficacy. However, there are only a few studies reporting the determination of chlorine in pharmaceutical samples.[4,5] The determination of chlorine can be performed by spectrometric techniques, such as inductively coupled plasma mass spectrometry (ICP-MS). However, the sample needs to be in solution form, requiring a sample decomposition step. Several methods have been used for this purpose, such as microwave-induced combustion (MIC), microwave-assisted alkaline extraction, alkaline fusion, among others.[5] The pyrohydrolysis is one of these methods and it has been applied for the decomposition of several matrices and further halogens determination.[4,5] However, no studies reported the use of this method for the subsequent determination of chlorine in drugs. In this sense, the main objective of this study was to develop a simple and environmentally friendly sample preparation method for antidepressant and antihypertensive drugs and further Cl determination by ICP-MS. For this, three antihypertensive and four antidepressant drugs were used, containing the following active ingredients: indapamide (IND), chlortalidone (CHLO), potassic losartan (LOS), imipramine hydrochloride (IMI), clomipramine hydrochloride (CLOM), amitriptyline hydrochloride (AMI), and nortriptyline hydrochloride (NOR). The sample IND was used for the optimization of the method. For this, some parameters were evaluated: absorbing solution (H_2O; 25, 50, 100 and 200 mmol L^{-1} NH_4OH), reaction time (5 to 20 min), oxygen flow rate (0.2 to 1.0 L min^{-1}), water flow rate (0.5 to 1.5 mL min^{-1}), reactor temperature (800 to 1000 °C), and sample mass (100 to 750 mg). The optimized parameters were: 10 mL of 100 mmol L^{-1} NH_4OH as absorbing solution, 10 min reaction time, 0.8 L min^{-1} of oxygen as carrier gas, 1.0 mL min^{-1} of water flow, reactor temperature at 1000 °C, and 200 mg of sample mass. The accuracy of the proposed method was evaluated using certified reference materials (CRMs) of aquatic plant (BCR-60) and bituminous coal (NIST 1632C) and agreement with certified values ranged from 95 to 105%. The results obtained after pyrohydrolysis were compared with those obtained after a reference method based on microwave-induced combustion (MIC) and no statistical difference was observed (t-test, 95% of confidence level). Additionally, standard addition experiments were performed in three levels (50, 100 and 150%) and recoveries ranged from 90 to 110%. The limit of quantification of the pyrohydrolysis method in combination with ICP-MS determination was 0.015 mg g^{-1} for Cl. The proposed method was considered suitable for chlorine volatilization from the matrix, and allowed the use of diluted solutions, reducing the generation of residues.

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[CNPq, FAPERGS, CAPES, and UFSM]

096 - MICROWAVE-INDUCED COMBUSTION FOR Hg DETERMINATION IN ORAL TABLETS WITH HIGH INORGANIC CONTENT BY CVG-ICP-MS

Ana P. F. Padilha[a], Vitoria H. Cauduro[a], Vinícius P. de Souza[a], Alessandra S. Henn[a], Rochele S. Picoloto[a], Erico M. M. Flores[a*]

[a]Universidade Federal de Santa Maria, Departamento de Química, Santa Maria, RS, Brazil, 97105-900
*e-mail: ericommf@gmail.com

