Scientific Program

15th Rio Symposium on Atomic Spectrometry

6 · 11 OCTOBER 2019 · Mendoza · Argentina
Hotel Intercontinental Mendoza

Welcome letter

It is our honor and pleasure to welcome you to the 15th Rio Symposium on Atomic Spectrometry.

Once again, we have the opportunity of joining together scientists, students and professionals from Latin America with distinguished researchers from different parts of the world to present and discuss our latest works in a very friendly environment.

The 15th Rio Symposium on Atomic Spectrometry is held in Mendoza city. In the middle of the mountains, Mendoza is one of the great wine capitals of the world and a great place to explore high quality wines and food. You will enjoy an amazing time in a sunny climate while discovering the Andes Mountains, drinking some of the best wines of the world, tasting our delicious food, and living memorable experiences that will make very special this edition of the Rio Symposium.

So, be welcomed to Mendoza! We are sure this symposium will meet your expectations and you will have a great opportunity for discussion of your achievements, evaluation of ongoing projects and the exchange of views on novel initiatives. We also assure you all a memorable touristic experience and friendly social events so you will return home with the feeling that your visit was not only productive and worthwhile but enjoyable.

Organizing Committee

Committees

Local Organizing Committee

Rodolfo G. Wuilloud – Chairman
Instituto Interdisciplinario de Ciencias Básicas – ICB
Facultad de Ciencias Exactas y Naturales
Universidad Nacional de Cuyo/CONICET
Mendoza, Argentina

Patricia Smichowski
Comisión Nacional de Energía Atómica – CNEA
CONICET
Buenos Aires, Argentina

National Organizing Committee

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Mauricio Llaver
Emiliano Franco Fiorentini
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Pamela Yanina Quintas
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Instituto Interdisciplinario de Ciencias Básicas – ICB
Facultad de Ciencias Exactas y Naturales
Universidad Nacional de Cuyo/CONICET
Mendoza, Argentina

Committees

Scientific Committee

Marco Aurélio Zezzi Arruda – Campinas, SP, Brazil
Ramon Barnes – Amherst, USA
Ewa Bulska – Warsaw, Poland
Maria Tereza W. D. Carneiro – Vitória, ES, Brazil
Maria Luisa Carvalho – Lisboa, Portugal
Marinela Colina – Maracaibo, Venezuela
Sergio Luis Costa Ferreira – Salvador, Brazil
Alessandro D'Ulivo – Pisa, Italy
Miguel de la Guardia – Valencia, Spain
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Jiří Dědina – Praha, Czech Republic
Joerg Feldmann – Aberdeen, Scotland
Érico M. M. Flores – Santa Maria, MS, Brazil
Zoltán Mester – Ottawa, Canada
Javier Laserna – Málaga, Spain
Joaquim A. Nóbrega – São Carlos, SP, Brazil
Nicoló Omenetto – Gainesville, USA
Mariela Pistón – Montevideo, Uruguay
Waldo Quiroz – Valparaíso, Chile
Dirk Schaumlöffel – Pau, France
Patricia Smichowski – Buenos Aires, Argentina
Mabel B. Tudino - Buenos Aires, Argentina
Maria Goreti R. Vale – Porto Alegre, RS, Brazil
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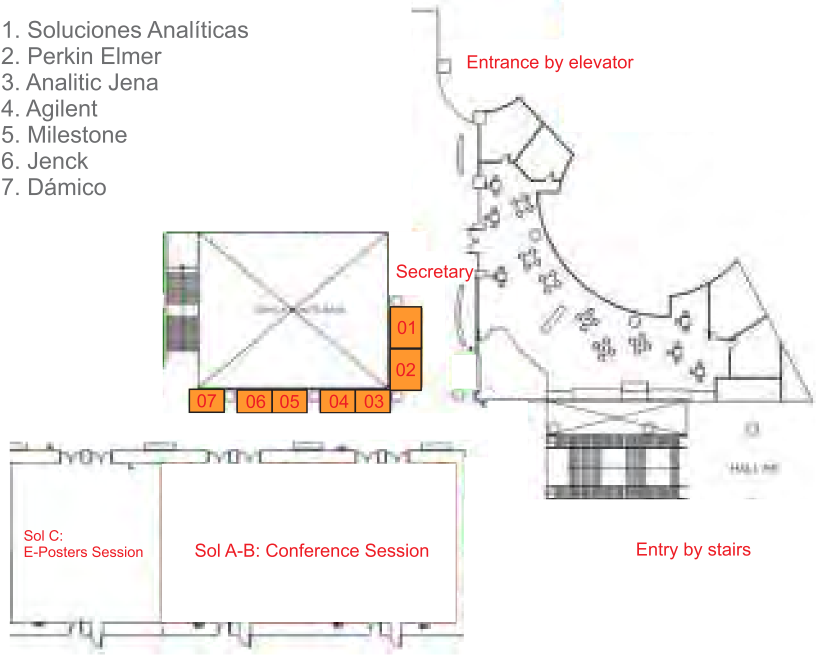

Useful Information

Currency

Argentina's currency is the Argentinean peso. Notes: 1000, 500, 200, 100, 50, 20, 10 and 5 pesos. Coins: 1, 2 and 5 Pesos and 50 and 25 cents.

Time

Mendoza's standard time zone is UTC/GMT -3 hours.

Weather

In general, the climate in Mendoza is known for its sunshine. It is dry and temperate continental with significant temperature fluctuations between day and night.

Useful numbers

- Emergencies: 911
- Firefighters: 100
- Mendoza Police: 101
- Federal Police: 1049, Peru street. Telephone: +54-0261-423-8710
- Lost Documents: 0800-2222-999 / +54-0261-449-9024 (from 8 to 17hs)
- Coordinated Health Emergencies: 107

City Transport

Public transport runs from 06:00-01:00. The journey, either bus, trolley or metrotranvía, is paid through a machine located inside each vehicle, which only receives coins and doesn't give change back. Another form of payment is by Redbus card, which is purchased in kiosks and shops offering this service. (You can ask for further information in the bus station or: http://www.transportes.mendoza.gov.ar/mi-red-bus/)

Taxis

Taxis are always metered. The fare depends on where you're going, but a short ride will cost about 100 Pesos while a longer one could cost about 300 Pesos. Taxis are generally safe, but if you're staying in a hotel, you can ask the concierge to call one for you. **Uber** and **Cabify** services are operative in the city as well.

Touristic activities

Below follows a list of Tourist Information Centers (TIC) in Mendoza and major tourist destinations that may be contacted for information on hotels, restaurants and excursions:

Tourism Ministry: San Martin St, 1143. Phone: 0810-666-6363/ +54-0261-4132101
E-mail: turismo@ciudaddemendoza.gov.ar

TIC I: 9 de Julio St, 500. Floor 7. Municipality of Mendoza Capital. Phone: +54-0261-4495185/6 Opening hours: Monday to Friday from 08:15-13:30.

Useful Information

TIC II: San Martin and Garibaldi St. Phone: +54-0261- 4201333 / 4238745 Opening hours: Every day from 09:00-21:00

TIC III: Las Heras St.,700. Phone: +54-0261-4296298 Opening hours: Monday to Saturday from 09:00-20:00

TIC General San Martin Park: Av Los Plátanos s/n San Martin Park. Phone: +54-0261-4205052 ext. 22

For pre and post Congress tours please contact:

SB División Turismo
E-mail: turismo@sbcongresos.com
Phone and Whatsapp: +54 9 261 5793166

Banks

Banks are open from Monday to Friday from 8:00 - 13:00. However, you can make cash withdrawals and other transactions at ATMs, which operate 24 hours.

Voltage

The electrical supply in Argentina is 220 volts, 50 Hz.

LOCATION OF THE VENUE

HOTEL INTERCONTINENTAL MENDOZA
Blvd Perez Cuesta esq. Acceso Este: Mendoza.
ZIP code: M5521AAR
Tel: +54 0261 5218800

Secretariat

Registration and general information will be available at our secretariat stand on every day of the conference, from 09:00 to 18:00

Restaurants

The INTERCONTINENTAL HOTEL has a restaurant and is also located next to Mendoza Plaza Shopping, the city's largest shopping mall. Several lunch and dinner options are available at the mall; open all day up to around 01:00 am.

Lectures and Oral Presentations

The Plenary Lecture (PL) will be 60 min including discussion. Invited Lectures (IL) will be 30 min including discussion and Oral Presentations (OP) will be 15 min including discussion. All speakers are requested to respect their allotted time and chairpersons are advised to avoid delays to the daily program. Files for oral presentations should be saved as *.ppt or *.pptx, since the organization cannot assure the well-functioning or projection quality of any other format/s.
Morning session speakers are kindly requested to provide their presentations in a USB flash drive before the day previous to their lecture. Meanwhile, afternoon speakers are kindly requested to provide their presentation in a USB flash drive before the lunch break of their corresponding presentation day.

E-poster Presentation

Each e-poster will be projected for 30 minutes in a screen during the corresponding daily session, during which the author must be present in order to be eligible for the corresponding award. The presentation should include at least 20 minutes of exposition and 10 minutes of discussion. During the rest of the daily activities, the e-posters will be sequentially projected (author presence not required). The daily e-poster presentation schedule will be:

Monday, Oct. 7	Tuesday, Oct. 8	Thursday, Oct. 10	Friday, Oct. 11
AAS01 – AAS08 AES01-AES06 XR01-XR05 LIBS01-LIBS03 SP01-SP07	AAS09-AAS17 MS01-MS10 SP08-SP15 CS01	AES07-AES11 XR06-XR10 MS11-MS20 CVG1-CVG8	ChemS01-ChemS06 SMet01-SMet08 SP16-SP22 MS21-MS29

Special issue

Selected papers from the 15th Rio Symposium on Atomic Spectrometry will be published as a Special Issue of Spectrochimica Acta B: Atomic Spectrometry. Please, follow instructions about abstract submission and deadlines available in our official webpage: www.15riosymposium.com.

Scientific Program

Sunday October 6	Monday October 7	Tuesday October 8	Wednesday October 9	Thursday October 10	Friday October 11
Registration <u>Sunday to Friday</u> 8:00 - 18:00	*Chairperson: Marco Zezzi Arruda*	*Chairperson: Joanna Szpunar*	***Starting 8:15*** ***FULL DAY EXCURSION***	*Chairperson: Mariela Pistón*	*Chairperson: Erico M.M. Flores*
	9:00 IL1: Ryszard Lobinski	9:00 IL7: Frank Vanhaecke		9:00 IL13: Joerg Feldmann	9:00 IL19: Pilar Bermejo-Barrera
	9:30 IL2: Ewa Bulska	9:30 IL8: Maria Goreti Vale		9:30 IL14: José Almirall	9:30 IL20: Jiří Dědina
	10:00 IL3: Javier Laserna	10:00 IL9: Víctor Cerdà		10.00 IL15: Vincent Motto-Ros	10:00 IL21: Marco Zezzi Arruda
	10:30 IL4: Márcia Foster Mesko	10:30 IL10: Alessandro D'Ulivo		10.30 IL16: Érico M. M. Flores	10:30 IL22: Waldo Quiroz
	11:00 - 11:30 Coffee Break			*11:00 - 11:30 Coffee Break*	
11:30-13:00 Thermo Scientific Seminar	*Chairperson: Pablo Pacheco*	*Chairperson: Leticia Escudero*		*Chairperson: Marta Costas Rodríguez*	*Chairperson: Mirna Sigrist*
	11:30 OP1	11:30 OP10		11:30 OP18	11:30 OP27
	11:45 OP2	11:45 OP11		11:45 OP19	11:45 OP28
	12:00 OP3	12:00 OP12		12:00 OP20	12:00 OP29
	12:15 OP4	12:15 OP13		12:15 OP21	12:15 OP30
13:00 -14:00 Lunch	*12:30 -14:00 Lunch*			*12:30 -14:00 Lunch*	
14:00-18:00 Short Course: Víctor Cerdà	14:00-15:30 Poster Session AAS01-AAS08; AES01-AES06; XR01-XR05; LIBS01-LIBS03; SP01-SP07	14:00-15:30 Poster Session AAS09-AAS17; MS01-MS10; SP08-SP15; CS01		14:00-15:30 Poster Session AES07-AES11; XR06-XR10; MS11-MS20; CVG01-CVG08	14:00-15:30 Poster Session ChemS01-ChemS06; SMet01-SMet08; SP16-SP22; MS21-MS29
	Chairperson: Márcia Foster Mesko	*Chairperson: Ewa Bulska*		*Chairperson: Vincent Motto-Ros*	*Chairperson: Pilar Bermejo-Barrera*
	15:30 IL5: Mariela Pistón	15:30 IL11: Joanna Szpunar		15.30 IL17: Dirk Schaumlöffel	15.30 IL23: Pablo Pacheco
	16:00 IL6: Eva Krupp	16:00 IL12: Viktor G. Mihucz		16.00 IL18: Rebecca Brodie	16.00 IL24: Sofia Pessanha
	16:30-17:00 Coffee Break			*16:30-17:00 Coffee Break*	
	Chairperson: Jorge Yañez	*Chairperson: Fernando Iñón*		*Chairperson: Victor Mihucz*	*Chairperson: Daniel Borges*
	17:00 OP5	17:00 Sponsor presentation - Milestone		17:00 OP22	17:00 OP31
	17:15 OP6	17:15 OP14		17:15 OP23	17:15 OP32
	17:30 OP7	17:30 OP15		17:30 OP24	17:30 OP33
	17:45 OP8	17:45 OP16		17:45 OP25	17:45 OP34
	18:00 OP9	18:00 OP17		18:00 OP26	18:00 OP35
18:15-19:00 Opening Ceremony		18:15 Sponsor presentation - Analytik Jena			18:15 - 18:45 Poster Awards / Closing Ceremony
19:00-19:30 Tribute to Bernhard Welz					19:00 Bottle Party
19:30-20:30 PL: Gary Hieftje					
20:30 Welcome Cocktail		20:30 Atomic Dinner			

PL: Plenary Lecture; **IL:** Invited Lecture; **OP:** Oral Presentation

Sunday, October 6, 2019

9:00 – 18:00	**Registration & Materials** | Hotel Intercontinental
11:30 – 13:00	**Thermo Scientific seminar** | Salón Sol A-B Discover the right tools for elemental analysis: key technologies to expand the border of your applications *Ana Rita Cristiano*
13:00 – 14:00	**Lunch**
14:00 – 18:00	**Short Course** | Salón Sol A-B Automation of atomic spectroscopy methods using flow techniques *Víctor Cerdà*
18:15 – 19:00	**Opening Ceremony** | Salón Sol A-B
19:00 – 19:30	**Tribute to Bernhard Welz** | Salón Sol A-B *Marco Aurélio Zezzi Arruda – UNICAMP, Brazil*
19:30 – 20:30	**Plenary Lecture** | Salón Sol A-B Analytical atomic spectrometry and the arrow of time *Gary M. Hieftje – Indiana University - USA*
20:30	**Opening Cocktail** | Hotel Intercontinental

Monday, October 7, 2019

Chairperson: Marco Zezzi Arruda
Invited Lectures | Salón Sol A-B

09:00 – 09:30 **IL 01**	Mass spectrometry-driven studies of metal ion trafficking and function in bacteria and plants *Ryszard Lobinski – CNRS, France*
09:30 – 10:00 **IL 02**	The use of mass spectrometry for environmental and clinical purposes: advantages and limitations *Ewa Bulska – University of Warsaw, Poland*
10:00 – 10:30 **IL 03**	LIBS analysis of individual nanoparticles: attogram detection limits in optical traps *Javier Laserna – University of Málaga, Spain*
10:30 – 11:00 **IL 04**	Green analytical methods for determination of metals and non-metals by mass spectrometric techniques *Márcia Foster Mesko – Federal University of Pelotas, Brazil*
11:00 – 11:30	**Coffee Break** | Hotel Intercontinental

Chairperson: Pablo Pacheco
Oral presentations | Salón Sol A-B

11:30 – 11:45 **OP 01**	Sulfur determination using the SiS molecule via HR-CS GF MAS and direct solid samples analysis: a reliable method for different matrices *Wiliam Boschetti*

Monday, October 7, 2019

11:45 – 12:00 **OP 02**	Multi-flow calibration: a novel approach applied to inductively coupled plasma techniques *Raquel C. Machado*
12:00 – 12:15 **OP 03**	Atomization of bismuthane and sensitive bismuth determination by atomic fluorescence spectrometry *Barbora Štádlerová*
12:15 – 12:30 **OP 04**	A new procedure to determine the composition of alloys based on the technique calibration free: time resolved calibration free *I. Urbina*
12:30 – 14:00	**Lunch**

E-poster session | Salón Sol C

14:00 – 15:30	AAS01-AAS08; AES01-AES06; XR01-XR05; LIBS01-LIBS03; SP01-SP07

Chairperson: Márcia Foster Mesko

Invited Lectures | Salón Sol A-B

15:30 – 16:00 **IL 05**	Challenges in sample preparation for trace elements determination using microwave-induced nitrogen plasma optical emission spectrometry *Mariela Pistón – University of the Republic, Uruguay*
16:00 – 16:30 **IL 06**	Does the use of HPLC-ICPMS answer all questions how the elements occur in a sample? *Eva Krupp – University of Aberdeen, Scotland*

Monday, October 7, 2019

16:30 – 17:00 **Coffee Break** | Hotel Intercontinental

Oral presentations | Sol A-B

17:00 – 17:15 **OP 05**	Photochemical vapor generation of transition metals – expanding to new analytes *Stanislav Musil*
17:15 – 17:30 **OP 06**	Simultaneous on-line preconcentration and determination of Cd, Hg, Mn, Pb and Sb in rice and rice-based products by ICP-MS. Optimization using chemometric approaches *Agustín Londonio*
17:30 – 17:45 **OP 07**	Qualitative imaging using laser ablation inductively coupled plasma mass spectrometry applied in dendrochemical analysis *Renata S. Amais*
17:45 – 18:00 **OP 08**	Study of the matrix effects in flowing liquid anode atmospheric pressure glow discharge optical emission spectrometry (FLA-APGD-OES) *Krzysztof Greda*
18:00 – 18:15 **OP 09**	Bioaccessibility and total concentration of Cr and Ni in different varieties of cooked rice *María Laura Ortiz*

Tuesday, October 8, 2019

Chairperson: Joanna Szpunar
Invited Lectures | Salón Sol A-B

09:00 – 09:30 **IL 07**	Multi-collector ICP-MS high-precision isotopic analysis of essential mineral elements in health & disease *Marta Costas-Rodríguez – Ghent University, Belgium*
09:30 – 10:00 **IL 08**	Direct analysis of complex matrices: overcoming the interferences by HR-CS AAS *Maria G. M. Vale – Federal University of Rio Grande do Sul, Brazil*
10:00 – 10:30 **IL 09**	Automatic radiochemical analysis using flow techniques *Víctor Cerdà – University of the Balearic Islands, Spain*
10:30 – 11:00 **IL 10**	Fundamental aspects of chemical vapor generation by aqueous boranes *Alessandro D'Ulivo – University of Pisa, Italy*
11:00 – 11:30	**Coffee Break** | Hotel Intercontinental

Chairperson: Leticia Escudero
Oral presentations | Salón Sol A-B

11:30 – 11:45 **OP 10**	Application of different strategies in partial least squares regression models for the determination of Mn, Cr, and Ni in steel samples using LIBS *Aderval S. Luna*

Tuesday, October 8, 2019

11:45 – 12:00 **OP 11**	Spark discharge-assisted single-standard calibration in laser-induced breakdown spectroscopy: determination of Al and P in agroindustrial samples *José A. Gomes Neto*
12:00 – 12:15 **OP 12**	Microextraction and preconcentration technique based on magnetic ionic liquid for the determination of chromium by electrotermal atomic absorption spectrometry applied to honey sample *Emiliano F. Fiorentini*
12:15 – 12:30 **OP 13**	Critical evaluation of the analytical performance of commercial nebulizers in microwave-induced plasma optical emission spectrometry *Julymar M. Higuera*
12:30 – 14:00	**Lunch**

E-poster session | Salón Sol C

14:00 – 15:30	AAS09-AAS17; MS01-MS10; SP08-SP15; CS01

Chairperson: Ewa Bulska
Invited Lectures | Salón Sol A-B

15:30 – 16:00 **IL 11**	Methodological developments for ultratrace and large-scale biological selenium speciation analysis *Joanna Szpunar – CNRS, France*
16:00 – 16:30 **IL 12**	Integrated approach for the chemical characterization of indoor $PM_{2.5}$ subordinated to oxidative potential assessment *Victor G. Mihucz – Eötvös Loránd University, Hungary*

