European Winter Conference on Plasma Spectrochemistry

10-15 February 2013, Krakow, Poland

Department of Analytical Chemistry
Faculty of Chemistry, Jagiellonian University
Krakow 2013

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on Plasma Spectrochemistry
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CONTENTS

Oral presentations

Poster presentations

European Winter Conference
on Plasma Spectrochemistry
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general information

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Mobile phones are active from 9th to 17th February 2013.

CONFERENCE VENUE

Auditorium Maximum, Jagiellonian University
Krupnicza 33, Kraków

The Conference will be held in Auditorium Maximum, Jagiellonian University. All oral and poster presentations, the exhibition, as well as the Welcome Reception, Opening of the exhibition and social mixer and lunches will be organized there.

The Conference Office in Auditorium Maximum UJ will be open from Sunday to Friday during the conference session hours. We kindly inform that admission to Auditorium Maximum UJ is allowed only upon presenting the conference ID badge.

EXHIBITION

During the Conference there will be a display of analytical instrumentation, laboratory equipment and specialist literature. Stalls of the exhibitors will be located on level -1.

Official opening of the exhibition will take place on 11th February at 18:00.

All participants of the conference are cordially invited to the opening of the exhibition joined with a social mixer.

COFFEE BREAKS

Beverages, coffee, tea and snacks will be available for all participants during the Conference. They will be constantly served on level -1 from 10:30 to the last lecture.

PAPERS

Submitted papers, based on oral or poster presentations given at the 2013 Winter Conference on Plasma Spectrochemistry, will be considered for publication as original research papers in a themed issue of JAAS (i.e. full papers, urgent communications or technical notes).

The submission deadline is 1st April 2013.

Submitted manuscripts should be prepared in the format laid out in the "Instructions to Authors" available on the website (www.rsc.org/jaas).

Each manuscript deemed suitable for consideration as a submission will be reviewed by at least two referees, whose names are not disclosed to the authors. Papers will only be accepted if they conform to the normal high standards required for publication in the journal.

Accepted papers will be published on the RSC website as Advance Articles as soon as they are ready. The printed issue is provisionally scheduled to be published in August 2013. A PDF file will be supplied (and distributed) free of charge to the corresponding author of each paper published so that they can produce reprints on demand.

CONFERENCE PRESENTATIONS

Lectures and communications

All multimedia presentations which are to be displayed with the use of conference computers should be prepared in Power Point 2013 format or lower. Participants are kindly requested to pass on their presentations to the service staff at least half an hour before the session during which their presentation will be given, in order to copy them onto the conference computer. Participants who wish to make use of their own computers are requested to test them beforehand to assure correct communication with a multimedia projector in a conference room.

Posters

The maximum dimensions of the posters: 90 cm × 120 cm (width × height). Poster sessions will take place on level -1. The organizers supply all the materials needed to fasten posters onto the boards. The posters should be put up on the morning of the presentation day and removed when the poster session has finished.

Symbol	Explanation	Time	Total number
H	Honorary Lecture	40 + 5 min	7
P	Plenary Lecture	40 + 5 min	5
K	Keynote Lecture	25 + 5 min	10
E	Emerging Scientist Lecture	25 + 5 min	4
O	Oral Presentation	10 + 5 min	99
P	Poster Presentation	90 min	223

LIST OF CONFERENCE PRESENTATIONS

ORAL PRESENTATIONS

SYMBOL AND SECTION TOPIC		H	P	K	E	O	Total number
	Opening session	2					2
A	**Fundamentals and instrumentation**	1	1	2	1	30	35
B	**Stable isotope analysis & HR ICP MS**	1	1	2	1	18	23
C	**Glow discharge**	1	1	2	0	6	10
D	**Elemental speciation**	1	1	2	1	21	26
E	**Laser ablation**	1	1	2	1	24	29
	Total number	**7**	**5**	**10**	**4**	**99**	**125**