The long-term use of pharmaceutical tablets in the treatment of type 2 diabetes is necessary for the control of the patient's glucose levels[1]. For this reason, strict quality control regarding the presence of elemental impurities is necessary. The ICH 3QD guidelines established permitted daily exposure (PDE) values for elemental impurities,[2] which must be monitored in the starting materials and final product. Out of the elements included in the guidelines, Hg can be highlighted due to its risks for human health. Plasma-based techniques, such as inductively coupled plasma mass spectrometry (ICP-MS) allow for sensitive detection of these impurities. For this, the sample needs to go through a pre-treatment to become a liquid solution. In this sense, microwave-induced combustion (MIC) is a well-established sample preparation method that could potentially be used for elemental impurities determination in oral tablets. This method provides the complete digestion of the organic matrix in samples followed by a reflux step, improving the recovery of the analytes.[3]. However, samples with high inorganic content, such as tablets containing inorganic excipients, can be a challenge for combustion-based methods, as the necessary heat for analyte volatilization might not be achieved, since the organic matter works as the fuel for combustion,[3], Thus, the aim of the present study was to develop a MIC method for further Hg determination in oral tablets with high inorganic excipient content. For this, three generic pharmaceutical tablet samples containing sitagliptin phosphate, metformin hydrochloride, and canaglifozin as the active pharmaceutical ingredients were used. Sitagliptin phosphate was chosen for method optimization. Samples were ground and pressed as pellets and placed on a quartz holder containing a disk of filter paper moistened with 50 µL of 6 mol L^{-1} NH_4NO_3 (igniter solution). After, the quartz holders were transferred into quartz vessels containing 6 mL of absorbing solution, which were then closed, placed in a rotor, pressurized at 20 bar with O_2, and placed in the microwave oven. The irradiation program consisted of the following steps: *i*) 900 W for 5 min (ignition and reflux step) and *ii*) 0 W until reaching 50 °C (cooling step). Cold vapor generation coupled to inductively coupled plasma mass spectrometry (CVG-ICP-MS) was used for Hg determination. The following method parameters were evaluated: sample mass (150 to 600 mg) and the composition and concentration of absorbing solution (H_2O or 0.5 to 5 mol L^{-1} HNO_3). The efficiency of digestion was evaluated considering analyte recovery and the visual aspect of the digests. For method accuracy evaluation, standard addition experiments at 50%, 100% and 150% of the PDE level were performed according to chapter 233 of the United States Pharmacopeia[4], as well as by decomposing a certified reference material (CRM) of dogfish liver (DOLT-4) mixed with the sample matrix. The optimized conditions for the proposed method were 600 mg of sample and 0.5 mol L^{-1} HNO_3 as absorbing solution. Quantitative analyte recoveries were obtained for all samples at all standard addition levels, and no significant differences were observed between experimental and certified values for CRM analysis (Student's *t*-test, 95% of confidence). Thus, the proposed MIC method allowed efficient decomposition of pharmaceutical oral tablets with high inorganic content for further Hg determination by CVG-ICP-MS. This was achieved using only 6 mL of diluted HNO_3, and LOQ values were adequate according to ICH Q3D limits for Hg for oral route.

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[CNPq, CAPES, FAPERGS]

097 - SAMPLE DECOMPOSITION USING DILUTED NITRIC ACID IN A CLOSED-VESSEL CONDUCTIVELY HEATED DIGESTION SYSTEM FOR INORGANIC SPECTROSCOPIC ANALYSIS

Guilherme O. Ferreira[a*], José A. Gomes Neto[a], Alex Virgilio[b], Alan L. Vieira[c], Gabriel Gustinelli A. Carvalho[c]

[a]São Paulo State University (UNESP), Institute of Chemistry, Araraquara, São Paulo, Brazil, 14800-060.
[b] University of São Paulo, Center for Nuclear Energy in Agriculture, Piracicaba, São Paulo, Brazil, 13400-970
[c] Vert Technology in Chemical Separations, São Paulo, Brazil, 01544-000
*e-mail: guilherme.orlandin@unesp.br