Tuesday, October 8, 2019

16:30 – 17:00	**Coffee Break** | Hotel Intercontinental

Oral presentations | Salón Sol A-B

17:00-17:15 **Sponsor presentation – Milestone**	*State-of-the-art* sample preparation technologies to maximize elemental analysis. *Mattia Locatelli*
17:15 – 17:30 **OP 14**	Space-charge effect and internal standardization *Fernanda C. Pinheiro*
17:30 – 17:45 **OP 15**	Subcellular metal partitioning in *Steno bredanensis* from southeastern Brazil *Rocha, R.C.C*
17:45 – 18:00 **OP 16**	A highly efficient ionic liquid-assisted cloud point extraction technique for preconcentration and speciation analysis of tellurium in environmental samples using electrothermal atomic absorption spectrometry *Mauricio Llaver*
18:00 – 18:15 **OP 17**	Optimization of sample injection in TS-FFAAS for determination of trace elements *Guillermo A. Carrone*
18:00-18:15 **Sponsor presentation – Analytik Jena**	Analysis of metals in naphtha by PQMS® accordingly to ASTM D8110-17 *Rui Miguel Santos*

Thursday, October 10, 2019

Chairperson: Mariela Pistón
Invited Lectures | Salón Sol A-B

09:00 – 09:30 **IL 13**	Are nanoparticles and speciation important in the oil and gas industry? *Joerg Feldmann –University of Aberdeen, Scotland*
09:30 – 10:00 **IL 14**	The use of LA-ICP-MS databases to calculate likelihood ratios in the forensic evaluation of glass evidence *José Almirall – Florida International University, USA*
10:00 – 10:30 **IL 15**	LIBS imaging: a breakthrough in material and biomedical sciences? *Vincent Motto-Ros – University Claude Bernard Lyon, France*
10:30 – 11:00 **IL 16**	How simple can be the sample preparation for further determination of halogens in organic matrices? *Érico M. M. Flores – University of Santa Maria, Brazil*
11:00 – 11:30	**Coffee Break** | Hotel Intercontinental

Chairperson: Marta Costas Rodríguez
Oral presentations | Salón Sol A-B

11:30 – 11:45 **OP 18**	XANES spectrometry in the laboratory: S.I. traceable energy edges for calibration *Mauro Guerra*

Thursday, October 10, 2019

11:45 – 12:00 **OP 19**	Filter paper as calibration solid support for quantification of metals in tree-rings samples by LA-ICP-MS *Pedro S. Moreau*
12:00 – 12:15 **OP 20**	Method development for the determination of total mercury and mercury thermospecies in coal *Mpho W. Mathebula*
12:15 – 12:30 **OP 21**	Dielectric barrier discharge-assisted determination of methylmercury in atmospheric particulate matter by AAS *Gilberto S. Coelho Junior*
12:30 – 14:00	**Lunch**

E-poster session | Salón Sol C

14:00 – 15:30	AES07-AES11; XR06-XR10; MS11-MS20; CVG01-CVG08

Chairperson: Vincent Motto-Ros

Invited Lectures | Salón Sol A-B

15:30 – 16:00 **IL 17**	Elemental and isotopic imaging at nanometer scale using Nano Secondary Ion Mass Spectrometry *Dirk Schaumlöffel – CNRS, France*
16:00 – 16:30 **IL 18**	How to publish in high impact journals *Rebecca Brodie – JAAS/Royal Society of Chemistry*

Thursday, October 10, 2019

16:30 – 17:00 **Coffee Break** | Hotel Intercontinental

Oral presentations | Salón Sol A-B

17:00 – 17:15 **OP 22**	Magnetic ionic liquid-based microextraction and preconcentration technique for arsenic speciation analisys by electrothermal atomic absorption spectrometry *María N. Oviedo*
17:15 – 17:30 **OP 23**	Atomic fluorescence spectrometry for determination of mercury in polymeric solutions from treatment of petroleum sludge *Mateus O. Müller*
17:30 – 17:45 **OP 24**	A new approach for trace Hg determination in crude oil by CVG-ICP-MS following wet digestion *Gabriel T. Druzian*
17:45 – 18:00 **OP 25**	Determination of mineral species by laser induced breakdown spectroscopy and chemometric methods *Jonnathan E. Álvarez*
18:00 – 18:15 **OP 26**	Green and simple micro-extraction of free seleno-amino acid from powder and lyophilized milk samples whit natural deep eutectic solvents *Paul E. Hasuoka*

Friday, October 11, 2019

Chairperson: Erico M. M. Flores

Invited Lectures | Salón Sol A-B

09:00 – 09:30 **IL 19**	The use of sp-ICP-MS for the analysis of titanium dioxide and silver nanoparticles *Pilar Bermejo-Barrera – University of Santiago de Compostela, Spain*
09:30 – 10:00 **IL 20**	Laser-induced atomic fluorescence for the development of hydride atomizers and for ultratrace determination of hydride forming elements *Jiǿ Dì dina – Charles University, Czech Republic*
10:00 – 10:30 **IL 21**	Speciomics: integrating bioanalytical information through mass spectrometry *Marco Aurélio Zezzi Arruda – University of Campinas, Brazil*
10:30 – 11:00 **IL 22**	Sb(III) vs. As(III): who represents a greater ecotoxicological risk? *Waldo Quiroz – Pontificial University of Valparaíso, Chile*
11:00 – 11:30	**Coffee Break** | Hotel Intercontinental

Chairperson: Mirna Sigrist

Oral presentations | Salón Sol A-B

11:30 – 11:45 **OP 27**	Validation of methodology to identification, characterization and quantification of dissolved gold (I) and gold nanoparticles in cosmetic products by SP-ICP-MS *L.M.G dos Santos*

Friday, October 11, 2019

11:45 – 12:00 **OP 28**	Total sulphur determination in automotive gasoline samples via CS diatomic molecule by high-resolution continuum source molecular absorption spectrometry using dried-matrix spot sampling *Leandro Kolling*
12:00 – 12:15 **OP 29**	Atmospheric pressure glow discharge system generated in contact with a hanging drop electrode as an excitation source in optical emission spectrometry *Krzysztof Świderski*
12:15 – 12:30 **OP 30**	Ultratrace impurities determination in silver for nuclear applications: signal optimization in ICP-MS with artificial neural networks and response surface methodology *Ezequiel Morzan*
12:30 – 14:00	**Lunch**

E-poster session | Salón Sol C

14:00 – 15:30	ChemS01-ChemS06; SMet01-SMet08; SP16-SP22; MS21-MS29

Chairperson: Pilar Bermejo-Barrera
Invited Lectures | Salón Sol A-B

15:30 – 16:00 **IL 23**	Hydride trapping on nanomaterials. Tunable nanoparticles studies towards a novel hydride generation approach *Pablo Pacheco – National University of San Luis, Argentina*

Friday, October 11, 2019

16:00 – 16:30 **IL 24**	Portability of EDXRF spectrometers: challenges and perspectives *Sofia Pessanha – NOVA University of Lisbon, Portugal*
16:30 – 17:00	**Coffee Break** | Hotel Intercontinental

Oral presentations | Salón Sol A-B

17:00 – 17:15 **OP 31**	Development of isotopic dilution mass spectrometry with single and multiple collectors *Marta Bavio*
17:15 – 17:30 **OP 32**	Speciation of Sb(III) and Sb(V) in homeopathic drugs by cloud point extraction combined with hydride generation in homemade dual cyclonic aerosol chamber by ICP-OES *Fátima J. Rodriguez-Ramos*
17:30 – 17:45 **OP 33**	An eco-friendly sample preparation method development for animal feed nutrient analysis by MIP OES *Florencia Cora Jofre*
17:45 – 18:00 **OP 34**	Determination of inorganic constituents in urban dust using direct analysis by energy dispersive x-ray fluorescence spectrometry *Vaniele S. Ribeiro*
18:00 – 18:15 **OP 35**	Exploratory analysis of inorganic constituents in rumen fluid and feces of nelore beef cattle *Mykaelli A. Santos*

Friday, October 11, 2019

18:15 – 18:45	**Oral and Posters Awards and Closing Ceremony** | Salón Sol A-B The Awards are sponsored by SAB-Elsevier, JAAS-RSC and ABC-Springer.

SOCIAL PROGRAM

Sunday, October 6, 2019

20:30	Welcome Cocktail | Hotel Intercontinental *Free for participants and registered accompanying persons*

Tuesday, October 8, 2019

20:30	Atomic Dinner | Bodega del 900 *Tickets available until October 7*

Wednesday, October 9, 2019

08:15 – 18:00	Full Day Excursion | Bodega Norton, Gran Hotel Potrerillos, Olivícola Laur *Includes lunch, tickets available until October 8* *See on next page*

Friday, October 11, 2019

19:00	Bottle Party | Hotel Intercontinental *Free for participants and registered accompanying persons* *You are invited to bring a bottle of a typical drink from your country*

FULL DAY EXCURSION

WEDNESDAY – October 9, 2019

08:15 am Departure from Intercontinental Hotel towards Norton Winery.

BODEGA NORTON

Bodega Norton is a winery of Austrian origin, recognized by its trajectory in the viticulture of Argentina for the quality of its wines and sparkling wines.

Finca Perdriel is the original property of Norton, where the winery is located. With one hundredyears of continuous crops, it's made by 100hectares, at 950 meters above sea level, with vineyards between 30 and 50 years old.

We invite you to live the evolution of a dream. We go back to 1989, to the vision of the Austrian, glassware expert Gernot Langes Swarovski, who proposed to share the wealth of our terroir, with wine lovers from more than 60 countries in the world. Today, the Winery is a hallmark of awardwinning winemakers and the artisan work of passionate harvesters. More than a name, Bodega Norton is an indelible firm that connects history with terroir, talent with passion.

09:30 am Visit Malbec Experience. We start with a welcome spirit drink and later a guided visit of winery. We will taste a Malbec reserve and a wine of the Oenology line.

10:30 am Expected departure to Potrerillos Dam. Tour around the lake and later lunch at the traditional Gran Hotel Potrerillos.

12:30 pm Lunch planned according to the chosen menu (See the options of the menu in final pages). Neitherdrinks with alcohol nor tips are included.

GRAN HOTEL POTRERILLOS

The history of Gran Hotel Potrerillos dates back to 1940 when its construction began, marked by a significant increase in public works, specifically in the tourism sector. Twenty-five years later it went through a period of instability that caused its closing. From 2005 the idea of re-opening the Gran Hotel Potrerillos re-emerged, giving it the touristic and cultural value it deserves. Facing their recovery after years of neglect, both in their building structure and in their surrounding environment, entailed the responsibility of incorporating new requirements according to current needs, without denaturing their character strongly incorporated in the collective memory of Mendoza

4:15 pm Departure from Hotel Potrerillos towards Olivícola Laur.

5:30 pm Factory guided tour and tasting in Laur.

OLIVÍCOLA LAUR

Founded in 1906 by Don Francisco Laur, a French immigrant, from the Loire region located in the south of France, who settled in Cruz de Piedra-Maipú in the early 1900s, pioneered the implantation of olive groves in the province of Mendoza as so also in the elaboration of extra virgin olive oil.

Today its doors are open to Tourism where visitors can learn the secrets of elaboration, its history and taste its products.

ANALYTICAL ATOMIC SPECTROMETRY AND THE ARROW OF TIME

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Time moves inexorably forward, second by second, year by year, decade by decade. In contrast, progress in science seems to move by jumps, with periods of slow progress interrupted by unexpected breakthroughs, which can lead to true paradigm shifts, new ways of thinking and behaving and a subsequent period of slower evolutionary advancements. Analytical atomic spectrometry follows this trend closely, beginning with the pathbreaking work of Bunsen and Kirchhoff until the current era. In this lecture, some of the breakthroughs in atomic spectrometry will be highlighted, along with a few vignettes about the scientists responsible for them. The current state of atomic spectrometry will then be assessed, and possible future advances suggested.

AUTOMATION OF ANALYTICAL METHODS USING FLOW TECHNIQUES

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Advances in Science and Technology have resulted in an increasing demand for control analyses and posed various challenges to analytical chemists such as the need to develop new methods exhibiting as much selectivity, sensitivity, sample and reagent economy, throughput, cost-effectiveness, simplicity and environmental friendliness as possible. Automation and miniaturization of solution-based analysis are essential to make them fast and efficient for routine and research tasks.

Flow techniques have undoubtedly aroused especial interest in relation to many other automatic methodologies of analysis. Ever since, Segmented Flow Analysis was developed by Skeggs in 1957, flow techniques have been in continuous evolution towards new developments. They have gained importance for clinical, industrial and environmental purposes as they allow highly reproducible fast determinations. There is no solid argument in favour of using any particular flow technique separately; rather, substantial advantages can be derived from their combination.

Thus, a description of the evolution of the main flow techniques, their online analytical determination modes, the separation and preconcentration methods, their hyphenation advantages and a critical comparison between them are presented in this short course.

MASS SPECTROMETRY-DRIVEN STUDIES OF METAL ION TRAFFICKING AND FUNCTION IN BACTERIA AND PLANTS

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Metals are usually present in biological samples at low concentrations (picomolar range), are generally associated with organic molecules, and occur distributed in a plethora of chemical forms with various properties (covalent or noncovalent species and a wide range of molecular weights). These species are often unstable (labile and prone to oxidation), which makes the analysis cumbersome. Whereas covalent species can be approached by canonical metabolomic procedures, the identification of noncovalent metal complexes at basal concentrations remains a challenge. De novo identification of previously unreported species and detection of minor species are therefore difficult to achieve.

The introduction of coupled methods combining a chromatographic separation step with element-specific detection, most often by ICP MS has been a decisive factor in the rapid progress of metal speciation analysis. The success of these methods depends critically on the chromatographic separation power and the purity of peaks used for quantification. Therefore, the approach shows considerable limitation in the analysis of complex matrices as well as in the cases when standards of the analytes are unavailable.

The ultimate proof of the species identity can be obtained by its molecular signature confirmed by the fine isotopic structure. It can be achieved if the separation is good enough to distinguish species with masses differing by one electron. Hence, the analytical challenge is shifted from the chromatographic peak capacity to the peak capacity in a mass spectrum. The detected feature is not the elemental but the molecular isotopic pattern of the analyte compound. Resolution powers down to a single electron mass can be obtained by Fourier transform MS, either using ion cyclotron resonance (ICR) or Orbitrap which has opened new horizons in speciation studies of metal-containing compounds at trace concentration levels.

The lecture discusses the opportunities offered by FT-MS approaches for the large scale speciation analysis. In particular, comprehensive approaches aiming the identification of a large number of metal or metalloid containing species in a single run (metallomics) in plants and bacteria will be discussed. Special attention will be given to a mechanistic interpretation of MS data sets using biochemistry and molecular biology approaches.

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THE USE OF MASS SPECTROMETRY FOR ENVIRONMENTAL AND CLINICAL PURPOSES: ADVANTAGES AND LIMITATIONS

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The usefulness of the analytical techniques for the investigation of environmental and clinical objects grown significantly over the last years. This is due mainly to the improved analytical performance and the ability to provide novel set of the information about the composition of the samples. Several techniques, those elemental as well as molecular mass spectrometry are consider to be very useful for the investigation of the molecular, elemental as well as isotopic composition of e.g. plants, animal tissues, bacterial strains, urine, blood or saliva.

In the last years a lot of attention was focused on the investigation of the process ongoing in plants and animal tissues towards understanding the specific mechanism, when they are exposed to the various environmental conditions, e.g. toxic substances or drugs. Several analytical scenarios, those involving plasma based instrumental techniques were tested towards investigation of the elements transport as well as its bio-transformation via examination of the presence of specific compounds in various tissues.

Several examples will be given to illustrate growing application areas. Commonly used determination of the elemental composition of tissues will be exemplified by the evaluation of the transport efficiency of selected elements in plants, all towards understanding its respond to the environmental conditions. Chromatographic techniques coupled to ICPMS were used to identify chemical forms of selected elements. The analytical scenario for speciation studies which was developed toward the evaluation of the bio-mechanism of plants to adapt for unfavorable environmental conditions will be exemplified by the investigation of the selenium and zinc.

Various chromatographic techniques coupled to molecular mass spectrometry facilitate to performed the structural analysis towards proteomic investigation. This was used for the investigation either the identification of selected compounds or for the examination of the mechanism of protein expression in living organism exposed to various stressing conditions.

Acknowledgements

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LIBS ANALYSIS OF INDIVIDUAL NANOPARTICLES: ATTOGRAM DETECTION LIMITS IN OPTICAL TRAPS

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Single particle characterization still constitutes a challenge to contemporary chemical analysis. Considerable effort worldwide is being devoted to conceive experimental strategies providing detection capabilities compatible with the extremely low mass of micro- and nano-particles and the ability to determine the chemical composition of the individual entities. The notion of using optical levitation to trap individual particles was demonstrated in the past century. Recently we have proposed the multielemental analysis of individual nanoparticles in optical traps using LIBS. In this lecture, the fundamentals of optical trapping of nanoparticles in air will be presented. The specific excitation and ionization processes leading to efficient optical detection and an analysis of the photon emission efficiency will be discussed. Finally, some limiting factors involved in our approach and prospective directions for improvement will be presented.

GREEN ANALYTICAL METHODS FOR DETERMINATION OF METALS AND NON-METALS BY MASS SPECTROMETRIC TECHNIQUES

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Trace element determination has been performed in order to provide information about the influence of elements in several fields such as nutrition, health, toxicology, environment and technology. In spite of the technological developments in instrumentation, especially for mass spectrometric techniques, samples are generally introduced in the equipment as a solution in routine analysis. Classical methods are generally used for sample digestion and involve the use of a relatively high volume of concentrated reagents and take a long time for digestion. The use of concentrated reagents may require a dilution step of digests before the analyte determination, which could compromise the limits of detection. In addition, some systems present limitations for complete digestion of many matrices. In this sense, even using methods based on microwave-assisted closed vessels, some drawbacks can occur and incomplete digestions are frequently reported. Regarding to halogens determination, they can also be lost in their unstable volatile compounds in acid medium. Nowadays, there is a trend for the development of green analytical methods, which require lower reagent consumption and waste generation, less analytical steps combined with high-efficiency digestion. The suitability of the digests with the determination techniques are also important. On this aspect, the main trends for sample preparation for a variety of matrices (such as cosmetics, food and biological samples) will be presented in this lecture for further metals and also non-metals determination by mass spectrometric techniques. The use of diluted solutions, using systems assisted by microwave and UV radiations or using combustion systems, will be covered. Therefore, recent applications will be presented showing the advantages of methods using diluted reagents for the determination of metals and non-metals using mass spectrometric techniques.

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CHALLENGES IN SAMPLE PREPARATION FOR TRACE ELEMENTS DETERMINATION USING MICROWAVE-INDUCED NITROGEN PLASMA OPTICAL EMISSION SPECTROMETRY

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Microwave induced plasma optical emission spectrometry (MIP OES) has been used since 1950s and since 2012 there exists a commercial instrument that uses nitrogen as plasma gas. This made the technique very attractive due to its low maintenance cost since nitrogen can be obtained from an air compressor connected to a N_2 generator.[1] Despite the advantage of being economical, the use of a nitrogen plasma makes it prone to generate matrix interferences because the temperature of the plasma is lower than that reached by an argon plasma. On the other hand, the sample introduction technology has evolved in such a way that it is possible to introduce samples with a total dissolved solids content up to 3%. Several multi-element analysis applications in complex samples will be presented and discussed.

One of the reasons that MIP OES is not a widely used technique is that it does not reach detection limits comparable to other techniques such as ICP OES or ETAAS when used in a conventional manner. However, when the hydride generation is coupled (HG), the detection limits improve significantly for elements such as As, Se and Pb. Determination of As in water, vegetables and urine was successfully performed achieving limits of detection comparable with ETAAS. In the case of Se, determinations can be carried out by HG-MIP OES with interesting figures of merit in water, beef and forage.

Among the hydride forming elements, lead volatilization by plumbane generation is not very extended for its determination.[2] The incidence of acid and nitrate concentration in plumbane generation was studied as a first attempt of the use of HG-MIP OES for Pb determination in water with a promising performance for trace analysis.

The instrumentation has improved considerably which makes this technique can overcome analytical and technical challenges that in the past were considered as limitations. In addition to the known benefits of low operating cost, by coupling hydride generation, low detection limits can be achieved, in some cases comparable with ETAAS.

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DOES THE USE OF HPLC-ICPMS ANSWER ALL QUESTIONS HOW THE ELEMENTS OCCUR IN A SAMPLE?

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The keynote lecture will introduce the term speciation and discusses how this differ from nanoparticles. It will however also clarify that not only speciation analysis is important to understand processes in the environment and biology but also in some cases, illustrated by mass balance approaches, that nanoparticle analysis is crucial. Recent studies from TESLA will be shown involving the accumulation of selenium, mercury and arsenic in pilot whales and it will show that the exposure of gaseous mercury does not necessarily be elemental mercury.

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MULTI-COLLECTOR ICP-MS HIGH-PRECISION ISOTOPIC ANALYSIS OF ESSENTIAL MINERAL ELEMENTS IN HEALTH & DISEASE

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Multi-collector ICP-mass spectrometry (MC-ICP-MS) is a dedicated tool for isotopic analysis offering a precision – down to 0.001% RSD under ideal conditions – sufficient to reveal natural variation in the isotopic composition of (trace) elements resulting from isotope fractionation. Compared to thermal ionization mass spectrometry (TIMS), the "gold" technique for this type of application, MC-ICP-MS shows a higher ionization efficiency, rendering the formation of M^+ ions also feasible for elements with an ionization energy exceeding 7-7.5 eV. Additionally, the ICP is a robust ion source, operated at atmospheric pressure, thus allowing straightforward sample introduction via solution nebulization. Finally, the technique shows a substantially higher sample throughput. These advantages have led to an extension of the application range, both in terms of elemental coverage and research contexts.