POSTER PRESENTATIONS

SYMBOL AND SECTION TOPIC		Total number
F	**Fundamentals and instrumentation**	**17**
G	**Sample preparation and introduction**	**5**
H	**Applications of plasma spectrometry**	**45**
I	**Glow discharge**	**10**
J	**Atomic emission spectroscopy**	**19**
K	**Laser ablation and elemental imaging**	**41**
L	**Isotopic analysis**	**15**
M	**Speciation analysis, metallomics and nanoparticle analysis**	**71**
	Total number	**223**

LUNCH & LEARN SYMPOSIUM

Expand your horizons with Agilent Technologies

Join our interactive symposium on 12th February at 13:00, Auditorium Maximum UJ room F level +2, Krupnicza 33, Krakow, and learn about the benefits and application capabilities of the new technologies, such as the 8800 ICP-QQQ and the 4100 MP-AES. The session will include a panel discussion with key scientists using the latest innovations and will be moderated by Professor Ryszard Łobiński, the National Reaserch Council of France.

SOCIAL EVENTS

Welcome reception

Sunday, 10th February at 19:30, Auditorium Maximum UJ, Hall Level 0

Opening of the exhibition and social mixer

Monday, 11th February at 18:00, Auditorium Maximum UJ, Level -1

During official opening of the exhibitions all participants of the conference are cordially invited to an informal dinner. Traditional Polish cuisine will be served including selected fine liqueurs.

Vendors' event

Agilent Technologies Evening Event Stara Zajezdnia

Meet us on 13th February at 18:30 in Auditorium Maximum UJ, Krupnicza 33, Krakow, to depart for a friendly evening event with our atomic spectroscopy team. Reserve your seat now for our popular user group meeting, with dinner, drinks and music: seats are limited. Don't forget to come to booths no. 8&9 to pick up your evening event free pass.

Thermo Innovation Club Night

Join us on 13th February at the Lizard King Club (entertainment, food and drinks supplied). See the conference bag flyer for registration details and visit the Thermo Scientific booth to collect your entrance ticket. Visit www.thermoscientific.com/ewpc2013

PerkinElmer Users' Event

Let's go underground – take a walk with us through the Rynek Underground Museum.

We will start on 13th February at 18:00 at Main Square 1, Krakow, with a visit of the Rynek Underground Museum followed by a traditional dinner at the foot of the Wawel Hill. Registration/Tickets: available during the Conference at PerkinElmer booths no. 10&11

Sightseeing of Krakow Old Town – guided walk

Wednesday, 13th February
Meeting place: Auditorium Maximum UJ, Krupnicza 33, 8:30

Get to know Krakow with us! All participants of the Conference are invited to a walk through the streets of the Old Krakow. Our guides will show you around the Wawel Cathedral and after we will follow the Kings' Road towards one of the biggest market squares in Europe – the Main Market Square. The guided walk will give you the opportunity to familiarize yourselves with the history of the famous monuments: the medieval cloth hall – Sukiennice, St. Mary's Basilica with the traditional bugle call sounded every hour from the tower, and the oldest buildings of the university district including Collegium Maius Jagiellonian University.

Krakow and the surroundings (Pieskowa Skała) – only for registered accompanying person

Thursday, 14th February
Meeting place: Auditorium Maximum UJ, Krupnicza 33, 8:50

We will visit the Ojców National Park located in the vicinity of Krakow (30 km). Amongst beautiful scenery of limestone rocks and forest lies a medieval castle of Pieskowa Skała overlooking a famous rock formation called Herkules's Club. On our way back to Krakow there will be an opportunity to see a unique shrine on water and have a dinner in a traditional restaurant. Upon return to Krakow we will get familiar with the monuments and the history of the Jewish District and the tour will conclude in the Oscar Schindler's Factory Museum.