This study represents a significant advancement in spectrochemical analysis for agro-industrial samples through the utilization of the Simplify Digestor (Fig. 1), an innovative closed-vessel digestion system employing conductive heating recently proposed. This pioneering system[1] has been successfully employed to digest an array of samples such as plant tissues, meat, milk, chocolate, and coffee, predominantly employing around 2 ml of concentrated nitric acid. Moreover, this work extends the applicability of the commercial Simplify digestor by analysis for inorganic elemental constituents within plant materials exhibiting diverse compositions, as well as soils, employing diluted nitric acid and H_2O_2 (30% v/v). This approach not only underscores its potential for elemental analysis across diverse sample matrices but also further enhances the field of spectrochemical analysis in agro-industrial contexts. The digestion procedure for 200 mg of sample powder of plant and soil, respectively, was defined using 2 ml of HNO3 (50%, v/v) and 1.5 ml of H_2O_2 (30%, v/v) volumes, at a temperature of 240 ºC on the aluminum block. The performance of this novel sample preparation approach was rigorously assessed using certified reference materials, including apple leaves, Brachiaria Brizantha, and soil samples. After digestion, macro- and micronutrient elements (Mg, K, Ca, P, Mn, S, Cu, Zn, and Fe) were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). The samples were digested using a microwave-assisted closed system (MW-AD) and analyzed using ICP OES for comparison purposes. The results of this study demonstrated recovery ranges of 74% to 104% for the CHDS and 72% to 117% for the MW-AD method when applied to plant samples. For soil samples, variations ranged from 21% to 88% for CHDS and 14% to 96% for MW-AD. Furthermore, the efficiency of the digestion process was evaluated through the measurement of residual carbon content (RCC). The calculated RCC values, given in milligrams of carbon per 100 milligrams of the sample, ranged from 5.5 to 8.5 for CHDS and 4.5 to 8.9 for MW-AD. Using CHDS alongside diluted acids has shown satisfactory results in preparing plant and soil samples for ICP-OES analysis, particularly due to the reduction of reagent consumption and procedure time. This approach not only underscores its potential for elemental analysis across diverse sample matrices but also further enhances the field of spectrochemical analysis in agro-industrial contexts[2].

Fig. 1. The Simplify Digestor with 24 quartz tubes (45 mL) sealed with PTFE lids. The digestion vessels are equipped with safety disks that break at pressures > 20 bar. The heating program used a heating rate of 10 °C per minute up to 240 °C, with a dwell time at that temperature of 20 minutes, followed by 10 min cooling time, resulting in a total digestion procedure time of 50 min.

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098 - HALOGEN DETERMINATION IN EDIBLE INSECTS BY ICP-MS AFTER MICROWAVE-INDUCED COMBUSTION

Nicole W. da Silva[a], Vitoria H. Cauduro[a], Diuly S. O. Pazatto[a], Alessandra S. Henn[a], Cristian R. Andriolli[a], Érico M. M. Flores[a]*

[a]Federal University of Santa Maria (UFSM), Chemistry Department, Santa Maria, RS, Brazil, 97105-900
*e-mail: ericommf@gmail.com

Due to the growing demand for food, insects are being incorporated into the human diet as alternative protein sources. This practice can be beneficial due to the high protein content of insects, as well as the practical production aspects of this food product[1]. However, there is still little research addressing the presence of contaminants and micronutrients, with no data regarding halogen levels in this matrix[2]. Owing to the difficulty of halogen determination, the development of adequate sample preparation methods and determination techniques is necessary[2]. In this context, microwave-induced combustion (MIC) is a promising method aiming at halogen determination, due to the possibility of using relatively high sample masses and diluted alkaline absorbing solutions[2]. In this sense, the aim of this research was to develop a sample preparation method based on MIC for edible insect decomposition and further halogen determination by inductively coupled plasma mass spectrometry (ICP-MS). For the development of this study, seven insect samples of different geographical origins and species were used, specifically mealworm (*Tenebrio molitor*) from 2 different origins (Mealworm A and B), cricket (2 house cricket, *Acheta domesticus sp.*, and 1 mole cricket, *Gryllotalpidae sp.*) from 3 different origins (cricket A, B and C), june beetle (*Phyllophaga*), and rice-field grasshopper (*Oxya yezoensis sp.*). Samples were washed, dried at 75 °C for 4 h and pressed as pellets using a hydraulic press (3 tons for 1 min). Pellets were weighed and placed in quartz holders containing a filter paper wetted with 50 µL of 6 mol L^{-1} NH_4NO_3 (igniter solution) and introduced into quartz vessels containing 6 mL of absorbing solution. The vessels were then closed, pressurized with oxygen (20 bar) and introduced in the microwave system for sample combustion (irradiation program: 1400 W for 5 min and 0 W for 20 min). Sample cricket A was arbitrarily chosen for method optimization. The absorbing solution (H_2O or 25 to 200 mmol L^{-1} NH_4OH) and sample mass (100 to 600 mg) were evaluated, and results were compared to those obtained by a reference method based on microwave assisted extraction (MAE). The MAE procedure consisted of using 50 mg of sample, 200 mmol L^{-1} tetramethylammonium hydroxide as extracting solution and a 50 min microwave irradiation program (ramp to 1000 W for 10 min; permanence in 1000 W for 50 min; and cooling to 50 ºC)[3]. The accuracy of the proposed method was evaluated by standard addition experiments performed at two levels (50% and 100% of the sample concentration), and by decomposition of a cricket flour reference material (KRIK-1, National Research Council, Canada). Moreover, stability of the digests was evaluated during four weeks. The optimized conditions were set as 500 mg of sample and 100 mmol L^{-1} NH_4OH as the absorbing solution. Quantitative recoveries were obtained for Cl, Br and I for standard addition experiments (agreements from 94% to 102%). Agreements varying from 95 to 105% were obtained when results were compared to the reference method. Furthermore, no significant differences (t test, 95% confidence) were observed between obtained and certified values for KRIK-1 analysis, and halogen concentration in the digests remained steady throughout the entire stability test. Finally, using the proposed MIC method for insect decomposition made it possible to determine Cl, Br and I at trace levels. The limits of detection were 0.013 mg g^{-1}, 0.019 µg g^{-1} and 0.002 µg g^{-1} for Cl, Br and I, respectively. Compared to MAE, the proposed method was significantly faster and permitted lower relative standard deviations and blank values. Furthermore, the MIC method could be performed using a much safer reagent, which also resulted in digests with lower carbon content. Thus, the proposed MIC method may become an important instrument for halogen determination in edible insects by ICP-MS.