The A&MS research unit of Ghent University is exploring the use of high-precision isotopic analysis of essential mineral elements using MC-ICP-MS in a biomedical / clinical context[1]. The aims are exploring the diagnostic capabilities of this approach and obtaining an enhanced insight into the metabolism of these elements in health and disease.

Research carried out so far at A&MS-UGent has demonstrated that in patients with liver disease, the serum Cu isotopic composition is lighter (low δ65Cu) than in an age- and gender-matched reference population, while monitoring after successful liver transplantation showed a fast normalization. High-precision Fe isotopic analysis permitted a distinction between iron deficiency anemia and anemia as a result of altered production of erythropoietin (EPO) in the kidneys. Finally, the serum Mg isotopic composition is systematically affected in the case of type-I diabetes. Identification of the factors governing such changes in the isotopic composition of essential mineral elements is attempted by using in vitro cell-line experiments to evaluate the effect of single processes and in vivo experiments using murine (mouse) models.

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DIRECT ANALYSIS OF COMPLEX MATRICES: OVERCOMING THE INTERFERENCES BY HR-CS AAS

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Since our first publication based on slurry sampling, our research has been devoted to direct sampling analysis (DSA) using atomic absorption spectrometry (AAS)[1]. The motivation for choosing this kind of application was the difficulties that are encountered in the accurate determination of volatile trace elements in refractory matrices, the most notorious ones being the time and special equipment involved in complete digestion of these materials, and the risks of contamination and analyte loss involved in these procedures. In contrast, DSA, is fast, offers the highest sensitivity, as no dilution is involved, the risk of contamination and/or analyte loss is minimal and has a significant contribution to clean chemistry. In most publications, using conventional line source atomic absorption spectrometry (LS AAS), aqueous standards were reported as having been used for calibration after careful program optimization. Obviously, there are limitations, where even calibration with certified reference materials did not lead to accurate results. In these cases, the problem is typically associated with spectral interferences that cannot be corrected properly. Due to the limited information, by the systems available for conventional LS AAS, as we only can see the absorbance over time within the very small spectral interval emitted by the radiation source. And, if there is a problem with background correction, we can at maximum observe the artifact, but not the reason of the problem. However, using high-resolution continuum source atomic absorption spectrometry (HR-CS AAS), spectral interferences become visible owing to the display of the spectral environment at both sides of the analytical line at high resolution, which makes program optimization straightforward. Any spectrally continuous background absorption is eliminated automatically, and even rapidly changing background absorption does not cause any artifacts, as measurement and correction of background absorption are truly simultaneous. Any kind of fine-structured background can be eliminated by “subtracting” reference spectra using a least-squares algorithm. Aqueous standards are used for calibration in the majority published applications of DSA using HR-CS AAS. At least for samples that are difficult to be brought into solution and/or which are particularly affected by contamination problems, HR-CS AAS makes DSA very attractive. Several examples will be given where difficult elements, such as Pb or F, could be determined in complex samples, like fertilizer or road dust, using aqueous standards for calibration, i.e. without interference.

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AUTOMATIC RADIOCHEMICAL ANALYSIS USING FLOW TECHNIQUES

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Radiochemical analyses are increasingly demanded in routine laboratories for monitoring radionuclides from environmental samples, nuclear power plants, water treatment plants, nuclear medicine and industrial uses, among others. Thus, benefits of automation are of great interest in the radiochemical field. Features such as the minimization of sample and standards handling together with the decrease of waste generation are crucial, since the safety of the analyst is ensured and more environmentally friendly methods are developed. In this contribution, different strategies used for automating radiochemical analyses are discussed, encompassing fully and partially automated flow methodologies.[1,2] Thus, automated analytical protocols of extraction and preconcentration of radionuclides are presented, together with their coupling to radiometric detectors or inductively coupled plasma mass spectrometers (ICP-MS).

Acknowledgements
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FUNDAMENTAL ASPECTS OF CHEMICAL VAPOR GENERATION BY AQUEOUS BORANES

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Chemical Vapor Generation (CVG) by aqueous borane reagents has been employed as an analytical derivatization technique for the conversion of aqueous ions of several metals and semi-metals to their volatile derivatives. At present CVG is a popular technique and it has been widely employed in the determination and speciation of several elements at ultratrace level by atomic and mass spectrometry. More recently, starting since 2003, dedicated studies were developed with the aim to clarify the mechanisms governing the chemistry of CVG by using $NaBH_4$ (THB) and amine-boranes (ABs), NR_3BH_3 (R=H, alkyl) for aqueous phase derivatization.

In the recent years the studies on fundamental aspect of CVG served not only to reconcile CVG with the chemistry of aqueous boranes, but they also provide new evidence on the mechanism of hydrolysis of aqueous boranes which were unknown in the fundamental chemistry literature.[1,2]

This lecture presents and discusses some evidence indicating that the chemistry of aqueous boranes is essentially the chemistry of their hydrolysis products, which are generally referred as to ‘hydridoboron species’. The nature of the hydridoboron species formed during the hydrolysis of THB and ABs, is controlled by the reaction conditions employed in CVG (sample composition, pH, type of chemical reactor).

The evidence provided by CVG coupled with atomic or mass spectrometry combined with the study of the rate of dihydrogen evolution during borane hydrolysis can be useful for the implementation of improved CVG reaction systems, as well as they could stimulate investigations in the field of hydrogen storage where boranes play an important role.

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METHODOLOGICAL DEVELOPMENTS FOR ULTRATRACE AND LARGE-SCALE BIOLOGICAL SELENIUM SPECIATION ANALYSIS

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Selenium is a biologically important element with a very narrow toxicity/essentiality range. It can occur in several oxidation states and its incorporation into proteins (selenocysteine) in genetically encoded. It is efficiently metabolized by biological organisms producing hundreds of low molecular weight (less than 1000 Da) selenometabolites belonging to different chemical categories. The discrimination among the different chemical forms of selenium present in biological systems is essential to delineate its metabolomics pathways and has been addressed with different success rate more than two decades.[1,2]

HPLC with ICP MS detection has long been the principal tool for the selenium speciation studies.[1,2] In particular, it allowed the accurate determination of selenomethionine and selenocysteine, and the fingerprinting of distribution of selenometabolites. The selenium metabolome turned out to be a useful tool for the control of the reproducibility of the biotechnological processes used for the production of the most common Se supplement: Se-enriched yeast and is a marker of its manufacturer's origin.

The development of electrospray MS/MS for the identification of the Se peaks observed in HPLC-ICP MS led rapidly to the conclusion that the resolution and peak capacity of HPLC was by far insufficient to cope with the complexity of the selenium metabolome.[3] Electrospray MS/MS allowed the detection of over 200 metabolites over a concentration range starting two orders of magnitude below the ICP MS detection limits. It opened new perspectives for the detection of selenium species in complex biological matrices such as serum and soft tissues.

The lecture discusses electrospray mass spectrometry as a selenium specific detection in chromatography and compares it with ICP MS. In particular, the need for ultrahigh (1 000 000) resolution and high accuracy (< 1 ppm) and dedicated data mining strategies will be highlighted. New applications for the identification and quantification of low molecular selenium species in blood plasma and soft animal tissues will be discussed in the context of the animal physiology and nutrition.

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INTEGRATED APPROACH FOR THE CHEMICAL CHARACTERIZATION OF INDOOR $PM_{2.5}$ SUBORDINATED TO OXIDATIVE POTENTIAL ASSESSMENT

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Global climate change and increasing energy requirements have led to the development of energy-saving buildings typically characterized by low air-exchange rates. Given that people may spend more than 90% of their time in such enclosed spaces during the main activities of living, working and transportation, the investigation of indoor air quality (IAQ) in these micro-environments is of paramount importance. In the past decade, the number of chemical studies aiming at understanding the adverse effects of exposure to atmospheric particulate matter (PM) with an aerodynamic diameter smaller than 2.5 μm ($PM_{2.5}$) on human health at workplaces has increased substantially. The oxidative potential (OP) of PM, a measure of particle toxicology, can be estimated by acellular and *in vitro* cellular assays characterized by different sensitivities. The antioxidant depletion methods use dithiothreitol, ascorbic acid (AA) and reduced glutathione (GSH). There are many challenges in the multi-component analysis of indoor PM. Ideally, sampling solely during working hours would give useful information for exposure assessment. However, this limitation results in small mass collected on the filters. For indoor aerosol collection, sampling devices should be equipped with quiet oil-free pumps or sound reducing panels. Finally, concurrent parallel samplings on different filter materials should be avoided to ensure that unknown differential matrix effects are not encountered. Glass and quartz fiber filters (QFFs) have not often been used because of their high blank values for several elements. However, QFFs are suitable for PM EC/organic carbon (OC) determination, while cellulose ester, polycarbonate and Teflon filters should be discarded for such type of analysis due to their high carbon content. During the presentation, a robust, repeatable approach for the comprehensive assessment of indoor $PM_{2.5}$ characteristics of small sample masses will be presented. This entailed the assessment of acid and water extractable elemental and inorganic ionic compositions of indoor $PM_{2.5}$ through ICP-MS and ion chromatographic measurements, respectively, subordinated to concomitant OP and EC/OC analyses in the same loaded QFF.

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ARE NANOPARTICLES AND SPECIATION IMPORTANT IN THE OIL AND GAS INDUSTRY?

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Metals and metalloids are commonly occurring in petrochemical fractions. Most of the metals associated in crude oil[1]. But the gas and the condensate fraction is also often contaminated with mercury[2] and arsenic[3]. The lecture will give an overview where metals and metalloids occur and then focus on the mercury distribution in gas and gas condensates and where to install mercury removal units (MRUs) in a gas processing plant. The function of the MRUs are however optimised to absorb only elemental mercury; sometimes the MRUs do not work, because mercury occurs in a different molecular form. Speciation procedures for identifying organomercury compounds using GC-ICPMS and nanoparticles using field-flow fractionation (AF4-UV-MALS-ICPMS) and single particle (spICPMS) as well as TEM-EDX will illustrated the difficulty to determine the flux of mercury in a processing plant[4].

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THE USE OF LA-ICP-MS DATABASES TO CALCULATE LIKELIHOOD RATIOS IN THE FORENSIC EVALUATION OF GLASS EVIDENCE

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Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is the “gold standard” for the forensic analysis and comparison of glass evidence. A match criterion is used to compare the elemental profile of the known sample to a recovered sample and, if the glass samples are determined to be indistinguishable, this may be followed by the use of a verbal scale to report the examiner’s conclusion. This approach has several disadvantages: a fixed match criterion suffers from the “fall-off-the-cliff effect,” the rarity of an elemental profile is not taken into account, and the use of a verbal scale to assign a weight of evidence may be considered as subjective and can vary by examiner. An alternative approach includes the use of a continuous likelihood ratio that provides a quantitative measure of the significance of the evidence and accounts for the rarity of an elemental profile through the use of a glass database. In the present study, three glass databases were used to evaluate the performance of the likelihood ratio; the first database includes 420 automotive windshield samples, the second database includes 385 glass samples from casework and the third is a combination of the two. The multivariate kernel model was used for the calculation of the likelihood ratio. However, this model led to unreasonably large (or small) likelihood ratios. Thus, a calibration step, using the Pool Adjacent Violators (PAV) algorithm, was necessary in order to limit the likelihood ratio to reasonable values. The calibrated likelihood ratio led to improved false exclusion rates (< 1.0 %) and comparable false inclusion rates (< 1.0 %). In addition, the likelihood ratio limited the magnitude of the misleading evidence, providing only weak support for the incorrect hypothesis. Finally, most of the pairs found to be falsely included were explained by similarity of manufacturer of the glass source.

LIBS IMAGING: A BREAKTHROUGH IN MATERIAL AND BIOMEDICAL SCIENCES?

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The imaging capability of laser-induced breakdown spectroscopy (LIBS) has a high potential in various domains including biology, industry, geology and medicine. This approach can be distinguished by its ease in use, multi-elemental capability, detection of light elements, as well as operation at ambient conditions. This is furthermore the only all-optical technique providing space-resolved elemental information with ppm-scale sensitivity and µm-range resolution. These advantages, make LIBS imaging very attractive to be used in research laboratories for routine investigations.[1]

However, advanced technological solutions must be found for this application since elemental imaging requires high sensitivity, sharp spatial resolution, high speed of acquisition as well as the ability to process a huge quantity of data. In this presentation, we will summarize the recent progresses made in the Light and Matter Institute concerning the implementation of the LIBS imaging. Different examples will be shown with the aim of illustrating the specificities of LIBS among other elemental imaging approaches, such as the possibility to detect and image light elements, the coupling with optical and Raman imaging and the analysis of large-scale samples. Different perspectives and remaining challenges will be finally proposed.

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HOW SIMPLE CAN BE THE SAMPLE PREPARATION FOR FURTHER DETERMINATION OF HALOGENS IN ORGANIC MATRICES?

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The classical methods for sample decomposition and subsequent halogen determination by various analytical techniques (ion chromatography, atomic spectrometry, inductively coupled plasma mass spectrometry, etc.) involve the use of a relatively high volume of concentrated reagents and in general a long time for digestion making difficult achieving suitable throughput. In addition, the efficiency of digestion employing these systems has some limitations for many matrices, especially those having stable structures or high fat content. In this sense, even using methods based on microwave-heated closed vessels, some drawbacks may occur and incomplete decomposition and low analyte recoveries have been frequently reported. In this regard, the main trends for sample preparation for further halogen determination will be presented and the use of dilute solutions and the use of some alternatives systems will be discussed. Recent applications will be presented showing the advantages of methods using diluted reagents (combustion, MW-UV digestion, etc.) for halogen determination using atomic spectrometry and chromatography techniques.

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ELEMENTAL AND ISOTOPIC IMAGING AT NANOMETER SCALE USING NANO SECONDARY ION MASS SPECTROMETRY

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Trace element imaging in biological cells and tissues provide an important contribution to the investigation of biochemical functions, biosorption and bioaccumulation processes at cellular and subcellular level. Scientific progress in this field is directly related to new instrumental and methodological analytical developments. Nano secondary ion mass spectrometry (NanoSIMS) is an analytical technique which relies on the sputtering of ions from a solid surface by focused positive or negative primary ion beams and the subsequent analysis of the produced secondary ions by a mass spectrometer under high vacuum.[1] Thus, the NanoSIMS can be described as a scanning ion microprobe which can analyse at the sub-micrometre scale and produce elemental and isotopic images in 2D and 3D. NanoSIMS allows chemical imaging of a sample surface with lateral resolution below 50 nm combined with high sensitivity and thus it is perfectly suited to localize the distribution of chemical elements with high spatial resolution in biological samples. This lecture highlights advantages and challenges of elemental and isotopic NanoSIMS imaging at nanometer scale including different sample preparation strategies. Recent examples from our work will be presented from the biomedical and environmental field such as nanoparticles in lung cells, bacteria in macrophages, and essential and toxic metals in cells and tissues from environmental relevant organisms. Approaches for correlative imaging with other techniques will be briefly discussed.[2]

Acknowledgements

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HOW TO PUBLISH IN HIGH IMPACT JOURNALS

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This presentation will give an overview of scientific publishing, covering all the information you need to know about publishing your research. As well as providing an introduction to Royal Society of Chemistry we will discuss the peer-review process, how to write your paper, submission procedures, ethics and open access – along with an editor's top tips.

THE USE OF sp-ICP-MS FOR THE ANALYSIS OF TITANIUM DIOXIDE AND SILVER NANOPARTICLES

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The potential of Engineered nanomaterials (ENM) to improve the quality of life and to contribute to economic growth is today widely recognized. But, due to the fast expansion in the production of ENM and products incorporating these materials, there is a concern about their potential risks. Between these ENM metal-nanoparticles such as titanium dioxide nanoparticles (TiO_2 NPs) and silver nanoparticles (Ag NPs) are of a special concern because both NPs have many different applications. Although there are different analytical techniques adequate for the metal NPs characterization, quantitative information can only be assessed with techniques that use atomic detectors, such as ICP-MS, GF-AAS or ICP-OES. But, these techniques do not distinguish between dissolved species and metal nanoparticles. Metallic speciation can be performed by coupling atomic detectors with separation techniques, but in order to simplified the NPs analysis, the use of the ICP-MS in the mode single particle-ICP-MS is a promising technique for analysing complex samples that contain metal NPs and the corresponding ionic form, without a previous separation step. The possibilities of sp-ICP-MS using modern instrumentation allowing short dwell times for data acquisition has been investigated for different type of samples. With this technique is possible to obtain information about the NPs concentration and about their size distributions.

In this talk some examples of metal NPs analysis in different types of samples will be discussed. TiO_2 NPs and Ag NPs (NPs concentration and size distribution) has been studied in different types of mollusks samples after applying ultrasound assisted enzymatic hydrolysis of NPs. Moreover, the same edible mollusks have been subjected to an in vitro digestion procedure for TiO_2 NPs and Ag NPs for human risk evaluation. These NPs were also studied directly in human urine samples. On the other hand, several extraction methods using aqueous or glycerol mediums were also developed for isolating Ag NPs from textiles, samples and cosmetic products respectively. The development methods were applied for the analysis of real samples.

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LASER-INDUCED ATOMIC FLUORESCENCE FOR THE DEVELOPMENT OF HYDRIDE ATOMIZERS AND FOR ULTRATRACE DETERMINATION OF HYDRIDE FORMING ELEMENTS

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Hydride generation (HG) is ideally suited for trace and ultratrace element and speciation analysis of hydride forming elements since it involves analyte separation from the sample matrix and its high efficiency transfer from the sample to the spectrometer. HG coupled to the relatively low cost and simple detectors, atomic absorption (AA) or atomic fluorescence (AF) spectrometer, can thus serve as an alternative to the conventional approaches based on the liquid phase sampling inductively coupled plasma mass spectrometry. However, the final step of the whole procedure, hydride atomization, has to be optimized. The best way of doing that is to establish how the relevant operation parameters influence the distribution of hydrogen radicals (H radicals), temperature and analyte free atoms in hydride atomizers. The miniature diffusion flame (MDF) is a standard hydride atomizer for AF but it can be very useful also for AA spectrometry. MDF provides a very efficient analyte atomization. The other atomizer for AF, flame-in-gas-shield (FIGS), employs a hydrogen-oxygen microflame, burning at the top of a capillary, shielded by Ar flow. Compared to MDF, FIGS is more flexible and it offers better sensitivity and a higher potential in terms of miniaturization.

The aim of the present work was to quantify the distributions of all the three fundamental parameters (H radicals, temperature and analyte free atoms) in MDF and FIGS atomizers under relevant experimental conditions. H radical distribution was determined by two photon absorption laser induced fluorescence (TALIF). TALIF was also employed to derive temperature from the Gauss broadening of two-photon absorption Lβ line. Rayleigh scattering of the laser beam was tested as an additional approach to find temperature distribution. Laser-induced fluorescence (LIF) was used to derive spatial maps of absolute concentrations of analyte free atoms. Pb was employed as an analyte for the preliminary experiments. Pb atom concentration resulting from LIF measurements was reasonably close to that estimated from analyte supply from hydride generator.

The quantification of the distributions of all the three fundamental parameters together with a numerical model of the gas dynamics and heat transfer within the atomizer observation volume yield a complete information required for optimization of both studied atomizers. Outlooks of this research to further investigation of other hydride atomizers will be outlined and emerging possibilities of absolute analysis will be discussed.

Acknowledgements

The support of the Czech Science Foundation (project 17-04329S), Czech Academy of Sciences (Institutional support RVO:68081715) and Charles University (project SVV260440) is gratefully acknowledged.

SPECIOMICS: INTEGRATING BIOANALYTICAL INFORMATION THROUGH MASS SPECTROMETRY

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While the speciation analysis applied to analytical chemistry is defined as the analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample,[1] omics refers to the collective technologies, such as genomics, proteomics, metabolomics, metallomics, among others, which are used to explore the roles, relationship, and actions of various types of molecules that make up the cells of an organism,[2] The Speciome, adapted from biological area,[3] is then coined due to the synergism of both chemical speciation and omics, and defined as the entirety of the chemical species evaluated through omics strategies, and the Speciomics, the study/evaluation of chemical species applied to omics studies. In order to exemplify this new concept, some examples involving plant science, humor diseases, and forensic are presented[4] for contextualizing this proposal. As a conclusion, this concept is then presented as the “umbrella” containing all omics approaches devoted to speciation analysis.

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Sb(III) vs. As(III): WHO REPRESENTS A GREATER ECOTOXICOLOGICAL RISK?

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As_2O_3 has been classified as a class 1 carcinogen by IARC, while in the case of Sb_2O_3, it is classified as list 2 because there is no evidence of its effects in humans. Antimony shares the redox chemistry of As, sharing its same oxidation states. Inorganic Sb(III) shares structural similarities with As(III) being both triangular base pyramids. However, the solubility Sb_2O_3 is extremely low compared with As_2O_3 which has led to suggest that the availability of this compound is low from a trophic point of view.