Hot plasma party (Zalesie, 15 km from Krakow) – optional

Tuesday, 12th February
Meeting place: Auditorium Maximum UJ, Krupnicza 33, 18:45

You are most welcome to join us at the unforgettable HOT PLASMA PARTY which will take place outside Krakow in 'Folwark Zalesie' Inn – an old farm surrounded by forests, fields and meadows, where you can enjoy a beautiful panorama of the Beskid and the Tatra mountains. The participants will be transported to this magic rural place by bus along a scenic route leading through the Wielickie Foothills. The guests will be welcomed by a folk band playing traditional music and serving the local liqueur, and the group will give a short performance afterwards. Later on, the participants will have an occasion to taste exquisite traditional Polish cuisine including white borsch with egg, grilled meat and many others served with diverse types of salads and a wide variety of drinks.

This very special event, scheduled for the last night of the Carnival 2013, will be accompanied by a band playing folk and traditional dance music.

Conference Gala Dinner (Wieliczka Salt Mine) – optional

Thursday, 14th February
Meeting place: Auditorium Maximum UJ, Krupnicza 33, 18:45

You are cordially invited to the Conference Gala Dinner in the captivating interior of the Wieliczka Salt Mine, one of the most valuable monuments of Polish material and spiritual culture visited each year by more than one million tourists from all over the world. It is a world class monument with more than 700 years of history, featured on the UNESCO’s World Cultural and Natural Heritage List. Dazzling decor of the underground excavations makes the Wieliczka Salt Mine an ideal venue for a banquet with the served dishes cooked on site, in the underground kitchens, and prepared from local top-quality products.

The dinner will take place in the Warszawa Chamber – formed after salt mining, localised ca. 150 m under ground. The participants will be transported from Krakow to Wieliczka by bus. The guests will be welcomed by a salt mine kobold Skarbek and will also receive souvenirs. Miner’s orchestra will be performing before the dinner followed by dance music will be performed after the dinner. With respect to the venue and occasion all participants are kindly requested to wear semi-formal evening dress.