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[CNPq, FAPERGS, CAPES and UFSM]

099 - ASSESSMENT OF BROMINE AND IODINE CONCENTRATIONS IN DRILL CUTTINGS AND OILY SLUDGE BY ICP-MS

Renan G. Marim[a*] and Eduardo S. Chaves[a]

[a] Universidade Federal de Santa Catarina, Departamento de Química, Florianópolis, SC, Brazil, 88040-900
*e-mail: marimrenan@gmail.com

The oil and gas industry is amongst the most relevant sectors for the global economy.[1] However, the ecological concerns linked to oil and gas exploration require careful reflection due to the waste production inherent to this activity.[2] The data regarding the concentrations of non-metals in waste from the oil and gas industry, principally in wastes like drill cuttings and oil sludge, are still scarce.[3] Considering the organic content in these samples, an appropriate sample preparation is required to allow the determination of halogens by ICP-MS.[4] However, the sample preparation for halogen determination is a challenge, as these elements are volatile and can be lost during this step.[4] Microwave-induced combustion, pyrohydrolysis, and extraction are amongst the most used sample preparation procedures for further determination of halogens in different samples.[4] Thus, the determination of bromine and iodine in drill cuttings and oil sludge by ICP-MS after extraction in alkaline tetramethylammonium hydroxide (TMAH) media was performed. The extraction procedure was optimized through a Doehlert design. The best extraction conditions were achieved using 100 mg of sample, 500 µL of TMAH, at 75 °C, and 4h of time extraction. The optimized ICP-MS conditions were: 1400 W of RF power, 1.05 L min^{-1} nebulizer gas flow and the isotopes monitored were ^{79}Br and ^{127}I. The accuracy of the proposed method was evaluated through the analysis of certified reference materials (CRMs), and also by comparing the results with those obtained after the pyrohydrolysis sample preparation.[5] The bromine and iodine concentrations obtained by the proposed method showed good agreement with the reference concentrations (87 to 113%). No significant difference was observed between the concentrations found by the proposed method and the CRMs reference values (t-test, 95% confidence level). In addition, the concentration of the analytes obtained by the proposed method showed a good agreement with the values obtained by pyrohydrolysis (90 to 107%), and the paired t-test, at a 95% confidence level, also indicated no statistical difference between results obtained by the evaluation procedures. The precision (RSD < 10%) and the limits of detection for bromine and iodine, respectively 0.355 and 0.007 µg kg^{-1}, were suitable for drill cuttings and oil sludge analysis by the proposed method. However, TMAH extraction is not a selective process and other compounds from the sample matrix can also be extracted, increasing the risk of negative effects during the analysis. Thus, the bromine and iodine counts were monitored for 2 hours, and considering the dilution factor applied for sample analysis, no evidence of signal instability and/or particle deposits on the cone surfaces was noted (paired t-test, 95% confidence level). The method was applied for the analysis of two oily sludges and three drill cuttings samples. In the analyzed oily sludges, bromine concentrations ranged from 639 to 975 µg kg^{-1} and iodine from 553 to 905 µg kg^{-1}. Correspondingly, the drill cuttings samples displayed a concentration range of 616 to 31456 µg kg^{-1} for bromine, whereas iodine concentrations ranged from < 0.007 to 290 µg kg^{-1}. This discrepancy between the values found in drill cuttings and those found in oil sludge samples could be related to the distinct sample composition.