On the other hand Sb(III) is highly unstable in the presence of oxygen. This has generated skepticism about the reliability of the Sb(III) eco-toxicity experiments leading to the claim that these are biased or at least with underestimated effects. Does Sb_2O_3 have low toxicity or its classification is only an underestimation of its effects?.

There is lack of reliable analytical methods that work with adequate standards of Sb(III) and with a proper control of its redox stability both in the toxicity experiments or in the analytical methods, which hamper more robust conclusions.

Our research group has worked both in the development of analytical methods and also in the ecotoxicology of the inorganic species of As and Sb with special emphasis on the use of adequate standards and the control of the oxidation of Sb(III). We have demonstrated that Sb(III) must be stabilized by the use of complexing agents to avoid biases and false negatives. In addition, we demonstrated that Sb(V) partially reduced to Sb(III) generating redox imbalances in the chemistry of erythrocytes and macrophages[1]. On the other hand, our results show that Sb(III) as well as As (III) are both capable of generating renal cell deformations[2] decreasing protein mobility in similar proportions. However, the complexes of Sb(III) with proteins like the BSA are extremely labile for chromatographic methods[3].

We believe that the ecotoxicity of Sb(III) has not been underestimated in a trophic sense. However, considering that a non-trophic pathway through particulate material is highly plausible, the evidences of effects on protein mobility and cell morphology are a good start to thinking about to put both species at the same ecotoxicological risk.

Acknowledgements
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HYDRIDE TRAPPING ON NANOMATERIALS. TUNABLE NANOPARTICLES STUDIES TOWARDS A NOVEL HYDRIDE GENERATION APPROACH

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Gaseous sample introduction into atomic spectrometric instruments is always aspiring, since it represents many advantages compared to conventional liquid sample introduction techniques. Interactions between hydrides and nanomaterials have been studied for their preconcentration, as well as generation. As and Se hydrides were trapped on oxidized multiwall carbon nanotubes (oxMWCNTs) in a gas-solid system.[1, 2] The system avoids sophisticated temperature controlled traps and cloggings, common in liquid-solid systems involving nanomaterials. In addition elution volumes were reduced and sensitivity was improved. Recently hybrid nanoparticles (HNPs) of oxMWCNTs-TiO_2 were introduced for Sb hydride trapping. HNPs possess an increased number of new binding sites that improves hydrides adsorption kinetic on their surface.[3]

The modification of NPs provides them with new characteristics for different applications. Palladium-decorated TiO_2 NPs under UV light radiation (UVA 315-400 nm) can be tuned to adsorb Bi and Sb ions upon ethanol oxidation. Sb adsorption is faster in tuned NPs compared to TiO_2 NPs without modification. Tunable NPs are versatile catalysts and under the same conditions they can generate H_2.[4] Hydrogen generation by tunable NPs opens a path for hydride generation (HG) of different elements as shown in a recent review.[5] Variations of decorations and irradiation under different UV wavelengths extends applications of tunable NPs to the analysis of a wide range of detectable hydride forming elements.

The introduction of tunable NPs to HG encompass Green Chemistry statements since hazard reagents are not used and solvents like methanol are decomposed during HG. Low amounts of tuned NPs are necessary for HG thanks to their elevated specific surface. This point also favors miniaturization with decreased use of reagents and minimal waste generation. NPs can also be re recycled to be reused.

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PORTABILITY OF EDXRF SPECTROMETERS: CHALLENGES AND PERSPECTIVES

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Portable Energy Dispersive X Ray (EDXRF) spectrometers have gained protagonism in the past 30 years for the fast, *in situ,* multielemental analysis of samples. With the advent of low-power x-ray tubes and peltier-cooled detectors, the miniaturization of EDXRF from laboratory-built to commercially available hand-held systems improved.[1]

In this talk, a brief summary of the evolution of portable EDXRF systems will presented and the advantages, challenges and misconceptions will be discussed. Several case studies, with applications to Cultural Heritage, forensic and environmental studies will be presented as illustration of the capabilities of these systems for qualitative and quantitative atomic spectrometry.[2-4]

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POSTER PRESENTATIONS

E-POSTERS - PROGRAMME

Screen Number	Monday October 7	Tuesday October 8	Thursday October 10	Friday October 11
Coordinators: Maurico Llaver - Leticia Escudero				
#1	14:00 AAS01	14:00 AAS09	14:00 CVG01	14:00 MS21
	14:30 AAS02	14:30 CS01	14:30 CVG03	14:30 MS22
	15:00 SP01	15:00	15:00 AES07	15:00 SMet01
Coordinator: William Boschetti				
#2	14:00 AAS03	14:00 AAS10	14:00 CVG02	14:00 MS23
	14:30 AAS04	14:30 AAS16	14:30 XR06	14:30 MS24
	15:00 SP02	15:00 MS01	15:00 AES08	15:00 SMet02
Coordinator: Natalia Oviedo				
#3	14:00 AAS05	14:00 AAS11	14:00 CVG04	14:00 MS25
	14:30 AAS06	14:30 MS02	14:30 CVG05	14:30 SP16
	15:00 SP03	15:00 MS03	15:00 AES09	15:00 SMet03
Coordinator: Emiliano Fiorentini				
#4	14:00 AAS07	14:00 AAS12	14:00 CVG06	14:00 MS26
	14:30 AAS08	14:30 MS04	14:30 XR07	14:30 MS28
	15:00 SP04	15:00 MS05	15:00 AES10	15:00 SMet04
Coordinator: Mauana Schneider				
#5	14:00 AES01	14:00 AAS13	14:00 CVG07	14:00 MS27
	14:30 AES02	14:30 MS06	14:30 CVG08	14:30 MS29
	15:00 SP05	15:00 MS07	15:00 AES11	15:00 SMet05
Coordinator: Pamela Quintas				
#6	14:00 AES03	14:00 AAS14	14:00 MS11	14:00 ChemS01
	14:30 AES04	14:30 MS08	14:30 MS12	14:30 SP17
	15:00 SP06	15:00 MS09	15:00 XR10	15:00 SMet06
Coordinator: Pedro Moreau				
#7	14:00 AES05	14:00 AAS15	14:00 MS13	14:00 ChemS2
	14:30 AES06	14:30 MS10	14:30 MS14	14:30 SP18
	15:00 SP07	15:00 SP08	15:00	15:00 SMet07
Coordinator: Florencia Jofré				
#8	14:00 XR01	14:00 AAS17	14:00 MS15	14:00 ChemS3
	14:30 XR02	14:30 SP09	14:30 MS16	14:30 SP19
	15:00 XR03	15:00 SP10	15:00	15:00 SMet08
Coordinator: Brenda Canizo				
#9	14:00 XR04	14:00 SP11	14:00 MS17	14:00 ChemS04
	14:30 XR05	14:30 SP12	14:30 MS18	14:30 SP20
	15:00	15:00 SP13	15:00 MS20	15:00 ChemS06
Coordinator: Annaly Cruz-Sotolongo				
#10	14:00 LIBS01	14:00 SP14	14:00 MS19	14:00 ChemS05
	14:30 LIBS02	14:30 SP15	14:30 XR08	14:30 SP21
	15:00 LIBS03	15:00	15:00 XR09	15:00

ATOMIC ABSORPTION SPECTROMETRY – AAS

AAS01	A RAPID AND ENVIRONMENTALLY FRIENDLY METHOD BASED ON DISPOSIBLE PIPETTE EXTRACTION (DPX) AND NATURAL ADSORBENTS FOR METALIC IONS EXTRACTION *Vanessa N. Alves, Marina M. Ferreira*
AAS02	MICROSAMPLING DEVICES FOR THE DIRECT AND FAST DETERMINATION OF Hg IN BLOOD AND URINE VIA ATOMIC ABSORPTION SPECTROMETRY *Flávio V. Nakadi, Raúl Garde, Márcia A. M. S. da Veiga, Julio Cruces, Martín Resano*
AAS03	THE USE OF H_2SO_4 AS CHEMICAL MODIFIER FOR SIMULTANEOUS DETERMINATION OF Cr AND Fe IN DIETARY SUPPLEMENTS BY HR-CS GF AAS *Thais D. Maciel, Morgana B. Dessuy, Maria Goreti R. Vale, William Boschetti*
AAS04	SEQUENTIAL AND SIMULTANEOUS DETERMINATION OF Cd, Ni AND Fe IN SEED SAMPLES BY HR-CS GF AAS USING DIRECT SOLID SAMPLE ANALYSIS *Morgana B. Dessuy, Natália K. V. dos Santos, Leandro dos Santos, Maria G. R. Vale*
AAS05	SIMULTANEOUS DETERMINATION OF Ni AND Fe IN WATER OF OIL SHALE BY HR-CS GF AAS *Adenilde S. dos Passos, Eliseu S. Menger, Suenni P. Ferreira, Maria Goreti R. Vale*
AAS06	DETERMINATION OF YTTERBIUM IN URBAN DUST EMPLOYING SLURRY SAMPLING BY HIGH-RESOLUTION CONTINUUM SOURCE GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY *Sidimar S. Oliveira, Vaniele S. Ribeiro, Tarcísio S. Almeida, Rennan G. O. Araujo*
AAS07	THE REUTILIZATION OF DOMESTIC BIO-WASTES FOR THALLIUM REMEDIATION *Pamela Y. Quintas, Guilherme L. Dotto, Leticia B. Escudero*

AAS08

PHOTOCATALYTIC PRECONCENTRATION OF Bi ON TiO_2 NANOPARTICLES AND THEIR DETERMINATION BY ETAAS

Ariel Maratta, Gastón Villafañe, Pablo Pacheco, Rodolfo Lara, Vanesa Bazán

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AAS09

TOTAL MERCURY DETERMINATION IN THREE DIFFERENT MATRIX IN AN INTERNATIONAL COMPARISON

Osvaldo Acosta, Maximiliano Peralta, Mariano Stratico y Mabel Puelles

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AAS10

LEVELS OF Cd, Pb, As AND Hg IN SOME COMMERCIALLY AVAILABLE MEDICINAL HERBS FROM TUCUMÁN, ARGENTINE

Gabriela Juárez, Carla M. Rubio, Pilar Balverdi, Patricia F. Marchisio, Raquel Dellmans, Silvina Gómez, María L. Chayle, Adriana M. Sales

AAS11

GAS-LIQUID SEPARATION CELLS IN FI-CVG-AAS: DESIGN AND OPTIMIZATION FOR SAMPLE INTRODUCTION

Facundo Beraldo Victorica, Ezequiel M. Morzan, Mabel B. Tudino

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AAS12

IN SITU SOLID PHASE EXTRACTION METHODOLOGY FOR PRE-CONCENTRATION AND DETERMINATION OF Cr(III) IN INFUSIONS OF MEDICINAL PLANTS

Lincoln L. Romualdo, Aléssa G. Siqueira, Vanessa N. Alves

AAS13

THE USE OF HIGH RESOLUTION GARPHITE FURNACE MOLECULAR ABSORPTION SPECTROMETRY (HR -MAS) FOR TOTAL FLUORINE DETERMINATION IN EXTRACTABLE

Abdullah Akhdhar, Mauana Schneider, Alice Orme, Lara Schultes, Andrea Raab, Eva M. Krupp, Jonathan P. Benskin, Bernhard Welz, Jörg Feldmann

AAS14	TOTAL MERCURY AND MERCURY THERMOSPECIES IN SOUTH AFRICAN COAL *Mpho W. Mathebula, Nikolai Panichev, Khakhathi L. Mandiwana*
AAS15	DEVELOPMENT OF SULFUR DETERMINATION METHOD IN HUMAN HAIR BY HIGH-RESOLUTION CONTINUUM SOURCE GRAPHITE FURNACE MOLECULAR ABSORPTION *Vitor Cornaqui P. Marrocos, Tatiana D. Saint'Pierre, Fabio G. Lepri*
AAS16	VALIDATION OF A METHODOLOGY FOR DETECTING LEAD IN CITRUS FRUITS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY *Gabriela A. Juárez, Raquel Dellmans, Evelina Valdivieso, José Barrionuevo, Norma Kamiya, Marcelo Ruiz*
AAS17	APPLICATION OF MAGNETIC NANOPARTICLES TO REMOVE ARSENIC FROM MOLYBDENUM CONCENTRATES *Gastón Villafañe, Ariel Maratta, Rodolfo Lara, Vanesa Bazán*

ATOMIC FLUORESCENCE/OPTICAL EMISSION SPECTROMETRY - AES

AES01	ELECTROLITES DETERMINATION IN HUMAN SERUM USING INDUCTIVELY COUPLED PLASMA - OPTICAL EMISSION SPECTROMETRY (ICP-OES) *Hernan Lozano, Mabel Puelles*
AES02	METAL CONCENTRATIONS IN SEDIMENTS FROM BEACHES OF GREATER VITORIA AREA, BRAZIL *Rafael Mantovaneli, Bruna M. Dalfior, Geisamanda P. B. Athayde, Jacqueline Albino, Maria T. W. D. Carneiro*
AES03	DETERMINATION OF MACRO AND MICROELEMENTS USING MIP OES IN URUGUAYAN SWEET PEPPER AND STRAWBERRIES *Marcelo Belluzzi, Valery Bühl, Sebastián Dini, Facundo Ibáñez, Mariela Pistón*
AES04	DETERMINATION OF TOTAL ARSENIC IN VEGETABLES USING HYDRIDE GENERATION- MICROWAVE INDUCED NITROGEN PLASMA ATOMIC EMISSION SPECTROMETRY (HG-MIPOES) *Florencia Tissot, Mónica Pereira, Ignacio Machado, Sebastián Dini, Valery Bühl, Marcelo Belluzzi, Facundo Ibáñez, Mariela Pistón*
AES05	DETERMINATION OF MERCURY IN FRESH FISH OF THE RIVERS FROM RORAIMA- BRAZIL USING ATOMIC FLUORESCENCE SPECTROMETRY *Gabrielly V. Mesquita, Victor Georges S. Elgamal, Klaiani B. Fontana, Sylvio R. B. Ferreira, Ivanise M. Rizzatti, Tatiane de A. Maranhão*

AES06	MICROWAVE INDUCED PLASMA OPTICAL EMISSION CAPABILITIES FOR THE DETERMINATION OF TRACE ELEMENTS IN NATURAL WATERS AFTER COPRECIPITATION WITH IRON *Luiza G. Santos, Anderson A. Rocha, Wendy S. Rojeno, Tatiana Saint'Pierre and Christiane B. Duyck*
AES07	APPLICATION OF A LAB-MADE TERNARY Fe-Cr-Al COIL VAPORIZER COUPLED TO ICP OES FOR BORON DETERMINATION IN POWDERED FOOD AFTER THE SAMPLE PREPARATION IN TMAH *Paulo S. de O Cezário, Aderval S. Luna, Jefferson S. de Gois*
AES08	ANALYSIS OF ELEMENTS IN DIFFERENT LUNG TISSUES USING ICPOES AND ICPMS AFTER MICROWAVE DIGESTION *Ciro Márquez, Mayra E. Alemille, Carlos Díaz, Raquel Huerte*
AES09	USE OF MODIFIED CELLULOSE FOR SEPARATION AND PRECONCENTRATION OF RARE EARTH ELEMENTS FROM WATER FOR DETERMINATION BY ICP OES *Lucas E. O. Porto, Gabriel G. de Carvalho, Denise F. S. Petri, Pedro V. Oliveira*
AES10	HANGING DROP CATHODE ATMOSPHERIC PRESSURE GLOW DISCHARGE AS A NEW SAMPLE INTRODUCTION SYSTEM IN INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION *Krzysztof Świderski, Maja We³na, Krzysztof Grêda, Pawe³ Pohl, Piotr Jamróz*
AES11	FUGITIVE EMISSIONS ANALYSIS FROM INDUSTRIAL IN THE URBAN PM_{10} USING X-RAY FLUORESCENCE SPECTROMETRY *Lincoln L. Romualdo, Marcos E. G. do Carmo, Nara L. S. Sousa*

CHEMOMETRICS IN SPECTROMETRY - ChemS

ChemS01	ULTRASOUND ASSISTED EXTRACTION FOR DETERMINATION OF INORGANIC CONSTITUENTS IN FLAVORING ESSENCE SAMPLES EMPLOYING ICP OES AND FRACTIONARY FACTORIAL DESIGN *Samir H. dos Santos, Carlos Alexandre B. Garcia, Sarah Adriana R. Soares, Rennan Geovanny O. Araujo, Silvânio Silvério L. Costa*
ChemS02	CLASSIFICATION OF MENDOZA (ARGENTINA) RED WINES BY ICP-MS MULTI-ELEMENT ANALYSIS AND MULTIVARIATE STATISTIC TECHNIQUES *Brenda V. Canizo, Lucila Brusa, Mirna Sigrist, Roberto G. Pellerano and Rodolfo G. Wuilloud*
ChemS03	BORON AND COBALT QUANTIFICATION IN INCOLOY BY ICP-OES USING FIRST-ORDER MULTIVARIATE CALIBRATION *Damián Piuselli, Silvana Martin, Jorge Magallanes, Diego Onna, Ezequiel Morzan*
ChemS04	CHEMOMETRICS ANALYSIS OF XRF-QUANTIFIED INORGANITY MATTER IN SAMPLES FROM BRANCHES OF ANIBA ROSAEODORA DUCKE FROM DIFFERENT REGIONS *Lucas G. C. de Souza, Paulo de T. B. Sampaio, Cláudia C. Silva*
ChemS05	OPTIMIZATION OF VOLCANIC ASH LEACHING METHODOLOGIES *Nicolas K. Vallejo Azar, Sabrina I. Permigiani, Paul E. Hasuoka, Raúl A. Gil, Luis A. Escudero*
ChemS06	GEOGRAPHICAL ORIGIN IDENTIFICATION OF BLACK PEPPER BY ICP-MS AND ICP OES *Luiza V. Vieira, Maiara Krause, Otávio A. Heringer, Geisamanda P. Brandão, Ricardo M. Kuster, Maria Tereza W. D. Carneiro*

COMPUTATIONAL SPECTROSCOPY IMAGING TECHNIQUES - CS

CS01	DIFFUSE REFLECTANCE SPECTROSCOPY AND HYPERSPECTRAL IMAGING FOR CHARACTERIZATION OF MINERAL SPECIES IN COPPER CONCENTRATES *Claudio Sandoval Muñoz, Martín Bravo, Rodrigo Fuentes, Jonathan Álvarez, Pablo Cohelo, Marizú Velásquez, Ashwin Kumar Myalkalwar, Daniel Sbarbaro, Sergio Torres, Jorge Yáñez*

CHEMICAL VAPOR GENERATION – CVG

CVG01	MULTIVARIATE OPTIMIZATION OF PHOTOCHEMICAL VAPOR GENERATION FOR FAST AND LOW-COST DETERMINATION OF MERCURY BY CVAAS IN FOOD SAMPLES *Nilvan A. Silva, Tamyris A. Gondim, Nandressa F. Nobre, Wladiana O. Matos, Gisele S. Lopes*
CVG02	SELENIUM DETERMINATION USING HG-MIP OES IN BEEF AND LIVESTOCK FEED *Javier Silva, Marcelo Belluzzi, Fiorella Iaquinta, Analía Suárez, Florencia Cora Jofré, Marianela Savio, Mariela Pistón*
CVG03	MULTIVARIATE OPTIMIZATION OF PHOTOCHEMICAL VAPOR GENERATION FOR DETERMINATION OF COBALT IN BLOOD PLASMA BY ICP-OES *Tamyris A. Gondim, Nilvan A. Silva, Nandressa F. Nobre, Wladiana O. Matos, Gisele S. Lopes*
CVG04	CHEMICAL VAPOR GENERATION OF CADMIUM FOR ANALYTICAL ATOMIC SPECTROMETRY *Linda Sagapova, Milan Svoboda, Stanislav Musil, Jan Kratzer*
CVG05	PHOTOCHEMICAL VAPOR GENERATION OF COBALT WITH AAS AND ICP-MS DETECTION *Jaromír Vyhnanovský, Stanislav Musil*
CVG06	IN ATOMIZER TRAPPING OF SELENIUM HYDRIDE IN GOLD MODIFIED QUARTZ TUBES *Aline Fernandes de Oliveira, Ignacio Machado, Dominik Vanì k, Milan Svoboda, Stanislav Musil, Jiǿ Dì dina, Jan Kratzer*

CVG07	PLUMBANE DETERMINATION BY HG-MIP OES: STUDY OF THE VARIABLES AFFECTING ITS GENERATION, INTERFERENCE ANALYSES AND APPLICATION *Alicia Mollo, Florencia Cora Jofré, Alexandra Sixto, Mariela Pistón, Marianela Savio*
CVG08	ARSENIC DETERMINATION IN URINE USING HG-MIP OES: A TOXICOLOGYCAL APPLICATION *Valery Bühl, Paulina Pizzorno, Lucía Falchi, Florencia Cora Jofré, Marianela Savio, Nelly Mañay, Mariela Pistón*