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programme timetable

time	**Sunday**	**Monday**		**Tuesday**		**Wednesday**		**Thursday**		**Friday**		**time**
	Opening of the conference	**Fundamentals and instrumentation**		**Stable isotope analysis & HR ICP MS**		**Glow discharge**		**Elemental speciation**		**Laser ablation**		
8^{30}-8^{45}		Honorary lecture **AH**		Honorary lecture **BH**		Sightseeing of Krakow Old Town		Honorary lecture **DH**		Honorary lecture **EH**		8^{30}-8^{45}
8^{45}-9^{00}												8^{45}-9^{00}
9^{00}-9^{15}												9^{00}-9^{15}
9^{15}-9^{30}		Plenary lecture **AP**		Plenary lecture **BP**				Plenary lecture **DP**		Plenary lecture **EP**		9^{15}-9^{30}
9^{30}-9^{45}												9^{30}-9^{45}
9^{45}-10^{00}												9^{45}-10^{00}
10^{00}-10^{15}		Keynote lecture **AK-1**		Keynote lecture **BK-1**				Keynote lecture **DK-1**		Keynote lecture **EK-1**		10^{00}-10^{15}
10^{15}-10^{30}												10^{15}-10^{30}
10^{30}-10^{45}		Coffee break		Coffee break				Coffee break		Coffee break		10^{30}-10^{45}
10^{45}-11^{00}												10^{45}-11^{00}
11^{00}-11^{15}		Emerging scientist lecture **AE**		Emerging scientist lecture **BE**				Emerging scientist lecture **DE**		Emerging scientist lecture **EE**		11^{00}-11^{15}
11^{15}-11^{30}						Coffee break						11^{15}-11^{30}
11^{30}-11^{45}		Keynote lecture **AK-2**		Keynote lecture **BK-2**				Keynote lecture **DK-2**		Keynote lecture **EK-2**		11^{30}-11^{45}
11^{45}-12^{00}						Honorary lecture **CH**						11^{45}-12^{00}
12^{05}-12^{20}		**A-a01**	**A-b01**	**B-a01**	**B-b01**			**D-a01**	**D-b01**	**E-a01**	**E-b01**	12^{05}-12^{20}
12^{20}-12^{35}		**A-a02**	**A-b02**	**B-a02**	**B-b02**			**D-a02**	**D-b02**	**E-a02**	**E-b02**	12^{20}-12^{35}
12^{35}-12^{50}		**A-a03**	**A-b03**	**B-a03**	**B-b03**	Keynote lecture **CK-1**		**D-a03**	**D-b03**	**E-a03**	**E-b03**	12^{35}-12^{50}
12^{50}-13^{05}		**A-a04**	**A-b04**	**B-a04**	**B-b04**			**D-a04**	**D-b04**	**E-a04**	**E-b04**	12^{50}-13^{05}
13^{05}-13^{15}	Registration open from 13^{00} to 20^{00}	Lunch		Lunch		Lunch		Lunch		Lunch		13^{05}-13^{15}
13^{15}-13^{30}												13^{15}-13^{30}
13^{30}-13^{45}												13^{30}-13^{45}
13^{45}-14^{00}												13^{45}-14^{00}
14^{00}-14^{15}	Short courses session											14^{00}-14^{15}
14^{15}-14^{30}												14^{15}-14^{30}
14^{30}-14^{45}		**A-a05**	**A-b05**	Poster session (section: **F**, **G**, **H**) and exhibition		Poster session (section: **I**, **J**, **K**, **L**) and exhibition		Poster session (section: **M**) and exhibition		**E-a05**	**E-b05**	14^{30}-14^{45}
14^{45}-15^{00}		**A-a06**	**A-b06**							**E-a06**	**E-b06**	14^{45}-15^{00}
15^{00}-15^{15}		**A-a07**	**A-b07**							**E-a07**	**E-b07**	15^{00}-15^{15}
15^{15}-15^{30}		**A-a08**	**A-b08**							**E-a08**	**E-b08**	15^{15}-15^{30}
15^{30}-15^{45}		**A-a09**	**A-b09**							**E-a09**	**E-b09**	15^{30}-15^{45}
15^{45}-16^{00}		Coffee break								**E-a10**	**E-b10**	15^{45}-16^{00}
16^{00}-16^{15}				**B-a05**	**B-b05**	Plenary lecture **CP**		**D-a05**	**D-b05**	**E-a11**	**E-b11**	16^{00}-16^{15}
16^{15}-16^{30}		**A-a10**	**A-b10**	**B-a06**	**B-b06**			**D-a06**	**D-b06**	**E-a12**	**E-b12**	16^{15}-16^{30}
16^{30}-16^{45}		**A-a11**	**A-b11**	**B-a07**	**B-b07**			**D-a07**	**D-b07**	**Closing ceremony**		16^{30}-16^{45}
16^{45}-17^{00}		**A-a12**	**A-b12**	**B-a08**	**B-b08**	Keynote lecture **CK-1**		**D-a08**	**D-b08**			16^{45}-17^{00}
17^{00}-17^{15}	**Opening session**	**A-a13**	**A-b13**	**B-a09**	**B-b09**			**D-a09**	**D-b09**			17^{00}-17^{15}
17^{15}-17^{30}		**A-a14**	**A-b14**			**C-a01**	**C-b01**	**D-a10**	**D-b10**			17^{15}-17^{30}
17^{30}-17^{45}		**A-a15**	**A-b15**			**C-a02**	**C-b02**	**D-a11**				17^{30}-17^{45}
17^{45}-18^{00}						**C-a03**	**C-b03**					17^{45}-18^{00}
18^{00}-18^{15}		Opening of the exhibition and social mixer										18^{00}-18^{15}
18^{15}-18^{30}												18^{15}-18^{30}
18^{30}-18^{45}						Vendors' event						18^{30}-18^{45}
18^{45}-19^{00}				Hot plasma party in Zalesie				Gala dinner in Wieliczka Salt Mine				18^{45}-19^{00}
19^{00}-19^{15}												19^{00}-19^{15}
19^{15}-19^{30}												19^{15}-19^{30}
19^{30}	Welcome reception											19^{30}