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[CNPq, CAPES, Petrobras and UFSC]

100 - STUDY OF GOLD NANOPARTICLES ON SOMATIC EMBRYOGENESIS OF SOYBEAN BY SINGLE-PARTICLE ICP-MS

Elisânia Kelly Barbosa Fonseca[a*], Ana Beatriz Santos da Silva[a],
Marco Aurélio Zezzi Arruda[a,b]

[a] Spectrometry, Sample Preparation and Mechanization Group, Institute of Chemistry, University of Campinas- Unicamp, Campinas, São Paulo, Brazil, 13083-970
[b] National Institute of Science and Technology for Bioanalytics, Institute of Chemistry, University of Campinas- Unicamp, Campinas, São Paulo, Brazil, 13083-970
*e-mail: elisaniakelly@gmail.com

Soybean has been a model in studies of toxicity and accumulation of nanomaterials[1]. Gold nanoparticles (AuNPs) have been investigated in plants to evaluate their absorption and bio-interaction, which are dependent on particle size and morphology mainly. Techniques such as dynamic light scattering (DLS) have been employed to provide information about the characterization of nanoparticles. Besides this technique, single-particle ICP-MS (spICP-MS) can be useful for characterizing and quantifying nanoparticles in cell cultures[2]. Additionally, for extracting nanoparticles of samples, ultrasound-assisted extraction has been proposed as an alternative to the more intensive sample preparation methods. Therefore, this work aims to characterize and quantify AuNPs in soybean cell culture by spICP-MS. To evaluate the extraction of NPs, high-frequency ultrasound was used in the sample preparation, varying the exposure time. Then, AuNP suspensions were submitted to the cup-horn ultrasound for 3, 5, and 8 min, 75% amplitude, and 1 min on-off. Then, the DLS analysis was carried out, and the exposure time does not seem to influence the hydrodynamic size of the NPs. When compared to the control suspension, the recovery varied from 92% (3 min), 94% (8 min) to 103% (5 min). On the other hand, AuNPs certified suspension with a diameter size of 30 nm was employed to assess the transport efficiency using the number frequency method by spICP-MS[3]. Around 300 mg of soybean callus, cultured with 10 mg kg^{-1} AuNPs (15 nm), were submitted to the same extraction method already described to cup-horn, using 3 mL of deionized water. Additionally, the extracts were filtered (0.22 µm) and diluted 10 and 1000-fold before the total analysis through ICP-MS and spICP-MS analysis, respectively. Regarding AuNPs certified, a high number of detected particles and high recovery values number-based concentration were observed, varying from 100 to 123%. However, for the samples, no occurrence of AuNPs was observed with a dilution factor of 1000 fold. This way, was assessed the gold tracked by the soybean callus samples. The gold in the soybean callus was quantified at 82.0 ± 1.4 ng g^{-1}, corresponding to 0.82 ± 0.14% of the amount tracked. This indicates that the gold is present in almost 100% ionic form, and corroborating with spICP-MS analysis previously mentioned. Finally, high-frequency ultrasound is efficient in the extraction of NPs. Samples of soybean callus will be prepared with the assistance of cup-horn ultrasound, having the perspective analysis of spICP-MS and single cell ICP-MS to investigate the effects of AuNPs. In addition, these studies can contribute to understanding nanoparticle interaction in cell culture.