LASER-INDUCED BREAKDOWN SPECTROSCOPY – LIBS

LIBS01	DETECTION OF HONEY ADULTERATION BY LASER-INDUCED BREAKDOWN SPECTROSCOPY ASSISTED BY SPARK DISCHARGE (SD-LIBS) ASSOCIATED WITH CHEMOMETRICS. *Maurílio G. Nespeca, Alan L. Vieira, José Anchieta Gomes Neto, Dário Santos Júnior, Edilene C. Ferreira*
LIBS02	DETERMINATION OF NITROGEN IN BIOCHAR FERTILIZERS USING LASER-INDUCED BREAKDOWN SPECTROSCOPY *Samia R. Dib, Maurílio G. Nespeca, Dário Santos Júnior, Clovis A. Ribeiro, Marisa S. Crespi, José Anchieta G. Neto, Edilene C. Ferreira*
LIBS03	MULTI-ELEMENTAL QUANTIFICATION IN COPPER CONCENTRATE ORES BY LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR CUSTOMS VALUATION OF EXPORTS *Marizú Velásquez, Martin D. Bravo, Claudio Sandoval Muñoz, Jonathan Álvarez, Rodrigo A. Fuentes, Daniel Sbarbaro, Danny Luarte, Jorge C. Yáñez*

MASS SPECTROMETRY – MS

MS01	PLATINUM GROUP ELEMENT DETERMINATION BY ICP-MS: A STUDY OF METALS AND ACID MEDIUM INTERFERENCES *Gabriel T. Druzian, Mariele S. Nascimento, Rodrigo C. Bolzan, Rochele S. Picoloto, Jussiane S. Silva, Erico M. M. Flores*
MS02	BROMINE AND CHLORINE ISOTOPE RATIO MEASUREMENTS USING MC-ICP-MS WITH A CONVENTIONAL SAMPLE INTRODUCTION SYSTEM *Jefferson S. de Gois, Paul Vallelonga, Daniel L. G. Borges, Frank Vanhaecke*
MS03	VALUE ASSIGNMENT OF REFERENCE MATERIAL FOR QUINOA FLOUR *Osvaldo Acosta, Maximiliano Peralta, Mariano Stratico y Mabel Puelles*
MS04	ETHANOL-ASSISTED PHOTOCHEMICAL VAPOR GENERATION FOR THE DETERMINATION OF IODINE IN ALCOHOLIC BEVERAGES BY ICP-MS *Richard M. Oliveira, Bárbara S. Soares, Daniel L. G. Borges*
MS05	PLATINUM-BASED ATTENUATION OF THE NITRATE INTERFERENCE ON THE PHOTOCHEMICAL VAPOR GENERATION OF HALOGENS FROM PETROCHEMICAL AND BIOLOGICAL SAMPLES PRIOR TO ICP-MS DETECTION *Richard M. Oliveira, Bárbara S. Soares, Daniel L. G. Borges*
MS06	ANALYSIS OF METALS IN NAPHTHA BY PQMS® ACCORDINGLY TO ASTM D8110-17 *Rui Santos*

MS13	WASHING EFFECTS ON TRACE ELEMENTS CONCENTRATION IN URBAN GARDEN PRODUCED LETTUCE (Lactuca Sativa L.) *Camila N. Lange, Lucilena R. Monteiro, Suzana das Neves Santos, Bruna M. Freire, Tatiane A. Jesus, Bruno L. Batista*
MS14	ICP-MS DETERMINATION OF METALS AND METALLOIDS IN RICE AND RICE-BASED PRODUCTS *Agustín Londonio, Ezequiel Morzán, Patricia Smichowski*
MS15	STRATEGIES FOR THE DETERMINATION OF MERCURY IN EYE SHADOW: EVALUATION OF A SIMPLE ELECTROTHERMAL VAPORIZATION SYSTEM COUPLED TO ICP-MS *Jussiane S. Silva, Alessandra S. Henn, Rodrigo C. Bolzan, Paola A. Mello, Valderi L. Dressler, Érico M. M. Flores*
MS16	GUNSHOT RESIDUE ANALYSIS USING LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY IMAGING *Isabela M. de S. Ferreira, Ricardo E. Santelli, Ladário da Silva, Bernardo F. Braz*
MS17	TOXIC ELEMENTS IN SEDIMENTS OF THE SANTOS- SÃO VICENTE ESTUARINE SYSTEM *Thais P. Gabulho, Roberto C. F. Barsotti Patricia C. C. Ladeira, Ítalo B. Castro, Heloisa F. Maltez*
MS18	METAL ELEMENTS IN LIVER AND MUSCLE OF TUNA BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY *Roberto C. F. Barsotti, Patricia C. C. Ladeira, Ítalo B. Castro, Heloisa F. Maltez*

MS07	ISOTOPIC ANALYSIS OF URANIUM IN A SINGLE PARTICLE FOR THE IMPLEMENTATION OF THE FISSION TRACK - THERMAL IONIZATION MASS SPECTROMETRY TECHNIQUE *Lisandro M. Ronconi, Fernando N. Grau, Ricardo N. Garavaglia, Mauricio A. Fernández*
MS08	MATRIX-MATCHING CALIBRATION APPROACH TO QUANTIFY Cd AND Pb IN TREE-RINGS BY LA-ICP-MS *Rafael Magnusson, Pedro S. Moreau, Renata S. Amais, Marco A. Z. Arruda*
MS09	COMPARISONOF THE BIOACCESSIBILITY OF MINERALS IN WHOLE COW'S MILK AND SOY MILK USING AN IN VITRO GASTROINTESTINAL DIGESTION METHOD AND DRC-ICP-MS *Isis S. Permigiani, Maria V. Principe, Cecilia Della Vedova, Cristian Bazan, Marcos Kaplan, Raúl Gil*
MS10	CORRELATION OF CONCOMITANT ELEMENTS OF ARSENIC IN EXPOSURE BIOMARKERS *Paola A. Cuello, Claudia M. Inga, Carolina A. Hernandez, Yanina G. Giusto, Raúl G. Badini*
MS11	Fe, Cu AND Zn ANALYSIS BY ICP-DRC-MS APPLIED TO IN VITRO BIOACCESSIBILITY STUDIES OF SPIRULINA DIETARY SUPPLEMENTS WITH DIFFERENT EXCIPIENTS COMPOSITION *María V. Principe, Isis S. Permigiani, María C. Della Vedova, Elisa Petenatti, Pablo Pacheco, Raúl A. Gil*
MS12	USE OF MASS SPECTROMETRY IN THE DETERMINATION OF METALS IN PARTICULATE MATTER FOR THE CONTROL OF ATMOSPHERIC POLLUTION (CDTN/CNEN) *Helena E. Leonhardt Palmieri, Ricardo G. Passos*

MS19

LEAD ISOTOPIC COMPOSITION BY THERMAL IONIZATION MASS SPECTROMETRYFOR PROVENANCE STUDIES IN ARCHEOLOGY

Marta A. Bavio, Mauricio A. Fernández, Erica N. Zubillaga, Nicolás C. Ciano, R. Gell, Eduardo A. Gautier

MS20

METHODOLOGY DEVELOPMENT AND VALIDATION FOR THE SIMULTANEOUS DETERMINATION OF AS, Cd, Pb AND Hg IN HUMAN BLOOD

Santos A. V. Neto, Lisia M. G. dos Santos, Mayssa F. de Andrade, Carolina D. Magalhães, Cristiene B. Silva, Silvana do C. Jacob

MS21

DISTRIBUTION OF TRACE ELEMENTS ALONG THE COAST OF ESPÍRITO SANTO

Melara Krause, Jefferson Rodrigues Souza, Bruna Miurim Dalfior, Tiago Pereira Cunha, Sonara Gonçalves Silva Cassa, Matheus Barbosa Rasch, Bruno Marino Damm, Bruna Silva Correa, Geisamanda Pedrini Brandão, Maria Tereza W. D. Carneiro

MS22

DIRECT DETERMINATION OF TRACE METALS IN CRUDE OIL DESALTER EFLUENT (DE) BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP – MS)

Débora Selene Cardone, Mikaele S. dos Santos, Sherlan G. Lemos, Elma Neide V. Carrilho, Anderson N. do Nascimento, Geórgia Labuto

MS23

EVALUATION OF TRACE ELEMENT CONTENTS IN WATER AND SEDIMENT SAMPLES FROM REIS MAGOS RIVER (ESPÍRITO SANTO, BRAZIL)

Eldis M. Sartori, Bruna M. Dalfior, Maria Tereza W. D. C. Lima, Geisamanda P. B. Athayde

MS24	DIMENSIONING OF BIOSYNTHESIZED SILVER NANOPARTICLES IN BEVERAGES BY spICP-MS *André L. Marques de Souza, Rodrigo M. Pereira, <u>Camila N. Lange</u>, Amedea B. Seabra, Wallace R. Rolim, Bruno L. Batista*
MS25	DIRECT DETERMINATION OF REE IN OIL AND DERIVATIVES BY ICP-MS *<u>Laís N. Viana</u>, Wendy J. S. Rojano, Christiane B. Duyck, Tatiana D. Saint'Pierre*
MS26	RARE EARTH ELEMENTS IN WATER CERTIFIED REFERENCE MATERIALS: RELIABLE MEASUREMENTS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY EQUIPPED WITH TRIPLE *<u>Mariana Ortega Garcia</u>, Lucas Porto, Bruno Menezes Siqueira, Valeska Meirelles, Rodrigo Papai, Ivanise Gaubeur, Maciel Santos Luz*
MS27	DETERMINATION OF RARE EARTHS ELEMENTS IN PETROLEUM AND DERIVATIVES BY ICP-MS *<u>Wendy J. S. Rojano</u>, Laís N. Viana, Christiane B. Duyck, Tatiana D. Saint'Pierre*
MS28	LA-ICPTOF ANALYSIS OF GEOLOCIAL SAMPLES: DEMONSTRATING FAST-WASHOUT, AND TIME RESOLUTION *<u>Mariana Ortega Garcia</u>, Bruno Menezes Siqueira, Valeska Meirelles, Martin Tanner*
MS29	DETERMINATION OF REE IN LEACHATES SIMULATING THE EFFECT OF ACID RAIN IN FLUORESCENT LAMP POWDER BY ICP-MS *<u>Wendy J. S. Rojano</u>, Laís N. Viana, Daniel L. Guimaraes, Jiang Kai, Tatiana D. Saint'Pierre*

SPECIATION ANALYSIS / METALLOMICS – SMet

SMet01	SPECIATION OF IRON AND COPPER BY FAAS-COMPLEXOMETRY IN GRAPE POMACE: TOWARDS REVALORIZATION OF A BY-PRODUCT FROM CHILEAN PISCO INDUSTRY *Fátima J. Rodríguez-Ramos, Vilbett Briones-Labarca, Raúl Cañas*
SMet02	EFFECT OF SELENOMETHIONINE AS A PROTECTIVE AGENT AGAINST INJURY INDUCED BY ISCHEMIA IN TRANSPLANT ORGANS *Paul E. Hasuoka, Marcos M. Kaplan, Nelson H. Ferrúa, Pablo H. Pacheco*
SMet03	SPECIATION AND PRECONCENTRATION METHOD FOR THE DETERMINATION OF Hg(II) AND MeHg IN DIETARY SUPPLEMENTS BY THE ON-LINE COUPLING SPE-HPLC-ICP-MS. FUNCTIONALIZED CARBON NANOTUBES AS A SUITABLE SORBENT FOR SPECIES PRECONCENTRATION *Agustín Londonio, Paul Emir Hasuoka, Pablo Pacheco, Raúl Andrés Gil, Patricia Smichowski,*
SMet04	PERFORMANCE OF DICARBOXYLIC ACIDS AS MOBILE PHASES FOR ARSENIC SPECIATION ANALYSIS BY HPLC-ICPMS *Candela Simonetto, Jonatan Schlotthauer, Juana Pedro, Diana Magni, Mirna Sigrist*
SMet05	FAST UHPLC-ICP-MS METHOD FOR MERCURY SPECIATION *Patricia C. C. Ladeira, Bruno L. Batista*

SMet06	ARSENIC SPECIATION IN RICE: EXPLORING A METHOD FASTER THAN FDA. DEVELOPMENT AND VALIDATION *Melissa Verger, Lorena D. Tchorbadjian. Elena Darré, Raquel Huertas*
SMet07	EVALUATION OF THE LEVELS AND ABSORPTION OF ARSENIC IN CHILEAN RICE ACORDING TO THE AGRONOMIC MANAGEMENT *Elmmy E. Ramírez, Karen S. Bastías, Viviana I. Becerra, Gabriel H. Donoso, Mario O. Paredes. Jorge C. Yáñez*
SMet08	EFFICIENCY OF CENTRIFUGAL FILTERS TO REDUCE BIAS ON ESTIMATION OF HEMOGLOBIN CONTENT IN BLOOD THROUGH TOTAL IRON DETERMINATION *Thiago O. Araujo, Lee L. Yu, Michael Whinchester*

SAMPLE PREPARATION – SP

SP01	REVERSED-PHASE DISPERSIVE LIQUID-LIQUID MICROEXTRACTION AS A SAMPLE PREPARATION METHOD FOR ALKALINE AND ALKALINE-EARTH METALS DETERMINATION IN CRUDE *Mariele S. Nascimento, Cristian R. Andriolli, Paola A. Mello, Eder L. M. Flores, Rochele S. Picoloto, and Erico M. M. Flores*
SP02	COMPARISON OF ALKALINE METHODS FOR THE EXTRACTION OF Cu AND Zn IN BEEF SAMPLES *Fiorella Iaquinta, Ignacio Machado, Analía Suárez, Mariela Pistón*
SP03	STUDY OF SAMPLE PREPARATION METHODOLOGY USING CHELEX-100 RESIN FOR DETERMINATION OF TRACE ELEMENTS IN SEA WATER BY ICP-MS *Bruna M. Dalfior, Raysa N. Chioato, Vitor N. da Conceição, Maria Tereza W. D. C. Lima, Geisamanda P. Brandão*
SP04	USE OF PRE-CONCENTRATION VIA COPRECIPITATION $Mg(OH)_2$ FOR TRACE ELEMENTS DETERMINATION IN FISH AND SHELLFISH BY MIP OES *Luana S. Moreira, Ívero P. Sá, Raquel C. Machado, Ana Rita A. Nogueira, Clarice D. B. Amaral*
SP05	OPTIMISATION OF ULTRASOUND-ASSISTED EXTRACTION PROCEDURE FOR MULTI-ELEMENTARY DETERMINATION IN TOBACCO SAMPLE *Hyrlam S. Ferreira, Sidimar S. Oliveira, Samir H. dos Santos, Tarcísio S, de Almeida, Rennan Geovanny O. Araujo*

SP06	SOLID PHASE BIOSORPTION, PRECONCENTRATION AND DETERMINATION OF LEAD IN INFANT FRUIT JUICES USING AN ECO-FRIENDLY BIOHYBRID MATERIAL *Pamela Y. Quintas, Elizabeth Agostini, Ana L. Wevar Oller, Leticia B. Escudero*
SP07	METHOD DEVELOPMENT FOR THE DETERMINATION OF TRACE-ELEMENTS IN ANTIFOULING PAINT BY ICP OES *Thaiane N. da Silva, Marcos A. Fernandez, Diego B. Batista, Ricardo E. Santelli, Bernardo F. Braz, Aderval S. Luna, Jefferson S. de Gois*
SP08	FEASIBILITY OF Cl^- AND F^- EXTRACTION FROM OILY SAMPLES BY RP-DLLME AND DETERMINATION BY HR-CS GF MAS *Thebny Thaíse Moro, Eduardo S. Chaves, Tatiane de A. Maranhão*
SP09	MULTI-ENERGY CALIBRATION AS A NOVEL STRATEGY FOR ANIMAL FEED ELEMENTAL DETERMINATION BY ICP OES *Marianela Savio, Ariane I. Barros, Joaquim Nobrega*
SP10	A GREENER MICROWAVE ASSISTED DIGESTION METHOD FOR RAPID EXTRACTION AND SPECTROSCOPIC DETERMINATION OF TOTAL SULFUR IN SOUTH AFRICAN CRUDE OIL-SAMPLES *Evah M Tjabadi, Nomvano Mketo*
SP11	BIOACCESSIBILITY OF Ca, Cu, Fe, Mg, P, AND Zn IN RAW SHEEP MEAT AND SUBMITTED TO VARIOUS HEAT TREATMENTS *Julymar M. Higuera, Herick M. Santos, Aline F. Olivera, and Ana Rita A. Nogueira*

SP12

EXTRACTION INDUCED BY MICROEMULSION BREAKING FOR TRACE ELEMENTS DETERMINATION IN PETROLEUM DERIVATIVES BY HR-CS F AAS

Diane O. Laroque, Juliana Vieira, Jennifer da Silva, Ana Carla Boeira, Alexandre de Jesus, Márcia Messias da Silva

SP13

ULTRASOUND-ASSISTED EXTRACTION FOR DETERMINATION POTENTIALLY TOXIC ELEMENTS IN LEATHER USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Bernardo Otávio Gemmer, Tatiane de Andrade Maranhão, Eduardo Sidinei Chaves

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SP14

ULTRASOUND-ASSISTED ACID DIGESTION OF GEOLOGICAL SAMPLES FOR ANALYSIS BY ICP-MS IN THE URANIUM MINING

Fernanda Bresina, Patricia Anzil, Marcos Salvatore, Sabrina Miyno, Carina Bello, Susana Rosa

SP15

INCREMENTAL VS DISRUPTIVE INNOVATION IN MICROWAVE SAMPLE PREPARATION

Camillo Pirola

SP16

EVALUATION AND COMPARISON OF DIFFERENT TYPES OF SAMPLE PREPARATION CONTAINING GOLD NANOPARTICLES BY SP-ICP MS

C. Barata-Silva, L.M.G dos Santos, S.A.V. Neto, M.A. Fonseca, C.D. Magalhaes, S.C Jacob, J.C. Moreira

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SP17

MULTISYRINGE FLOW INJECTION ANALYSIS OF URANIUM (VI) WITH 2-(5-BROMO-2-PYRIDYLAZO)-5-DIETHYLAMINOPHENOL

Víctor Cerdà, Kaewta Danchana, Sergio L.C. Ferreira

SP18	DISPERSIVE LIQUID-LIQUID MICROEXTRACTION FOR CADMIUM DETERMINATION IN ATMOSPHERIC PARTICULATE MATTER *Mariana A. Vega, Claus Samuelsen Lucea, Mariano Garrido, Claudia E. Domini, Marcelo T. Pereyra*
SP19	DEVELOPMENT OF AN EXTRACTION METHOD FOR RARE EARTH ELEMENTS FROM FLUORESCENT LAMPS PHOSPHOR *Marcelo F.M.F. Azevedo, Pedro H.M. Weingärtner, Gabriel A. Freitas, Rafael C.C. Rocha, Jiang Kai, Tatiana D. Saint'Pierre*
SP20	DETERMINATION OF ELEMENTAL IMPURITIES IN OMEPRAZOLE DRUG SAMPLES *Fernanda C. Pinheiro, Ariane I. Barros, Joaquim A. Nóbrega*
SP21	ULTRASOUND-ASSISTED EXTRACTION PROCEDURE FOR POTENTIALLY TOXIC ELEMENTS DETERMINATION IN OILY SLUDGE BY ICP-MS *Marcos Antônio Rodrigues Tenorio, Bernardo Otávio Germer, Victor Georges Santos Elgamal, Eduardo Sidinei Chaves, Vera Lúcia Azzolin Frescura Bascuñan*
SP22	METHODOLOGY FOR DETERMINATION OF RARE EARTH ELEMENTS IN URBAN DUST BY ICP OES *Sidimar S. Oliveira, Vaniele S. Ribeiro, Tarcísio S. Almeida, Sarah Adriana Rocha, Rennan G. O. Araujo*

POSTER PRESENTATIONS

X-RAY SPECTROMETRY - XR

XR01	GOLD ON SILVER: NON-INVASIVE DETERMINATION OF GOLD THICKNESS OVER SILVER IN A PORTUGUESE MONSTRANCE FROM THE 19th CENTURY *Sofia Pessanha, Jorge Sampaio, Sara Valadas, António Candeias, José Mirão, Marta Manso, Maria L. Carvalho, Fátima Fernandes, Vanessa Antunes*
XR02	EDXRF QUANTITATIVE ANALYSIS OF BIOLOGICAL SAMPLES WITH EXTERNAL STANDARD METHOD *Patrícia M.S. Carvalho, Sofia Pessanha, Ana Luísa Silva, João Veloso, José Paulo Santos*
XR03	APPLICATION OF WAVE DISPERSION X-RAYS FLUORESCENCE (WDXRF) METHODS TO COMPARISON OF INORGANIC COMPONENTS OF COMPOSITE RESINS *J. Victor M. de Albuquerque, Cláudia C. Silva, Jeffer H. R. da Silva, Diego F. Regalado*
XR04	CRYSTALOGRAPHIC STUDY OF THE AMAZON REGION ZIRCON STRUCTURES *Fernando A. de Oliveira, Adriane M. C. Horbe, Cláudia C. Silva*
XR05	WATERLILY PISTILS AS UNCONVENTIONAL EDIBLE PLANT: AN INORGANIC NUTRITION APPROACH *Cláudia C. Silva, Sara K. Loiola, Patricia S. P. Hidalgo*
XR06	RECOVERY OF RHENIUM OXIDE BY PYROMETALLURGICAL PROCESSES, ANALYZED BY DRX *Vanesa Bazan, Ariel Maratta, Gastón Villafañe, Rodolfo Lara, Elena Brandaleze*