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detailed programme

Sunday, 10th February 2013

13:00 – 20:00 REGISTRATION *Hall, Level 0*

14:00 – 16:30 SHORT COURSES SESSION

14:00 SC-1 *Introduction to ICP-MS*
Robert Samuel Houk
Room A, Level 0

14:00 SC-2 *Isotopic analysis via ICP-mass spectrometry: what, how and why*
Frank Vanhaecke
Room B, Level 0

14:00 SC-3 *Quality in analytical sciences*
Ewa Bulska
Room C, Level 0

14:00 SC-4 *From speciation analysis to metallomics*
Maria Montes-Bayón
Room D, Level 0

14:00 SC-5 *Laser ablation ICP MS*
Detlef Günther
Room E, Level 2

17:00 – 19:30 OPENING SESSION *Room A & B*

17:00 *Opening ceremony*
Joanna Szpunar, Paweł Kościelniak

18:00 *Winter Conference on Plasma Spectrochemistry: The background*
Ramon Barnes

18:30 *Plasma Award laudation*
Klaus Heumann

18:45 *Lecture of the Plasma Award laureate*
Norbert Jakubowski

19:30 WELCOME RECEPTION *Hall, Level 0*

Monday, 11th February 2013

SECTION A FUNDAMENTALS AND INSTRUMENTATION

8:30 – 10:30 **SESSION A1** ***Room A***
Chair: Joseph Caruso

8:30 AH *Historical development and recent advances in ICP mass spectrometry*
Robert S. Houk

9:15 AP *Novel models and methods for plasma spectrochemistry*
Gary Hieftje, George Chan, Steven J. Ray, Andrew Schwartz, Yan Cheung

10:00 AK-1 *Development of high performance triple tube concentric nebulizer for plasma spectrometry*
Kazumi Inagaki, Shin-Ichiro Fujii, Shinichi Miyashita, Alexander S. Groombridge, Keisuke Nagasawa, Tetsuya Okahashi, Akiko Takatsu, Koichi Chiba

10:30 – 11:00 Coffee break *Level -1*

11:00 – 12:00 **SESSION A2** ***Room A***
Chair: José Broekaert

11:00 AE *Characterization and application of the thermal inkjet-based aerosol generator as an alternative tool for sample introduction in plasma spectrometry*
Nicolas H. Bings, Jan O. Orlandini v. Niessen, J. Niklas Schaper, Jan H. Petersen, Tobias J. Fiedler

11:30 AK-2 *Selecting plasma source based on multi-electrode systems*
Krzysztof Jankowski

12:05 – 13:05 **PARALLEL SESSION A3-a** ***Room A***
Chair: Andreas Prange

12:05 A-a01 *Improvement of analytical performance of droplet direct injection ICP-TOFMS using desolvation system and high speed data acquisition*
Yuki Kaburaki, Tomokazu Kozuma, Akito Nomura, Takahiro Iwai, Hidekazu Miyahara, Akitoshi Okino

12:20 A-a02 *Organic solvent analysis using a ICP-QQQ-MS (MS/MS capable) inductively coupled plasma-mass spectrometer*
Glenn Woods

12:35 A-a03 *Single-particle analysis using ultra-fast quadrupole ICP-MS*
Hamid Badiei, Kaveh Kahen

12:50 A-a04 *Automatic sample pretreatment instrument for solid phase extraction of trace elements prior to the determination by ICP-MS*
Yanbei Zhu, Akiharu Hioki, Koichi Chiba

12:05 – 13:05 **PARALLEL SESSION A3-b** ***Room B***
Chair: Wolfgang Buscher

12:05 A-b01 *Optimization of geometrical and operating parameters of an inductively coupled plasma mass spectrometer: a computational study*
Maryam Aghaei, Helmut Lindner, Annemie Bogaerts

12:20 A-b02 *Expanding the direct analysis capabilities of plasma-based ambient mass spectrometry sources*
Jacob T. Shelley, Carsten Engelhard

12:35 A-b03 *Technological progress in construction of rotating plasma sources*
Krzysztof Jankowski, Sławomir Piotrowski, Andrzej Ramsza, Edward Reszke, Anna Tyburska-Staniewska