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101 - ULTRASOUND-ASSISTED EXTRACTION OF As, Cd AND Pb FROM SEAWEED

Thamires R. Silva[a], **Gustavo Gohlke**[a], **Vitoria H. Cauduro**[a], **Alessandra S. Henn**[a]
Érico M. M. Flores[a*]

[a] Federal University of Santa Maria, Department of Chemistry, Santa Maria, Rio Grande do Sul, Brazil, 97105-900
*e-mail: ericommf@gmail.com

Seaweed can be used for monitoring potentially toxic elements, such as As, Cd, and Pb, in the marine environment. These elements are known to cause severe environmental problems due to soil and water contamination and are harmful to human beings.[1] In this sense, the determination at low concentrations of these elements is necessary and can be performed by inductively coupled plasma mass spectrometry (ICP-MS). However, working with a conventional sample introduce system, this technique requires the sample in a solution form. Thus, a previous sample preparation step is necessary to convert the sample.[2] Among the sample preparation methods, ultrasound-assisted extraction (UAE) can be considered an alternative, since this method uses low cost instrumentation, requires less energy, in addition to the use of use diluted reagents.[3] Therefore, this study aims to develop a method for As, Cd, and Pb extraction from seaweed using UAE for further determination by ICP-MS. For the UAE optimization, a sample of Nori seaweed (*Porphyra yezoensis*) was used. Different ultrasound systems were evaluated: ultrasonic baths (25 and 45 kHz, 100 W; 37 and 80 kHz, 330 W; 35 and 130 kHz, 200 W), probe (20 kHz, 750 W; 20 kHz, 130 W), and cup horn systems (20 kHz, 750 W; 20 kHz, 130 W). The ultrasonic bath, operating at 25 kHz and 100 W, was selected for further experiments. In addition, the following parameters were optimized: amplitude (30 to 90%), temperature (25 to 90 ºC), sample mass (50 to 200 mg), volume (5 to 20 mL) and concentration (0.5 to 5 mol L^{-1} HNO_3) of the extraction solution, and time (5 to 30 min). The efficiency of As, Cd, and Pb extraction was evaluated by comparing results obtained after UAE with those obtained by the reference method (microwave-assisted wet digestion, MAWD). Moreover, the accuracy evaluation of the proposed UAE method was performed by the analyses of a certified reference material (CRM) of aquatic plant (BCR 60), spike recovery experiments (at tree levels: 50, 100 and 150%), and by comparison with results after MAWD. Agreement higher than 90% with MAWD results for all analytes was obtained using an ultrasonic bath operating at 25 kHz and 100 W, and the following conditions: 70% of amplitude, 200 mg of sample, 70°C of temperature, 10 mL of 2 mol L^{-1} HNO_3 as extraction solution and 30 minutes of extraction time. Comparison with magnetic stirring (silent condition) was performed and demonstrated that ultrasound had a positive significant effect on As, Cd, and Pb extraction from seaweed. No statistical difference (t-test, 95% of confidence level) was observed between certified, informed and obtained values for CRM BCR 60 for As, Cd and Pb after UAE and ICP-MS determination. Additionally, recoveries ranged from 90 to 107%. The proposed UAE method in combination with ICP-MS determination demonstrated to be suitable for the determination of As, Cd, and Pb at very low concentrations in seaweed, with limits of quantification of 80, 40 and 10 ng g^{-1} for As, Cd and Pb, respectively. The method combines the use of diluted acid solutions, low instrumentation cost, and reduces waste generation.