XR07	COMPARISON BETWEEN INDUCTIVELY COUPLED PLASMA AND X-RAY FLUORESCENCE PERFORMANCE OF ELEMENTARY ANALYSIS IN FOSSIL BONE SAMPLES *Sofia Fanioni, Camila Bidone, Maria Bavio, Gabriel Casal, Adriana Nillni, Pamela Tripodi*
XR08	EXAMINATION OF THE GROUND LAYERS OF AN EGYPTIAN MUMMY FROM THE ROMAN PERIOD USING X-RAY TECHNIQUES *Francis Anna C.R.A. Sanches, Raysa C. Nardes, Ramon S. Santos, Hamilton S. Gama Filho, Catarine C.G. Leitão, Renato P. Freitas, Alessandra S. Machado, Antônio Brancaglion Jr., Sheila M.F.M. Souza, J.T. Assis, Davi F. Oliveira, Marcelino J. Anjos, Ricardo T. Lopes*
XR09	CHARACTERIZATION OF PIGMENTS AND GROUND LAYER OF AN WOODEN PIETÁ SCULPTURE FROM THE XVIII CENTURY USING XRF AND XRD TECHNIQUES *Francis Anna C.R.A. Sanches, Raysa C. Nardes, Ramon S. Santos, Hamilton S. Gama Filho, Catarine C.G. Leitão, Teresa E. Calgam, Regina Bueno, Joaquim T. Assis, Davi F. Oliveira, Marcelino J. Anjos*
XR10	A SIMPLE METHOD FOR THE ELEMENTAL ANALYSIS OF GLASS USING TOTAL REFLECTION X-RAY FLUORESCENCE *Cassiano L. S. Costa, Clésia C. Nacente*

SULFUR DETERMINATION USING THE SiS MOLECULE VIA HR-CS GF MAS AND DIRECT SOLID SAMPLES ANALYSIS: A REALIBLE METHOD FOR DIFFERENT MATRICES

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In the last 10 years, several methods have been reported for sulfur determination, mostly using CS as target molecule, by high-resolution continuum source graphite furnace molecular absorption spectrometry (HR-CS GF MAS)[1]. These methods usually require different analytical conditions to guarantee the CS formation, mainly due to matrix effects and/or to the presence of different sulfur species[1]. It is also known that sulfur can be determined, via HR-CS MAS, using other diatomic molecules as SnS, PbS, GeS and SiS[1]. However, the SiS molecule was used only once in the determination of sulfur and the authors reported serious difficulties in the molecule generation[2]. The main goal of this work was the development of a simple and reliable method for sulfur determination, in different matrices, using the SiS molecule via HR-CS GF MAS and direct solid samples analysis. The SiS analytical line of 282.910 nm and the integrated absorbance values (A_{int}) of three pixels were used in this investigation. Six sulfur aqueous standard solutions (Na_2S, Na_2SO_4, $BeSO_4$, thiourea, L-cysteine and sulfamic acid) and six certified reference materials (CRM) (bovine muscle NIST 8414, non-fat milk powder NIST 1549, lake sediments LKSD-4, stream sediment STSD-3, citrus leaves NIST 1572 and tea DC73014) were evaluated. The use of 400 μg Zr, as permanent modifier, and 20 μg Si, as molecule forming reagent, was crucial to assure the SiS formation. The molecule highest A_{int} values and most symmetrical signals were obtained using the pyrolysis and vaporization temperatures of 1200 and 2000 °C, respectively. Under these conditions, the SiS analytical signals for the six sulfur standard solutions were statistically equal. In order to improve the sensitivity, the sum of the A_{int} values of ten SiS lines, available in the vicinity of 282.910 nm and with similar relative sensitivity, was explored. With this, calibration curves with a sulfur mass range of 0.01 to 2.5 μg, from Na_2SO_4 and thiourea standards, were used to obtain the limits of detection and quantification and the characteristic mass of 9.4, 31 ng mg^{-1} and 10 ng, respectively. Despite the differences in the CRM matrices, the SiS molecule was successfully employed for sulfur determination, as all values were in agreement with the certified ones at a confidence level of 95% (t-Student test).

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MULTI-FLOW CALIBRATION: A NOVEL APPROACH APPLIED TO INDUCTIVELY COUPLED PLASMA TECHNIQUES

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The analytical performance of inductively coupled plasma (ICP) techniques can be affected by nonspectral interferences, such as matrix effects, compromising the accuracy of the results during the analysis of complex samples.[1] Several strategies have been recently described to overcome matrix effects, among them, different calibrations methods. Multi-flow calibration (MFC) is one of these new strategies which employs multiple nebulization gas flow rates (Q) to change the plasma conditions, normalizing it and minimizing matrix effects.[2] The MFC curve is built with analytical signals from a single calibration standard (x-axis) and from the samples (y-axis), recorded at Q conditions. The analyte concentation in the calibration standard, along with the slope of a linear regression model obtained with the MFC plot (with each calibration point representing a different Q value) are then used to determine the analyte concentration in the sample. The MFC method was applied to ICP OES and ICP-MS to analyze four certified reference materials (CRMs) containing inorganic and organic matrices (*i.e.* soil, plant material, bovine liver and polymers). Five nebulization gas flow rates were used for data acquisition in both techniques, and the concentration of analyte in the calibration standard was evaluated considering the following sample/standard ratios: 1:0.5, 1:1 and 1:2. Arsenic, Cd, Co, Cu, Hg, Mo, Mn, Ni, Se, Sb, Pb, and V were determined by ICP-MS, and Al, As, Cd, Cr, Cu, Hg, Mn, Pb and Zn were determined by ICP OES. MFC results were compared with values obtained with the external standard calibration (EC) for both techniques. In all cases, MFC showed superior accuracy (recoveries in the 80-110% and 82-112% ranges for ICP OES and ICP-MS, respectively), and lower RSDs, demonstrating the efficiency of the new method for minimizing matrix effects in complex-matrix samples analyses.

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ATOMIZATION OF BISMUTHANE AND SENSITIVE BISMUTH DETERMINATION BY ATOMIC FLUORESCENCE SPECTROMETRY

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Hydride generation (HG) coupled to atomic fluorescence spectrometry (AFS) is an extremely sensitive method by which ultratrace amounts of hydride forming elements can be determined. In principle, AFS can be assembled in-house using commercially available components (radiation source, detector, lenses, interference filter and atomizer). In our laboratory, we designed such non-dispersive AFS spectrometer using an electrodeless discharge lamp (EDL) source with high radiation intensity and a solar blind photomultiplier as a detector. We found that in the case of arsenic we could easily attack the limits of detection typical of ICP-MS but at substantially lower investment and running costs.[1] In this work, we have moved our attention to bismuth. Bismuthane was generated in a flow injection system with the use of HCl as a reaction medium and $NaBH_4$ as a reducing agent. A miniature diffusion flame (MDF) and a flame-in-gas-shield (FIGS) were used as atomizers. Flow rates of argon and hydrogen as well as the observation height were optimized for MDF, while flow rates of argon, hydrogen and oxygen and flow rates of shielding argon were optimized for FIGS. Another part of this work dealt with an adjustment of the spectrometer components for efficient excitation, focusing and detection of Bi fluorescence radiation. A special attention was paid to optimization of the operating current and modulation of the EDL source and selection of a suitable wavelength for Bi fluorescence detection. Three interference filters were employed covering the most intense Bi fluorescence transitions with centre wavelength of 202.1, 222.63 and 307.1 nm all of them with full width at half maximum of 10 nm. As non-dispersive systems may be susceptible to interferences especially from other hydride forming elements, these filters were also used in an interference study in which the influence of As, Hg, Pb, Sn, Sb and Se on Bi determination was examined. No significant interferences were observed up to 100 ng mL^{-1} of Sn, Pb, Se and Hg. Negative interference (by ⊠ 30%) was observed for 100 ng mL^{-1} of As using all interference filters. Serious positive interference of Sb was observed, starting even at 1 ng mL^{-1} using both 202.1 and 222.63 nm filters but not with the 307.1 nm filter. An extremely sensitive methodology was finally achieved with the FIGS atomizer and the 307.1 nm filter, illustrated by an exceptionally low limit of detection 0.9 pg mL^{-1}. The method was applied to certified reference materials of water, hair and blood.

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PHOTOCHEMICAL VAPOR GENERATION OF TRANSITION METALS – EXPANDING TO NEW ANALYTES

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Photochemical vapor generation (PVG) is an emerging alternative sample introduction technique for analytical atomic spectrometry, yielding advantages of efficient separation of analyte from matrix and its significantly higher introduction efficiency than possible with pneumatic nebulization. Coverage of PVG continues to expand to more elements. It is currently applicable not only to mercury and hydride forming elements (Se, As, Sb, Te, Pb, Bi) but also nonmetals (I, Br, Cl, S) and transition metals.[1] Among them, PVG of Ni, Fe and Co from formic acid based media has garnered particular attention, including several analytical applications, due to its high efficiency and the intrinsic stability of the resultant volatile metal carbonyls that have been identified amongst the gaseous products. This presentation will focus on PVG of Mo and W that has been generated in our laboratory for the first time.[2,3] Efficient PVG was accomplished using a 19 W flow-through photoreactor operating in the flow injection mode using formic acid (30-50%) as the reaction medium. The generated volatile products (most probably $Mo(CO)_6$ and $W(CO)_6$) were directed by an argon carrier gas to a plastic gas-liquid separator and introduced into the spray chamber of an Agilent 7700x inductively coupled plasma mass spectrometer for sensitive detection. Details on optimization of generation conditions as well as the influence of various metal sensitizers will be presented. Particular attention was paid to the determination of overall PVG efficiency relative to that for liquid nebulization as well as on interferences from common inorganic anions (Cl^-, NO_3^-, SO_4^{2-}) likely to be encountered during analytical application to real samples. The accuracy and feasibility of this sensitive methodology (limits of detection ▯ 1 pg ml^{-1}) was verified by analysis of several Certified Reference Materials of water, seawater and fine fly ash. Mechanistic aspects of PVG of these two metals will be also pointed out and discussed.

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SIMULTANEOUS ON-LINE PRECONCENTRATION AND DETERMINATION OF Cd, Hg Mn, Pb AND Sb IN RICE AND RICE-BASED PRODUCTS BY ICP-MS. OPTIMIZATION USING CHEMOMETRIC APPROACHES

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A hyphenated system was developed for the simultaneous preconcentration and determination of Cd, Hg Mn, Pb and Sb by the on-line coupling of solid phase extraction (SPE) and inductively coupled plasma mass spectrometry (ICP-MS). The five analytes were retained on a microcolumn filled with oxidized multiwalled carbon nanotubes (MWCNTs). The optimization was performed by employing a multi-response process. The significant variables, obtained using Plackett-Burman screening design, are further evaluated using central composite design as response surface methodology with desirability functions to obtain the optimal levels of the significant parameters (pH, loading rate and eluent concentration). High enrichment factors were obtained (EF: 190-400) which allowed to reach LODs < 1 ng L^{-1}. The relative standard deviations resulted below 4% and recoveries of the five elements were never less than 96%. For checking accuracy, the standard reference material NIST1568a rice flour was analyzed and results were in good agreement with certified values. The developed method was applied to the determination of the five elements in rice and rice-based products.

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QUALITATIVE IMAGING USING LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY APPLIED IN DENDROCHEMICAL ANALYSIS

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Laser ablation and inductively coupled plasma mass spectrometry (LA-ICP-MS) has increasingly become a major tool for imaging the elemental distribution. This technique allows the investigation of trace metals in tree-rings with high spatial resolution. To ensure more efficient determination of micronutrients and potentially toxic elements, instrumental conditions were optimized based on analytical signal intensity, signal-to-background ratio (SBR) and background equivalent concentration (BEC) criteria. Pellets containing 10 mg kg^{-1} Ba, Cd, Cu, Fe, Mn, Ni, Pb, Zn and microcrystalline cellulose were employed for the optimization studies of ablation process and analytical detection. Cellulose powder was spiked by adding 400 L of standard solution to 0.2 g cellulose powder, dried for 48 h at 37 °C and homogenized with a mortar and pestle for 10 min.[1] Dried solid solution was pressed at 7 ton during 1 min. Under optimized conditions of the ablation process (laser intensity, 70%; frequency, 20 Hz; spot size diameter, 110 m) and elemental detection by ICP-MS (RF power, 1300 W; carrier and auxiliary gas flow rates, 1.2 L min^{-1} and 1.6 L min^{-1}, respectively), analytical signal acquisition by LA-ICP-MS in wood samples was conducted in line scan mode at 60 m s^{-1} speed. Carbon, which is naturally present in wood, was used as an internal standard during analysis to correct for signal fluctuations. Spatial elemental distributions in samples collected in the Peruaçu National Park located in Brazil were built using the free open source LA-iMageS software.[2] Results are presented as the ratio between the signal of the analytes and the internal standard ^{13}C and were correlated with digital X-ray image. Elemental distribution may vary according to the axial parenchyma, fibers, and vessels. LA-ICP-MS has demonstrate to be an effective technique for dendrochemical studies and the results may contribute to future investigations related to pollution and historical natural events in the region.

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STUDY OF THE MATRIX EFFECTS IN FLOWING LIQUID ANODE ATMOSPHERIC PRESSURE GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY (FLA-APGD-OES)

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Flowing liquid anode atmospheric pressure glow discharge (FLA-APGD) is a new excitation source that can be used for detection of elements by optical emission spectrometry (OES). This miniaturized plasma source offers very low detection limits of the elements (usually in the range of 0.005-0.050 μg L^{-1})[1,2], however, it is quite susceptible to matrix effects. In the present work, the effect of foreign ions on the analytes emission coming from FLA-APGD was studied in detail. It was revealed that most of the studied interfering ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Mn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) were not transported into the plasma phase and did not affect the atomization/excitation conditions. Interferents significantly reduced the efficiency of analytes transport from the liquid to plasma phase and the measured suppression in analytes transport strictly corresponded to the observed decrease in the intensity of emission lines of the studied analytes (Ag, Cd, Hg, Pb, Tl and Zn). The alkali metals and alkaline earth metals were recognized as the strongest interferents. Using different masking agents, an attempt was made to reduce the matrix effects. Among the tested compounds, there were different organic acids, crown ethers, thiourea, phenathroline, ammonium fluoride, EDTA and CDTA. Numerous of these compounds were found to be effective masking agents, especially in the determination of Pb and Zn. A simple method for quantification of Pb and Zn in the presence of Fe-matrix was developed and its analytical characteristic was assessed. Moreover, the application of this method for determination of Pb and Zn trace impurities in different samples was presented. The results of the research carried out can be used to develop other methods of analysis of complex matrix sample, both with FLA-APGD and other microplasma emission sources.

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BIOACCESSIBILITY AND TOTAL CONCENTRATION OF Cr AND Ni IN DIFFERENT VARIETIES OF COOKED RICE

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Rice (Oryza sativa) is a crop of great, economic and social importance worldwide. At present, the study of trace elements in foods, both beneficial to health and potentially toxic, has been prioritized, and rice grain is being one of the cereals characterized by a selective accumulation of these elements.[1] The total concentration of the different trace elements in food to be consumed, allows estimate the dose of exposure, while the soluble fraction present in the intestinal lumen after the digestive process, shows its bioaccessibility, wich is a more precise nutritional or/and toxic evaluation of the food.[2] The objective of the present work was to determine the total and bioaccessible concentration of cromium (Cr), and nickel (Ni) in samples of eight different varieties of cooked, lyophilized and ground rice. The bioaccessible fraction was determined by an in vitro solubility method which simulates the gastrointestinal digestion, by adding solutions of digestive enzimes and bile salts.[3] Finally, the total and solubilized minerals, after ashing, were determined by Atomic Absorption Spectrophotometry with Grafite Furnarce. The results were ranges of total values (μg /100g) of Cr: 18.88-43.43 and Ni: 21.45- 45.85; while the percentages of solubilized and bioavailable minerals were Cr: 15.04-28.18%; Ni: 34.36 - 63.61%. It is concluded that, both, the total content of minerals as the soluble fraction to be used by the organism, are influenced by the different physical and chemical characteristics of the studied varieties, and the bioaccessibility percentage values of these studied trace elements are high in comparison with other vegetable foods.

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APPLICATION OF DIFFERENT STRATEGIES IN PARTIAL LEAST SQUARES REGRESSION MODELS FOR THE DETERMINATION OF Mn, Cr, AND Ni IN STEEL SAMPLES USING LIBS

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Laser-induced breakdown spectroscopy (LIBS) analysis was carried out on eleven steel samples to quantify the concentrations of chromium, nickel, and manganese. The samples were certified reference materials provided by BAM (Berlin) in the framework of the LIBS 2008 Contest. LIBS spectral data were correlated to known concentrations of the samples using different strategies in partial least squares (PLS) regression models. For the PLS analysis, one predictive model was separately generated for each element, while different approaches were used for the selection of variables (VIP: variable importance in projection and iPLS: interval partial least squares) in the PLS model to quantify the content of the elements. The comparison of the performance of the models showed that there was no significant statistical difference using the Wilcoxon signed-rank test. The elliptical joint confidence region (EJCR) did not detect systematic errors in these proposed methodologies.

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SPARK DISCHARGE-ASSISTED SINGLE-STANDARD CALIBRATION IN LASER-INDUCED BREAKDOWN SPECTROSCOPY: DETERMINATION OF Al AND P IN AGROINDUSTRIAL SAMPLES

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The use of one standard to produce different signal intensities (instrumental signal dilution) by means of variation of any instrumental parameter of LIBS is feasible and promising to be used for calibration. Spark discharge coupled to LIBS (SD-LIBS) was recently proposed to improve sensitivity in the determination of P in fertilizers.[1] Data showed that emission intensities increased linearly with increasing voltage. Also, SD offers the possibility of overcoming low energies of lasers by reheating the plasma and increasing emission intensities, improving atomization and excitation processes which may contribute to eventual matrix effects minimization. However, the use of SD to perform calibration with a single standard is not described in the literature. This study reports on a new calibration strategy for LIBS called spark discharge-assisted single-standard calibration (SD-SSC). The SD-SSC requires the measurement of intensities (I) of the standard (C^{std}) and unknown sample (C^{sample}) at fixed voltage so that $C^{sample} = C^{std}(I^{sample}/I^{std})$. The efficiency of the proposed method was checked by determining aluminum in plant certified reference materials and phosphorus in commercial fertilizer samples. Accuracy was also evaluated by analyzing fertilizer samples by high-resolution continuum source flame atomic absorption spectrometry (HR-CS FAAS) comparative technique for P. No statistically significant differences were observed between analyte concentrations determined (*n*=3) by SD-SSC LIBS and certified values (for Al) and by HR-CS FAAS (for P) at 95% confidence level. The relative standard deviations (*n*=12) were typically 7% for Al, and in the 4-10% range for P. The SSC SD LIBS is first time presented and demonstrated for direct determination of Al and P in plants and fertilizers, respectively. The use of LIBS technique for direct solid analysis is attractive and even more so with simpler calibrations such as SSC. Besides simplicity and low cost, SD-SSC LIBS requires neither laborious, time consuming calibration methods nor changes in arrangements of the instrument.

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MICROEXTRACTION AND PRECONCENTRATION TECHNIQUE BASED ON MAGNETIC IONIC LIQUID FOR THE DETERMINATION OF CHROMIUM BY ELECTROTERMAL ATOMIC ABSORPTION SPECTROMETRY APPLIED TO HONEY SAMPLE

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The interest for chromium (Cr) is originated in the widespread use of this metal in several industries. Large quantities of Cr-containing residues reach the environment and can have significant adverse biological and ecological effects. The natural concentration of total Cr in food is at trace levels (μg L^{-1})[1]. However, these low concentrations are not compatible with the limits of detection (LOD) reached by some detectors based on atomic spectrometry. Therefore, emphasis has been placed on the development of sensitive analytical methodologies for preconcentration and determination of Cr at trace levels[2].

The ionic liquid (IL) trihexyl(tetradecyl)phosphonium chloride has been used as an extractant in liquid-liquid microextraction techniques (LLME) due to its ability to form ion pairs[1]. However, a more recent generation of ILs has emerged, called magnetic ionic liquids (MILs), which preserve the specific properties of ILs but also show magnetism. MILs brings more benefits to LLME techniques as it allows the development of analytical methods that avoid time-consuming steps such as centrifugation[3].