12:50 A-b04 *Dispersed particle extraction – a novel approach for analyte enrichment and matrix removal*
Winfried Nischkauer, Anastassiya Tchaikovsky, Rafael Janski, Marie-Alexandra Néouze, Andreas Limbeck

13:05 – 14:30 Lunch *Level -1*

14:30 – 15:45 PARALLEL SESSION A4-a *Room A*
Chair: Joerg Bettmer

14:30 A-a05 *Detection of cancer markers using surface modified metal/dye-doped magnetic silica nanoparticles in ICP-MS*
Jungaa Ko, Heung Bin Lim

14:45 A-a06 *3D ion optics for ICP-MS*
Iouri Kalinitchenko

15:00 A-a07 *Combination of the inductively coupled plasma and distance-of-flight mass spectrometry: exploring a new chapter in atomic mass spectrometry*
Alexander Gundlach-Graham, Elise A. Dennis, Steven J. Ray, Christie G. Enke, Charles J. Barinaga, David W. Koppenaal, Gary M. Hieftje

15:15 A-a08 *Determination of challenging elements in the context of marine environmental analysis: exploring the potential of ICP-MS-MS*
Daniel Pröfrock, Andreas Prange

15:30 A-a09 *Novel methodological approaches for the accurate and rapid analysis of elemental impurities in pharmaceutical products according to USP 232/233*
Lisa Fischer, Barbara Zipfel, Gunda Koellensperger, Jessica Kovac, Cornel Venzago, Stephan Hann

14:30 – 15:45 PARALLEL SESSION A4-b *Room B*
Chair: Kazumi Inagaki

14:30 A-b05 *Investigation of corrosion product deposits on nuclear fuel rods by means of ICP-MS and electron microscopy*
Ines Günther-Leopold, Marlene Krois, Judith Kobler Waldis, Hanspeter Linder, Sousan Abolhassani Dadras

14:45 A-b06 *Spectrometric techniques applied to the optimization and process control of a pilot plant for the recovery of rare earths from red mud*
Maria Ochsenkühn-Petropoulou, Lambrini Tsakanika, Theopisti Lymperopoulou, Leonidas Mendrinos, Rachel Argyropoulou, Klaus Ochsenkühn

15:00 A-b07 *Inorganic arsenic in seafood: Does the extraction method matter?*
Asta Heidrun Petursdottir, Helga Gunnlaugsdottir, Eva Krupp, Jörg Feldmann

15:15 A-b08 *Dissolution made easy for chromite ores, ferrochromes and chromium slags by peroxide fusions for ICP analyses*
Janice Pitre, Melanie Bedard, John A. Anzelm, Anne-Catherine Breton

15:30 A-b09 *Dynamic extraction of soluble surface layers with on-line ICP-OES detection – a novel approach for determination of depth profiles*
Andreas Limbeck, Ghislain Rupp, Herbert Hutter, Juergen Fleig

15:45 – 16:15 Coffee break *Level -1*

16:15 – 17:45 PARALLEL SESSION A5-a *Room A*
Chair: Maria Ochsenkühn-Petropoulou

16:15 A-a10 *Ultra-fast ICP-OES determinations of major, minor and trace elements in seawater using next generation sample introduction technology*
Glyn Russell, John Cauduro

16:30 A-a11 *Fast semi-quantitative and quantitative direct solids analysis using a fully simultaneous Mattauch-Herzog ICP-MS and transient signal acquisition*
Dirk Ardelt, Willi Barger, Aleksandra Polatajko, Oliver Primm, Maurice Reijnen

16:45 A-a12 *Determination of boron in high-temperature alloy steel using non-linear inter-element correction and microwave plasma – atomic emission spectrometry*
Terrance D. Hettipathirana

17:00 A-a13 *Background levels of metals in urine samples to assist with exposure assessments*
Jackie Morton, Elizabeth Leese, Emma Tan, John Cocker

17:15 A-a14 *Determination of trace-level amounts of lanthanides, thorium, plutonium and americium from uranium samples*
Judit Krajkó, Zsolt Varga, Adrian Nicholl, Maria Wallenius, Klaus Mayer