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[CNPq, FAPERGS and CAPES]

X-ray Spectrometry

102 - DETERMINATION OF NIOBIUM IN PHOTOCATALYTIC NANOMATERIAL BY X-RAY FLUORESCENCE SPECTROMETRY

**Claudir Gabriel Kaufmann Jr[a], Lourdes Maria Muraro Favarin[a], Ana Carolina Fadel Dalsin[b],
Cristiano Rodrigo Bohn Rhoden[a], Denise Crocce Romano Espinosa[b],
William Leonardo da Silva[a], Sergio Roberto Mortari[a*]**

[a]Franciscan University - UFN, Nanotechnology, Santa Maria, RS, Brazil, 97010-032
[b] University of São Paulo - USP, LAREX/ Polytechnic School, São Paulo, SP, Brazil, 05508-010
*e-mail: mortari@ufn.edu.br

Photocatalysis is a process used in water decontamination by the action of photocatalysts, which are usually alternative materials activated by ultraviolet (UV) irradiation, generating radicals that will activate oxidation-reduction reactions. In this work, in order to increase the surface area, multi-walled carbon nanotubes (MWCNT) were decorated with niobium (Nb) - MWCNT@Nb - aiming the degradation of organic pollutants trough a photocatalytic process[1,2]. Therefore, in this work, we present a semi-quantitative approach, using energy-dispersive X-ray fluorescence (ED-XRF) for determination of the concentration of Nb in this nanomaterial (EDX-7200, Shimadzu, Japan), according to the manufacturer's recommendations. The X-ray generator was operated at 50 kV and acquisition time of 120 s and silicon drift detector (SDD) was used. The original powder sample was placed in a 3.6 um polyester Mylar sample holder with a 3 mm opening, under an air atmosphere. The result obtained was 0.918 % Nb, indicating that the decoration was efficient. This instrumental technique has the advantage of being faster to processing of samples, generates less chemical waste and prevention of contamination. Quantitative analysis (using the ICP-OES technique) did not yield satisfactory results, due to the incomplete decomposition (HNO_3 65% + H_2O_2 30%, heating 130 °C for 4 hours). In the solid residue resulting from the digestion (14% of the mass used), it was possible to oberve a significant Niobium signal in the ED-XRF determination.

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[UFN, LAREX/USP, CNPq]

103 - ARE TOENAILS THE IDEAL SPECIMEN TO ACCESS THE EXPOSURE TO ARSENIC AND OTHER ELEMENTS IN EPIDEMIOLOGICAL STUDIES?

Camilla Faidutti[a], Louise Hair[a], Casey Doolette[b], Enzo Lombi[b], Joerg Feldmann[c]

[a] Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, UK
[b] Future Industries Institute, University of South Australia, Mawson Lakes, SA 5095, Australia
[c] TESLA – Analytical Chemistry, Institute of Chemistry, University of Graz, 8010 Graz, Austria
*e-mail: joerg.feldmann@uni-graz.at

The exposure to toxic elements especially arsenic, mercury and lead is commonly measured in occupational situation; less common in epidemiological studies (1). Often blood samples are used to assess the exposure to these elements. This has however several disadvantages: invasive sampling, storage costs and that it represents only the short-term exposure due to low residence time of these elements in the blood. In epidemiology, however long-term exposure is more important and therefore it has been suggested to use hair or nails as specimen to obtain total element concentrations to model the exposure. However, exogeneous contamination of the hair and nail through bathing, exposure to dirt and other environmental processes are the major drawbacks for using those specimens.

In this lecture we present

i) cleaning protocol to remove the exogeneous arsenic and other elements and its evaluation by using XRF synchrotron mapping and arsenic speciation using XANES (2) and
ii) its application to a case-control study investigating the influence of trace element exposure to myocardial infarction in Dhaka (Bangladesh) using ICPMS detection.

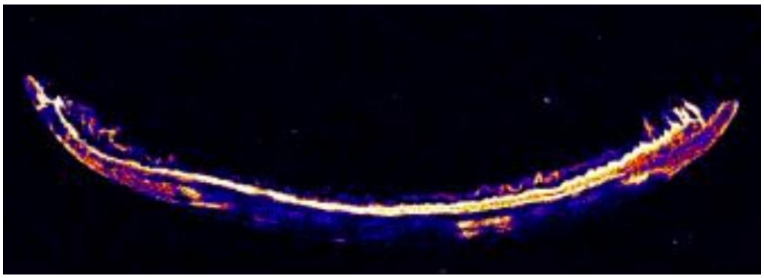

Fig.1. XRF Map for As in a toenail cross section (3)

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Notes

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