In the present work, a novel LLME technique based on the formation of ion pairs between the MIL trihexyl(tetradecyl)phosphonium tetrachloroferrate ($[P_{6,6,6,14}]FeCl_4$) and the anion $[Cr(H_2O)_2Cl_4]^-$ was developed for the preconcentration and determination of Cr by electrothermal atomic absorption spectrometry (ETAAS). The resulting method consisted in adjusting the acidity of samples to a concentration of 1 mol L^{-1} HCl, followed by the extraction of Cr with the MIL, the use of acetonitrile as a dispersant and vortexing. The MIL was collected with the use of a magnetic rod, diluted in $CHCl_3$ and an aliquot of the eluate was injected into the graphite furnace of ETAAS for Cr determination. Under optimal experimental conditions, an extraction efficiency of 95% was obtained, an LOD of 41 ng L^{-1} of Cr and a relative standard deviation (RSD) of 3.2% (for a Cr solution of 1 μg L^{-1} and n=10). The proposed methodology was successfully applied to honey samples previously treated in muffle oven and diluted.

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CRITICAL EVALUATION OF THE ANALYTICAL PERFORMANCE OF COMMERCIAL NEBULIZERS IN MICROWAVE-INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY

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The sample introduction is one of the most critical stages in the determination of elements by plasma spectrometry techniques. It is due to the characteristics of the aerosol formed in the nebulization directly influence the properties of the plasma, being able to affect the precision and accuracy of the analysis[1]. In this sense, the purpose of this study was to evaluate the analytical performance of four types of commercial nebulizers: OneNeb series 1, OneNeb series 2, Concentric, and Mira Mist in a microwave-induced plasma optical emission spectrometry (MIP OES). The plasma fundamental parameters, such as excitation temperature (T), number of electron density (n_e), and robustness (ratio Mg II/Mg I) were estimated. Also, solvent transport efficiencies were calculated. Precision, limits of detection, and accuracy were evaluated for the analytical performance of Al, Ca, Cu, Cr, Fe, Mn, and Zn. The nebulizers precision was estimated in different matrices: HNO_3(1% v v^{-1}), H_2SO_4(1% v v^{-1}), solutions containing high concentration of easily ionizable elements (EIEs), ethanol (1% v v^{-1}), and carbon (1000 mg L^{-1}). The accuracy was evaluated using the CRMs Tomato leaves (NIST SRM 1570), mineral fertilizer (NIST SRM 695), dogfish liver (DOLT-5 NRC), and lobster Hepatopancreas (TORT-3 NRC). According to the obtained results, the type of nebulizer used has a significant influence on each of the evaluated parameters, Mira Mist showed the highest T, n_e, and the ratio Mg II/Mg I. Nonetheless, it had the lowest transport efficiency. On the other hand, the lowest T, n_e, and the ratio Mg II/Mg I were found with the employment of OneNeb series 2. Moreover, this nebulizer had the lowest RSD and LOD values. Regarding the accuracy, all the nebulizers showed recoveries between 80 -120%.

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SPACE-CHARGE EFFECT AND INTERNAL STANDARDIZATION

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In ICP-MS, ions, atoms, photons and electrons formed in the argon plasma are transferred through the skimmer and sampling cone (interface region) before introduction into the mass spectrometer. In the interface region there is reduction of the pressure from 760 torr to 1-3 torr. After the interface region, the pressure continues to decrease along the ion lenses to 10^{-3} - 10^{-4} torr[1]. Thereby, electrons diffuse from the beam and ions begin to interact (electrostatic repulsion), this effect is known as space-charge effect. The ion lenses minimize space-charge effect, though the internal standardization has been used successfully to correct for this effect in ICP-MS measurements[2]. So far, the choice of the internal standard (IS) has been dependent on the mass of the analyte, once space-charge effect is more pronounced for light mass elements than for high mass elements[1]. However, with the evolution of instrumentation, the ion lenses configuration changed, consequently space-charge effect and IS performance should be reevaluated. Olesik and Jiao[2] showed that space-charge effect using ELAN 6000 ICP-MS (single ion lens) is different from that observed using ELAN 250 ICP-MS (three ion lenses) in different matrices containing elements with light, middle and high masses. Furthermore, a single internal standard was effective to correct for space-charge effect for light, middle and high masses elements. In order, to evaluate space-charge effect and internal standardization in ICP-MS with different set of ion lenses, changes in analyte ion sensitivities as a function of analyte ion mass ($^{11}B^+$, $^{24}Mg^+$, $^{45}Sc^+$, $^{60}Ni^+$, $^{71}Ga^+$, $^{75}As^+$, $^{111}Cd^+$, $^{138}Ba^+$ and $^{172}Yb^+$) due to the presence of seven different matrix elements ($^{23}Na^+$, $^{63}Cu^+$, $^{89}Y^+$, $^{115}In^+$, $^{159}Tb^+$, $^{175}Lu^+$ and $^{205}Tl^+$) were measured using Agilent 7800 Quadrupole ICP-MS (Agilent Technologies, Tokio, JHS, Japan). Elements with different masses (light, middle and high mass range) were evaluated as IS: $^{7}Li^+$, $^{88}Sr^+$ and $^{209}Bi^+$. As previously observed using ELAN 250[2], matrix effects generally became more severe for matrices containing elements with high masses ($^{115}In^+$, $^{159}Tb^+$, $^{175}Lu^+$ and $^{205}Tl^+$) but were not dependent on the mass of the analyte ion, differently from which was known about space-charge effect. Thus, as previously suggested[2], though the ISs evaluated had different behavior using Agilent 7800, a single internal standard was effective for correcting for space-charge effect for all analytes.

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SUBCELLULAR METAL PARTITIONING IN *Steno bredanensis* FROM SOUTHEASTERN BRAZIL

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Dolphins are considered excellent chemical exposure indicators, as they are long-lived apex predators and often exposed to chemical contamination, including metals, through the dietary route, which may lead to toxic effects along the aquatic trophic web. Most studies assess only total metal contents. However, metals are subject to internal subcellular compartmentalization, altering their bioavailability. Thus, subcellular metal data are essential in assessments concerning deleterious metal effects.[1] In this context, metal distributions in three subcellular liver (n=8), muscle (n=10) and kidney (n=3) fractions (insoluble, thermolabile and thermostable fractions) from *Steno bredanensis* from southeastern Brazil were determined and correlated to metallothionein (MT) levels. Metals were determined by inductively coupled plasma mass spectrometry in the subcellular after HNO$_3$ digestion. Quality control was conducted using DORM-4 with all recoveries ranging from 90 to 107% and, thus, considered satisfactory. Metal LOQ were as follows: ^{75}As (0.1200 mg kg^{-1}), ^{114}Cd (0.0200 mg kg^{-1}), ^{53}Cr (0.2100 mg kg^{-1}), ^{65}Cu (0.0280 mg kg^{-1}), ^{57}Fe (0.8800 mg kg^{-1}), ^{202}Hg (0.0240 mg kg^{-1}), ^{60}Ni (0.0130 mg kg^{-1}), ^{208}Pb (0.00300 mg kg^{-1}), ^{82}Se (0.0900 mg kg^{-1}), ^{118}Sn (0.0100 mg kg^{-1}) and ^{66}Zn (0.1800 mg kg^{-1}). Cu, Mn, Fe and Zn were associated to Hg and Ag in the insoluble fraction, indicating potential protective effects in place prior to MT-detoxification. Associations between Cu and Mn and Pb and As were noted in the thermolabile fraction. MT was associated with As, Pb, Mn, Cu and Zn. Se and Hg were associated in all subcellular fractions, indicating MT-mediated detoxification of these elements. Protective effects of Zn against Cd and of Se and Cu and Zn against Pb are postulated, due to high essential to toxic metal molar ratios. Inter-elemental correlations, thus, contain important detoxification information. The MT-mediated pathway in *S. bredanensis* was observed as significant for several metals, while some elements were quantified only in the non-bioavailable insoluble subcellular fraction, and thus, probably do not represent toxicity concerns.

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A HIGHLY EFFICIENT IONIC LIQUID-ASSISTED CLOUD POINT EXTRACTION TECHNIQUE FOR PRECONCENTRATION AND SPECIATION ANALYSIS OF TELLURIUM IN ENVIRONMENTAL SAMPLES USING ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Despite being one of the rarest elements in the earth's crust, tellurium has lately found several technological applications which have vertiginously augmented its demand.[1] Furthermore, Te is a toxic heavy metal with significant differences in the toxicity of its species.[2] Thus, the determination of Te in the environment is an increasingly important task, not only in terms of its total concentration, but also concerning its speciation analysis.

In this work, a novel, efficient and highly sensitive ionic liquid-assisted cloud point extraction (IL-CPE) and preconcentration technique was developed for the determination and speciation analysis of Te, using 1-octyl-3-methylimidazolium chloride as an additive for improving the extraction efficiency obtained with Triton X-114. Te(IV) was complexed with ammonium pyrrolidine dithiocarbamate, extracted into the micellar IL/surfactant phase and then directly measured by electrothermal atomic absorption spectrometry (ETAAS). Total Te concentration was obtained after a pre-reduction step of Te(VI), while Te(VI) was calculated by subtracting Te(IV) from total Te.

Different parameters related to the extraction and measurement processes, such as the type and concentration of IL and surfactant, time and temperature during the IL-CPE procedure and ETAAS conditions were thoroughly evaluated and optimized. An enhancement factor of 87 and a 90% extraction efficiency were achieved under optimal conditions. Limits of detection of 1.1 and 1.7 ng L^{-1} for Te(IV) and Te(VI), respectively, and relative standard deviations of 3.9% and 5.0% were obtained.

Furthermore, the action mechanism of the IL on CPE was studied using the fluorescence of LAURDAN as a polarity probe and a decrease in the internal polarity of the extractant micelles was observed. The developed IL-CPE technique was successfully applied for Te speciation analysis in different water samples (tap, underground and seawater) and in soil and sediment leachates.

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OPTIMIZATION OF SAMPLE INJECTION IN TS-FFAAS FOR DETERMINATION OF TRACE ELEMENTS

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TS-FFAAS (ThermpoSpray Flame Furnace Atomic Absorption Spectormetry) is a known analytical technique used for the determination of elementary traces. Over time, several modifications of the original configuration have been made that have allowed significant improvements related to the increase of the atomic population inside the oven. This work presents alternatives not yet explored related to the introduction of the sample in the flame-mounted oven. The effect on the analytical signal will be shown: the location of the injection capillary with respect to the oven, the number of internal holes in the capillary through which the sample passes or the multiple simultaneous injections.

Different alternatives for the injection of liquid samples in TS-FFAAS systems holding a stainless steel furnace as atomization cell are presented. The influence of different operational variables was studied with emphasis on the characteristics of the ceramic capillary employed for sample introduction. The classic one-hole capillary was compared to capillaries with different number of inner holes (one, four and six) and different spatial distribution. The influence on the analytical signal of a double simultaneous injection applied to different zones of the atomization furnace was also evaluated. Determination of elements with different atomization temperature (Ag, Cd and Se) was done. Results showed an optimization of the figures of merit with respect to the TS-FF-AAS conventional assembly. Applications of Multi Injection (MI-TS-FF-AAS) was evaluated for determination of analytes in different matrices; comparison of the obtained results using the proposed technique with referee methodology showed good agreement.

In order to develop a hypothesis that correlated the improvements obtained, with the temperature inside the oven, temperature determinations were made using an imaging method based on cameras with CMOS sensors with two-step calibration. The trends in the modification of the temperature and its distribution will be shown against the changes produced in the injection system.

A discussion focused on the importance of an efficient sample introduction on the figures of merit attainable with TS-FFAAS and the chance of broaden the analytical applications of the technique are provided.

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XANES SPECTROMETRY IN THE LABORATORY: S.I. TRACEABLE ENERGY EDGES FOR CALIBRATION

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Traceability of x-ray energy scales to the definition of the meter in the International System of Units (SI) was first made possible by the demonstration of an x-ray-optical interferometer by Deslattes and Henins in 1973[1]. The NIST lattice spacing comparator allows single crystal characterization with relative standard uncertainties of 10^{-8} which in turn permits the measurement of primary X-ray wavelength standards with accuracies in the ppm range. A Vacuum Double Crystal Spectrometer (VDCS) is being assembled in Lisbon with the goal of measuring reference-free (tied only to the S.I. definition of the meter), high-accuracy line shapes for transition metals. The use of a DCS will ensure measurements of line energies and shapes, with accuracies of a few parts per million, in the soft X-ray regime where most fundamental parameter databases are severely incomplete[2]. The apparatus will also allow the measurement of XANES (X-Ray Absorption Near Edge Spectrometry) in the fluorescence mode with a self-calibrated energy grid. In this way, this laboratory based measurements will allow a database for transition edges and XANES profiles to be created, in which the energy grid is directly traceable to the definition of the S.I. meter.

Future x-ray wavelength reference data will go beyond a list of transition peak and edges positions corresponding to the energy profile maxima or inflection points, respectively, as this procedure is not transferable and in principle does not allow traceable calibration of high-accuracy X-ray apparatus such as crystal diffractometers or crystal monochromators that are ubiquitous in large scale synchrotrons.

These line shapes and energies, will have to form part of a critically-evaluated database, which has to account for all instrumental and systematic effects, in order to provide a true and more transferable parameterization of the intrinsic spectra.

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FILTER PAPER AS CALIBRATION SOLID SUPPORT FOR QUANTIFICATION OF METALS IN TREE-RINGS SAMPLES BY LA-ICP-MS

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Laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful technique that provides major, minor and trace elements information from direct analysis of solid samples. Despite these advantages, some drawbacks must be overcome, especially in the quantitative steps, due to matrix effects and elemental fractionation. One way to overcome these problems is the preparation of matrix-matching standards to close the physical and chemical properties of the standards calibration and the sample matrix. In the analysis of botanical material, like leaves and wood, cellulose-based standard can be used as matrix matching material, such as filter paper[1]. The aim of this work is the study of filter paper as calibration solid support for quantification of Cu, Zn, Cd and Pb in tree-rings samples. To prepare the solid standards using filter paper supports, qualitative filter papers were cut in 8 mm disks using a LS 100 Gravograph machine, decontaminated in 10% v v^{-1} HNO_3 for 2 hours and dried overnight at 37°C. Dried filter disks were weighted and the average mass (0.00410 g) was used to calculate the concentration of the elemental standard solutions for addition on the disks. The addition volume of standard solutions was tested from 1.0 to 5.0 µL for the same final concentration of the analytes on the filters (10 µg g^{-1}). The optimal volume of 2.5 µL was found, taking into account the analytes distribution and homogeneity along the whole diameter of the filter. Using optimal volume of standard solution, analytical curves were obtained for Cu, Zn, Pb and Cd showing correlation coefficients varying from 0.99528 to 0.9990 in a linear range of 1-100 µg g^{-1}. The results showed the potentiality of the filter paper as a calibration solid support for quantification of Cu, Zn, Pb and Cd in cellulose-based samples, like tree-rings and botanical material. The next steps of this work are the evaluation of the analytical figures of merit, including the accuracy of the method using certified reference materials and the use of conventional ICP-MS and microwave acid digestion of the samples as a complementary technique. This method will be applied for the analysis of tree-ring samples, and the quantitative data are expected to contribute with the understanding of physiologic aspects of dendrochemistry and the record of trace elements in tree-ring due to environmental changes and extreme events.

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DIELECTRIC BARRIER DISCHARGE-ASSISTED DETERMINATION OF METHYLMERCURY IN ATMOSPHERIC PARTICULATE MATTER BY AAS

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The atmospheric particulate matter (APM) may contain several components, such as sooty particles made up largely of organic compounds, insoluble minerals and trace elements[1]. The presence of Hg in APM is not usual; however, some studies have shown concentrations of up to 21 ng m^{-3} of total Hg in airborne APM.[1] In contrast, very little information on the presence of methylmercury (MeHg), which is highly toxic,[2] in APM is available. The knowledge about its concentration in APM is of extreme importance, mainly in places where there is manipulation of this particular chemical compound, such as laboratories. The present study proposes a method for MeHg determination in APM using chemical vapor generation (CVG) to volatilize the analyte and a dielectric barrier discharge (DBD) associated at atomic absorption spectrometry (AAS) for the determination. The APM used in this study was collected in a laboratory environment using a portable medium volume sampler. CVG was performed in a batch system using NaBH$_4$ to volatilize the analyte and argon as the carrier gas. This system was coupled to a DBD device developed in the lab using a glass tube as dielectric barrier (5 mm i.d. and 1 mm of wall thickness), one copper electrode (wire) inside the glass tube and another in the outside (wire copper coil). The frequency and voltage applied were 15 kHz and about 60 kV, respectively. The role of the DBD was to convert MeHg into Hg^0, with subsequent detection by AAS. Initially, the signal difference observed when the DBD was switched between on and off modes when a MeHg solution (100 ng) was introduced in the system was evaluated. A significant difference was observed by switching modes using peak height for measurement (Unpaired *t*-test, confidence level of 95%). Afterwards, the experimental conditions associated to CVG were evaluated and 1 mL of 2% (m/v) NaBH$_4$ and 1 mL of 1.2 mol L^{-1} HCl were selected. The adsorption of MeHg in the APM filter was monitored in an interval of 0 to 50 min; signal suppression throughout this range was observed. The same test was performed using the blank filter and the signal remained constant in a range of 0 to 30 min, which was suppressed after 30 min, confirming the adsorption of MeHg by APM. In this sense, an extraction method for MeHg proposed in the literature was applied.[3] Significant difference (Unpaired *t*-test, confidence level of 95%) was observed when the results from direct analyses were compared to those from extraction (enriched sample). Thus, a calibration curve using the matrix was performed, obtaining a R^2 of 0.9935 in a range of 10 to 400 ng of MeHg. The limits of detection and quantification were 0.01 and 0.04 μg, respectively. Recovery tests were performed at two levels and recoveries of 107% and 116% were obtained. Based on the results, the proposed method which combines CVG, DBD and AAS was suitable for MeHg determination in APM.

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MAGNETIC IONIC LIQUID-BASED MICROEXTRACTION AND PRECONCENTRATION TECHNIQUE FOR ARSENIC SPECIATION ANALISYS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Arsenic is a highly toxic metalloid that can be present in low concentrations in water, soil, air and food. Its toxicity in environmental and biological systems is strongly dependant on chemical nature of its species[1]. It is well known that the inorganic species of As are more toxic than organic arsenicals, and the toxicity of As(III) is greater than As(V). Thus, speciation analysis of arsenic becomes highly necessary[2]. The natural concentration of total As in surface water is usually less than 10 µg L^{-1}. On the other hand, the concentration of the different species of As are of the order of ng L^{-1}. However, these low concentrations are not compatible with the limits of detection (LOD) reached by some detectors based on atomic spectrometry. Therefore, the development of sensitive analytical methodologies for preconcentration and speciation of As at trace levels is required. Ionic liquids (ILs) have been widely used as an extractant solvent in liquid-liquid microextraction techniques (LLME). Recently, a new family of ILs known as magnetic ionic liquids (MILs) has become the subject of interest in several analytical applications. MILs strongly respond to external magnetic fields, apart from possessing the unique and tuneable physicochemical properties of ILs[3].

In the present work, a novel LLME technique using the MIL trihexyl(tetradecyl)phosphonium hexachlorodisprosiate ($[P_{6,6,6,14}]_3DyCl_6$) (MIL_1) was developed for selective separation of As(III) with ammonium pyrollidine dithiocarbamate (APDC) as complexing agent. Then, the extraction and preconcentration of As(V) present in the aqueous phase was performed using the MIL trihexyl(tetradecyl)phosphonium tetrachloroferrate ($[P_{6,6,6,14}]FeCl_4$) (MIL_2) by electrothermal atomic absorption spectrometry (ETAAS). This method consists in adjusting the acidity of aqueous samples to a concentration of 1 mol L^{-1} HCl, followed by the extraction of As(V) with the MIL_2. After the vortex stage, the MIL_2 was collected with the use of a magnetic rod, diluted in $CHCl_3$ and an aliquot of the eluate was injected into the graphite furnace of ETAAS for As determination. Under optimal experimental conditions, an extraction efficiency of 92% was obtained, an LOD of 15ng L^{-1} of As(V) and a relative standard deviation (RSD) of 3.6% (for a As(V) solution of 100µg L^{-1} and n = 10). The proposed methodology was successfully applied to aqueous samples.