17:30 A-a15 *Determination of light elements in steel by optical emission spectroscopy*
Myriam Madani

16:15 – 17:45 PARALLEL SESSION A5-b *Room B*
Chair: Daniel Pröfrock

16:15 A-b10 *Microwave assisted high pressure flow digestion: New approaches to solve old problems*
Helmar Wiltsche, Günter Knapp

16:30 A-b11 *Elemental impurity compliance strategy for a large volume parenteral manufacturer*
Michael Fricke, James Fletcher, Neelam Varshney, Martin Hughes

16:45 A-b12 *ICP-MS study of role of microelements in the blood of oncologic patients*
Olesya Kovalenko, Irina V. Boltina

17:00 A-b13 *Optimisation of operative conditions for the determination of silicon concentrations in in vitro and ex vivo biological matrices by DRC-ICP-MS*
Dagmar Koller, Sarah Ratcliffe, Ravin Jugdaohsingh, Jonathan Powell,
Sylvaine Bruggraber

17:15 A-b14 *ICP-MS as monitoring tool to ensure the quality and safety of Norwegian marine fish*
Stig Valdersnes, Daniel Fliegel, Bente M. Nilsen, Sylvia Frantzen, Arne Duinker,
Kåre Julshamn, Amund Maage

17:30 A-b15 *Combining highest sensitivity with selectivity for quadrupole ICP-MS*
René Chemnitzer, Peio Riss, Meike Hamester, Andrew Toms

18:00 OPENING OF THE EXHIBITION AND SOCIAL MIXER *Level -1*

SECTION B STABLE ISOTOPE ANALYSIS & HR ICP MS

8:30 – 10:30		**SESSION B1** ***Room A*** **Chair: Gary Hieftje**
8:30	BH	*Isotope dilution mass spectrometry – an exhausting way from an exotic to a generally accepted method in elemental trace and elemental species determination* Klaus G. Heumann
9:15	BP	*High precision isotope ratio multiple collector ICP MS from planet formation to medicine* Alex N. Halliday, Kathrin Abraham, Jane Barling, Nick Belshaw, Pierre Bonnand, Raphaëlle Escoube, Louise Gall, Fiona Larner
10:00	BK-1	*Unleashing the full power of ICP-MS by exploiting isotopic information* Frank Vanhaecke, Maite Aramendia, Lieve Balcaen, Patrick Degryse, Veerle Devulder, Charo Florez, Lara Lobo, Martin Resano, Lana Van Heghe, Karen Van Hoecke
10:30 – 11:00		Coffee break *Level -1*
11:00 – 12:00		**SESSION B2** ***Room A*** **Chair: Frank Vanhaecke**
11:00	BE	*The potential of isotopic research in analytical ecogeochemistry* Thomas Prohaska, Johanna Irrgeher, Stefanie Kappel, Monika Horsky, Daniel Kofler, Gregor Laaha, Friedrich Leisch, Andreas Zitek
11:30	BK-2	*Mass-independent fractionation occurring in MC-ICPMS: a common phenomenon? And its implication for accurate isotope amount ratio measurements* Lu Yang
12:05 – 13:05		**PARALLEL SESSION B3-a** ***Room A*** **Chair: Peter Fodor**
12:05	B-a01	*Accurate plutonium isotope analysis using SF-ICP-MS provided evidence for the release of plutonium from the fukushima daiichi nuclear power plant accident* Jian Zheng, Keiko Tagami, Shigeo Uchida, Tatsuo Aono, Wenting Bu
12:20	B-a02	*Calibration of absolute* $^{13}C/^{12}C$ *isotope amount ratio measurements by MC-ICPMS using synthetic isotope mixtures* Dmitriy Malinovskiy, Philip Dunn, Heidi Goenaga-Infante
12:35	B-a03	*Precise Hg isotopic composition measurements at ultra-trace level: double stage gold-trap / MC-ICP-MS coupling* Sylvain Berail, Emmanuel Tessier, Zoyne Pedrero, Julien Barre, David Amouroux
12:50	B-a04	*Isotope ratio determinations: high sensitivity for highest precision* Meike Hamester, René Chemnitzer, Andrew Toms