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ATOMIC FLUORESCENCE SPECTROMETRY FOR DETERMINATION OF MERCURY IN POLYMERIC SOLUTIONS FROM TREATMENT OF PETROLEUM SLUDGE

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Contamination by mercury (Hg) is extremely dangerous to humans. This element is commonly found in oil sludge, a byproduct generated from oil refining, which consists of multiple wastes from this industry. However, it is already known that oil sludge may contain high concentrations of Hg, making it extremely important to develop an effective treatment technique and analytical methodologies that allow the monitoring of Hg in this residue. Thus, an alternative treatment for oily sludge is proposed, based on an adaptation of a technique employed in water treatment. The treatment was performed using flocculation with cationic polymers, a polyacrylamide, to promote the separation of oil sludge in two phases aiming at the higher proportion of retention of Hg in the dense (organic) phase. The optimal parameters for the treatment of the residues with polymeric solutions were: Un80 polymer solution with a concentration of 0.02% (m v^{-1}), pH 4.8 and 15 minutes agitation, followed by centrifugation at 3000 rpm for 5 minutes. After treatment optimization, a methodology for Hg determination in polymeric solutions from the processing of oily sludge by atomic fluorescence spectrometry (AFS) was proposed. The proposed methodology allowed the use of calibration with standards in aqueous solution in the concentration range of 50 to 1000 ng L^{-1}. The detection limit obtained for determination of Hg in polymer solutions was in the order of ng L^{-1}. The proposed method presented adequate accuracy and precision for Hg determination, with recovery values between 90-110% and relative standard deviation (RSD) were lower than 10%. The proposed methodology was applied to evaluate the efficiency of the treatment of oily sludge with cationic polymers. The performed experiments showed that the treatment allowed a proportion of retention of Hg in the dense phase, higher than 88%. These results indicate that the treatment of petroleum sludge with polymeric solutions may be an interesting alternative for these residues. Additionally, the proposed methodology proved to be simple, fast and efficient for the determination of Hg in polymeric solutions from the oil sludge treatment.

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A NEW APPROACH FOR TRACE Hg DETERMINATION IN CRUDE OIL BY CVG-ICP-MS FOLLOWING WET DIGESTION

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Crude oil is a hydrocarbon-based matrix, containing some elements, such as sulfur, nitrogen, oxygen and metals (e.g, Ni, V, and Hg). Regarding to Hg in crude oil, its concentration can range from 0.01 ng g^{-1} to 10 µg g^{-1} and is commonly related to the source. It is well known that Hg may cause poisoning of the catalysts, used in crude oil cracking and also corrosion, even at low concentration.[1] However, taking into account the complexity of the matrix, the difficulties for wet digestion, the low Hg concentration typically found in crude oil, as well as the low carbon content and low residual acidity required in digests by plasma-based techniques, the development of an accurate sample preparation method for further Hg determination in crude oil is required. In this work, crude oil digestion was performed with a microwave-assisted pressurized digestion cavity[2] for further Hg determination by cold vapor generation inductively coupled plasma mass spectrometry (CVG-ICP-MS). An ultra high pressure microwave-assisted digestion system (Multiwave 7000, Anton Paar, Austria) equipped with 5 quartz vessels (80 mL), with maximum temperature and pressure of 270 ºC and 160 bar, respectively, was used. The Hg determination was performed by using an inductively coupled plasma mass spectrometer (Elan DRC, Perkin Elmer, Canada). The determination of carbon content in digests and residual acidity were performed by inductively coupled plasma optical emission spectrometry (Optima 4300 DV, Perkin Elmer, USA) and by titration (836, Metrohm, Switzerland), respectively. Four samples and one certified reference material (CRM) of crude oil (NIST 2722) were used. Recovery experiments were carried out by adding 0.20 µg g^{-1} of Hg on the samples before the digestion. The following operational conditions were investigated: the sample mass (0.5 to 1.3 g), the HNO_3 volume (6 to 10 mL), the maximum temperature (220 to 270 ºC), and the microwave irradiation time (5 to 20 min). Using the optimized conditions (8 mL of 14.4 mol L^{-1} HNO_3, 270 °C, and 20 min), the proposed method allowed the digestion of 1.2 g of crude oil, resulting in a very low limit of quantification (0.52 ng g^{-1}). Recoveries close to 100% for Hg were obtained for all samples and CRM. The carbon content and residual acidity in digests were about 3.5 g L^{-1} and 10%, respectively.

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DETERMINATION OF MINERAL SPECIES BY LASER INDUCED BREAKDOWN SPECTROSCOPY AND CHEMOMETRIC METHODS

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In the copper industry there is a need of real time analytical techniques suitable for process monitoring and control. In this context, the characterization of mineralogical species in copper ores provides valuable information for key steps in the copper production processes. Conventional analytical methods used nowadays in the mining industry are time consuming requiring manual sampling, complex laboratory installations for chemical sample preparation and spectroscopic measurements. In contrast, LIBS owns the capabilities of real time and remote elemental analysis, no chemical pretreatment, thus reducing toxic wastes and emissions. LIBS also allows the access to complex installations such as melting furnaces, conveyor belts and piping. In this work we demonstrate that LIBS can be used to identify and classify natural mineral species in raw rocks without any sample pretreatment. The mineral species identified were pyrite (FeS_2), chalcopyrite ($CuFeS_2$), covellite (CuS), chalcocite (Cu_2S), bornite (Cu_5FeS_4), enargite (Cu_3AsS_4) and molybdenite (MoS_2). The measurements were performed using a LIBS device that includes a 266 nm Nd-YAG laser with energy 26 mJ/pulse and duration of 7 ns (Quantel, France). The detection was performed in ambient conditions with a 6 channel CCD spectrometer (Aurora, Applied Spectra, USA), spectral range from 185 to 1049 nm with an average resolution of 0.12 nm. The delay time was adjusted to 0.55 μs and the integration time to 1.05 ms optimized by the signal/noise ratio for the uniform measurement of all samples. To focus the laser pulse on the sample, a reference green diode laser was used. Principal component analysis (PCA) was considered for exploratory class analysis. Furthermore, Supervised classification models such as Partial Least Square Discriminant Analysis (PLS-DA), Soft Independent Modeling of Class Analogy (SIMCA), K-nearest neighbors (KNN) and Artificial Neural Network (ANN) were used for mineral identification and classification. The chemometric methods can resolve complex elemental LIBS spectra for achieving online recognition of mineral species in raw rocks with classification performance of up to 100% in the case of ANN. The classification performance of these chemometric methods is compared and discussed.

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GREEN AND SIMPLE MICRO-EXTRACTION OF FREE SELENO-AMINO ACID FROM POWDER AND LYOPHILIZED MILK SAMPLES WHIT NATURAL DEEP EUTECTIC SOLVENTS

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Recently, works have been published that apply new deep eutectic natural solvents (NADE) in replacement of conventional solvents for the extraction of proteins in different foods []. NADE in combination with ultrasonic energy is an ecological approach for protein solubilization. This research describes a new process for the extraction of free seleno-amino acids from cow's milk and sheep's milk samples with NADE. In dairy production, different amino acids are easily incorporated into the milk protein, becoming a good source of Se for humans []. Within the framework of a balanced diet, the ingestion of Se in organic form is recommended, mainly as amino acids present in food, since the human body assimilates it more easily than Se in its inorganic form. In this sense, it is important to evaluate in which form of selenium is being enriched in milk.

NADEs present a complex organic matrix that represents a challenge for the conventional inductively coupled plasma mass spectrometry (ICP MS) sample introduction system. An appropriate dilution of the NADE becomes an important strategy to overcome these difficulties along with the optimization of gas flow rate (GFR) and radio frequency (RF), to maintain a reproducible analysis without losing sensitivity. Extraction consists of adding the milk powder sample with NADE, shake it, perform an ultrasound extraction, centrifuge and analyze seleno-amino acids by liquid chromatography-ICP MS. The best extraction after different NADEs comparison was reached for the lactate-glucose NADE, reaching a 94% extraction of selenium. After the best NADEs performance for seleno-amino acid extraction, an experimental design was implemented to obtain accurate data on the most influential parameters in the system and the adequate quantities of sample and reagents. Results showed that the optimal working conditions were: 21.94% of LGH concentration (v v^{-1}), the ultrasound time of 33.26 minutes, the amount of sample of 0.94 g and the volume of extractant (NADE solution) of 3.09 mL. After optimization a LoD and LoQ of 2.18 and 6.61 g kg^{-1} were obtained respectively. A green extraction procedure developed that eliminates the use of highly polluting organic solvents. ICP-DRC-MS optimization increase sensitivity and precision during Se determination. The system was successfully applied to free seleno-amino acids determination in milk powder and milk lyophilized samples.

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VALIDATION OF METHODOLOGY TO IDENTIFICATION, CHARACTERIZATION AND QUANTIFICATION OF DISSOLVED GOLD (I) AND GOLD NANOPARTICLES IN COSMETIC PRODUCTS BY SP-ICP-MS

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Nanoparticle applications have recently gained more space in many product developments, mainly in cosmetology. As this is a very modern technology, uncertainties concerning health risks are still noted, indicating the need for regulations concerning NP product control and quality monitoring. The aim of the present study was to validate methodology single particle inductively couple plasma mass spectrometry (SP-ICP-MS) (Nexion 300D , Perkin Elmer) according to the parameters as described in ISO 17025, because is the unique technique which allows ability to provide information on nanoparticle size, size distibuition, element composition, and number concentration in single, rapid analysis of dissolved analyte in the sample. The limit of detection for nanoparticles diameter and for number concentration were determined with ultrapure water and dwell time of 50 μs and integration time 100 seconds. A LOD$_{size}$ of 16 nm, equivalent to a gold mass of 41.4 ag, and a LOD number distibuition of -3 x 10^{4}L^{-1}, were achieved. The LOD(I) 0.02μg L^{-1} for dissolved gold was obtained in standard mode conditions, calculated as three times the standard deviation of the blank divided by sensitivity. Suspensions containing gold nanoparticles at number concentrations below 10^{5} L^{-1} and/or dissolved Au(I) were introduced into the ICP-MS by Meinhard nebulization for determining the reccovery and precision. The recovery study for Au(I) 98% and AuNP 109% and the relative standard deviation was < 5% This validated methodology were applied in cosmetic products from diferente national and international industrial producers. The variability of the results detected between domestic and imported products demonstrates the importance of an adequate quality control for cosmetics containing AuNP in order to ensure consumer sanitary safety.

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TOTAL SULPHUR DETERMINATION IN AUTOMOTIVE GASOLINE SAMPLES VIA CS DIATOMIC MOLECULE BY HIGH-RESOLUTION CONTINUUM SOURCE MOLECULAR ABSORPTION SPECTROMETRY USING DRIED-MATRIX SPOT SAMPLING

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The presence of sulphur compounds in petroleum derivatives is undesirable once they are responsible for several problems in storage, processing, and transportation of fossil fuels.[1] In the environment, the SO$_x$ formed during the combustion of fossil fuels and emitted to the atmosphere is responsible for the acid rain formation, as well as the development of respiratory human diseases.[1,2] Thus, new environmental regulations are demanding lower sulphur fuels, which means oil industry analysts are facing new challenges in the field of sulphur analysis.[2] In this work, a simple and practical method for sulphur determination in automotive gasoline by high-resolution continuum source solid sampling graphite furnace molecular absorption spectrometry (HR-CS SS-GF MAS) was investigated. The proposed method is based on the dried-matrix spot sampling, in which a volume of sample is deposited and dried out onto a filter paper disk and then pulverised for trace element determinations.[3] Temperature program, chemical modifier, and the choice of sulphur compound for instrument calibration were investigated. The accuracy of the method was assessed by means of a reference method (ASTM D5453), spike-recovery tests at two levels (30 and 60 mg g^{-1}), and using a certified reference material (CRM NIST 2724b - Sulphur in Diesel Fuel Oil). Calibration curves from six different sulphur compounds were constructed and compared. All the calibration curves showed a correlation coefficient higher than 0.99 and sensitivities between 0.61 and 0.69 s mg^{-1}. A characteristic mass of 7 ng and limits of detection and quantification of 1.2 and 4.0 mg g^{-1}, respectively, were achieved using the optimized conditions. In the spike-recovery test, recoveries between 95 and 107% were obtained. The results obtained in the analysis of six samples showed no statistical difference at 95% confidence level using the Student's t-test when compared with those obtained using the reference method. In addition, the obtained values for the CRM were not statistically different at 95% confidence level to the certified values.

The filter paper was a noteworthy substrate that allowed the determination of lower sulphur levels than that established in the Brazilian legislation by HR-CS SS-GF MAS.

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ATMOSPHERIC PRESSURE GLOW DISCHARGE SYSTEM GENERATED IN CONTACT WITH A HANGING DROP ELECTRODE AS AN EXCITATION SOURCE IN OPTICAL EMISSION SPECTROMETRY

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Most common tools for trace elements determinations by optical emission spectrometry (OES) are commercially available instruments that use inductively coupled plasma (ICP) or microwave induced plasma (MIP) as the excitation source. Those apparatus offer very sensitive, simultaneous determinations of many elements. Their biggest disadvantages are their price and very high cost of operation. An alternative to them can be atmospheric pressure glow discharge (APGD) generated in contact with a flowing liquid electrode[1]. The discharge is generated between a pin-type electrode (e.g. made of W) at the top and the surface of a sample solution flowing from a quartz tube at the bottom. Usually, this kind of APGD is direct current driven, the solution is a flowing liquid cathode (FLC) while the W rod is the anode of the discharge system.

The current contribution presents a new APGD system in which the positon of the electrodes is reversed, i.e. the quartz tube is at the top while the solid electrode is at the bottom of the system. This is responsible for very low consumption of sample solutions (0.4 ml min^{-1}) and their complete evaporation by forming a hanging drop electrode (HDE). Under optimized operating conditions, limits of detection of Ag, Cd and Zn assessed with OES were 2.1, 2.4 and 6.0 μg L^{-1}, respectively, and they are comparable with those obtained for ICP. The effect of addition of low molecular organic compounds (methanol, ethanol, formic acid and acetic acid) into sample solution on the analytical performance of HDE-APGD-OES system was examined and discussed. Tolerance of the new APGD system to presence of easily ionizable elements, i.e. Ca, Mg, Na and K, in sample solutions was studied as well. Accuracy of the proposed HDE-APGD-OES method was verified by analysis of a pig kidney certified reference material (ERM-186). Additionally, tap and spring waters spiked with traces of Ag, Cd and Zn ions were analyzed and recoveries of these analytes were determined.

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ULTRATRACE IMPURITIES DETERMINATION IN SILVER FOR NUCLEAR APPLICATIONS: SIGNAL OPTIMIZATION IN ICP-MS WITH ARTIFICIAL NEURAL NETWORKS AND RESPONSE SURFACE METHODOLOGY

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Production of alloys for the nuclear application requires analyzing impurities in metals used as raw material. The specifications for nuclear grade silver-indium-cadmium alloys define maximum levels of impurities on each metal. Therefore, several impurities must be quantified in each individual metal.

Recently, the ICP-MS technique has acquired great relevance for impurities quantification since it allows multi-elemental analysis at the ultra-trace level. The quality of the measurement depends on the signal optimization that maximizes the sensitivity and leads to lower limits of detection. To improve the performance, operational variables must be optimized and, in general, the "one variable at a time" (OVAT) optimization has been used. However, this methodology is not the most efficient to obtain the maximum response values[1].

This work presents an empirical model using a full factorial design for the ICP-MS analytical signal optimization of several elements based on three variables: the torch position, the makeup gas flow, and the nebulizer flow. Response surface methodology and artificial neural networks (ANN) were compared to describe the empirical model and a better description was obtained with the ANN. The model was tested analyzing certified reference material and spiked samples in the optimal conditions, finding no significant bias. The figures of merit of the optimized method and the results of the analyzed silver samples will be shown.

In conclusion, the empirical model created by ANN helps to understand the influence of operational variables on the analytical signal. The optimized method helped quantify ultra-trace impurities in a complex matrix with maximum sensitivity.

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DEVELOPMENT OF ISOTOPIC DILUTION MASS SPECTROMETRY WITH SINGLE AND MULTIPLE COLLECTORS

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Isotope Dilution Mass Spectrometry (ID-MS) is the definitive method in quantitative trace and ultra-trace analysis. ID-MS uses highly enriched spikes of known concentration of an isotope absent or presented in very low quantity in the sample. The sample and spike are in the same chemical form and well-equilibrated, therefore a quantitative recovery of the analyte is not necessary to achieve and no differences in chemical behavior are presented.

Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) has a high resolution and it is one of the excellence technique for multi-element quantification at very low levels. Combining high-precision and high-sensitivity analytical techniques with the high accuracy of ID-MS correlates to the most powerful and accurate quantitative analytical method.

Some of the principal applications for ID-MS are geochronology and nuclear forensics .For forensic purposes, it is useful to know the date of the last purification of a nuclear sample in order to elucidate the production history and connections with other nuclear samples[1].Because if this, several parent-daughter radioisotope pairs (radiochronometers) are of special interest. For this work, the radiochronometers, ^{230}Th-^{234}U and ^{231}Pa-^{235}U, were applied to the analysis of a Radiochronometry Certified Reference Material (CRM) of Uranium, CRM 125. By determining the concentration of the parent-daughter isotopes and applying the decay equation, the age of the sample since the last time that the daughter was separated from the parent (Model Age) can be calculated.

A comparison between single collector mass spectrometers with high resolution (HR-ICP-MS) and MC-ICP-MS was performed by a spectrometric scientist from CNEA during her training with experts on Nuclear Forensic at LLNL in U.S.A. All results are consistent between analysis methods and with the certified purification date: August 18, 1994. The calculated combined uncertainties of the Model Age are 0.11% and 0.15% for Th-U and Pa-U by MC-ICP-MS respectively. Accurate and precise results can also be obtained by HR-ICPMS with uncertainties lower than 0.23% for both chronometers.

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AN ECO-FRIENDLY SAMPLE PREPARATION METHOD DEVELOPMENT FOR ANIMAL FEED NUTRIENT ANALYSIS BY MIP OES

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Feeds for farm animals must contain suitable nutrients concentration, since its composition may affect animal health and its productivity[1]. Thus, knowing nutrients in feed is of great importance. One of the main analytical chemistry challenges has been to overcome problems to bring samples into solutions, which should be compatible with the spectrochemical instrumental technique for inorganic trace analysis.

In the present work, a procedure for sample preparation of pig feeds using commercially available infrared radiation (IR) lamps was evaluated, as this technology could be extensively used based on its ability to promote fast heating. Microwave induced plasma atomic emission spectrometry (MIP OES) was used for Al, Ca, Cd, Co, Cu, Fe, K, Na, Mg, P, Sr and Zn determination in porcine food samples. The proposed procedure consisted in homogenizing and grinding the porcine food samples, adding 1 mL of diluted nitric acid (3.5 mol L^{-1}) to 0.15 g of the sample, and exposing it to IR until dry (this procedure was repeated again). Then, 1 mL of H_2O_2 -100 volumes- was added and samples were dried by exposing to IR (repeating the procedure twice). To validate the proposed methodology Certified Reference Materials (CRM) were analyzed using the same treatment as the samples; analytical recoveries were between 80-120%. Detection limits were found in the range between 0.87 mg kg^{-1} (Cd) and 148 mg kg^{-1} (Fe), and accuracy (expressed in terms of relative standard deviation, RSD) was better than 8%.

This treatment of complex samples, rich in organic compounds, through the use of IR was efficient, without residual carbon content and a low acidity in the final digest. In addition, the use of small volumes of diluted nitric acid makes it eco-friendly and recommended to improve the yield and productivity when quantifying the nutritional quality of pork foods. This could be verified by using the analytical eco-scale that is especially important in the search for new green methodologies because it clearly indicates the weaknesses of the analytical procedures.

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EXPLORATORY ANALYSIS OF INORGANIC CONSTITUENTS IN RUMEN FLUID AND FECES OF NELORE BEEF CATTLE

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Beef cattle require high consumption of mineral compounds for the maintenance of their health, production, and reproduction. Some minerals are considered essential, such as Ca, K, Mg, Fe, Zn, and Cu, while others are considered non-essential and may even be considered toxic, depending on their oxidation state, concentration, or species, such as As, Hg, Cd, Pb, and Hg[1,2]. Considering the essential and toxic factors, the determination of the mineral contents is usually required, and for both spectroscopic techniques that require the samples to be in liquid form are used. Thus, the sample preparation is needed, constituting the decisive step, and which presents countless challenges regarding its efficiency. In this context, a protocol for the preparation of ruminal fluid and feces samples of Nelore beef cattle, aiming at the determination of macro and micro minerals by ICP OES and ICP-MS was defined, by using diluted acid microwave-assisted digestion. To 100 mg of sample, the optimized digestion solution was 6 mL of HNO_3 (7 mol L^{-1}) plus 2 mL of H_2O_2 30% (m v^{-1}). The accuracy was assessed by certified reference materials. The samples were provided by a greenhouse nutrition experiment, with cattle submitted to two types of diet; one with high grain content and the other with total grains replacement by byproducts. Due to the large volume of results generated, statistical tests were performed for each evaluated analyte, in order to verify whether there was a statistical difference between the results obtained for animals submitted to the different diets. According to *t*-test, the macro minerals data indicated significant differences for the two evaluated diets for Ca, P, Fe, Mn, Na, Zn, S, K, and Mg in samples of feces. For rumen fluid, the normal distribution results, evaluated by t-test, or by Mann-Whitney for no normal distribution, showed significative differences for Ca, P, Fe, Mn, and Mg. Correlations were observed combining ower data with the ones collected by the partner research groups involved in the research[3]. The use of bioinformatics tools may generate valuable information about potentially functional genes and metabolic pathways related to minerals contents in the bovine tissues and may generate important observations that relate the biota with the generation of greenhouse gases.

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