12:05 – 13:05 PARALLEL SESSION B3-b *Room B*
Chair: Michael Sperling

12:05 B-b01 *Isotope ratio mapping by means of LA-single collector-ICPMS: Zn tracer studies in thin sections of daphnia magna*
María Rosario Flórez, Maite Aramendia, Martín Resano, Lieve Balcaen,
Frank Vanhaecke

12:20 B-b02 *Provenance studies on early gold of bronze ages using trace elements and isotope ratios*
Robert Lehmann

12:35 B-b03 *Initial experiments on monitoring two isotopes in single particle ICP-QMS*
Jörg Bettmer, Juris Meija

12:50 B-b04 *Fundamental ion beam study with respect to instrumental mass discrimination in multi-collector inductively coupled plasma mass spectrometry*
Niko Kivel, Ines Günther-Leopold, Frank Vanhaecke, Detlef Günther

13:05 – 14:30 Lunch *Level -1*

14:30 – 16:00 POSTER SESSION (section: F, G, H) AND EXHIBITION *Level -1*

16:00 – 17:15 PARALLEL SESSION B4-a *Room A*
Chair: Yang Lu

16:00 B-a05 *Sulphur metabolism studies with enriched stable isotopes using HPLC coupled to multicollector ICP-MS*
Oscar Galilea San Blas, Juan Manuel Marchante Gayon, J Ignacio Garcia Alonso

16:15 B-a06 *Transgenerational isotopic marking of carp Cyprinus carpio, l. using a ^{86}Sr/^{84}Sr double spike*
Andreas Zitek, Magdalena Cervicek, Johanna Irrgeher, Monika Horsky,
Manfred Kletzl, Thomas Weismann, Thomas Prohaska

16:30 B-a07 *Assesment of iron isotopic composition as a parameter for iron status.*
Lana Van Heghe, Joris Delanghe, Frank Vanhaecke

16:45 B-a08 *Method development for the determination of PBDEs in water samples by IDA-GC-ICP-MS: a new approach to meet the requirements of the EU-WFD?*
Adriana Gonzalez-Gago, Daniel Pröfrock, Andreas Prange

17:00 B-a09 *On the determination of trace elements in lead-bismuth eutectic by means of ICP-SFMS*
Tom Tindemans, Andrew Dobney, Dorine Wambeke, Frank Vanhaecke

16:00 – 17:15 PARALLEL SESSION B4-b *Room B*
Chair: Thomas Prohaska

16:00 B-b05 *Using enriched stable isotopes for traceability purposes: manufactured goods and living organisms*
Mariella Moldovan, Aida Reguera-Galan, Isabel Carames-Pasaron,
Gonzalo Huelga-Suarez, J. Ignacio García Alonso

16:15 B-b06 *Determination of geographical origin of rice based on multi-element fingerprinting by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS)*
Pracha Cheajesadagul, Carine Arnaudguilhem, Juwadee Shiowatana,
Atitaya Siripinyanond, Joanna Szpunar

16:30 B-b07 *Separation method for measurement of cadmium, lead and zinc in vegetal tissue samples by using isotopic dilution with ICP-SFMS*
Maria del Rocio Arvizu-Torres, Edith Valle-Moya, J. Velina Lara Manzano

16:45 B-b08 *Antimony isotopic analysis using multi-collector ICP-MS for provenancing Roman glass*
Lara Lobo Revilla, Patrick Degryse, Frank Vanhaecke

17:00 B-b09 *Highly accurate isotope composition measurements by a miniature laser ablation mass spectrometer designed for space research*
Andreas Riedo

18:45 **HOT PLASMA PARTY IN ZALESIE – optional**
Meeting place: Auditorium Maximum UJ, Krupnicza 33

POSTER SESSION

SECTION F FUNDAMENTALS AND INSTRUMENTATION

FP-1 *Application of MS/MS reaction cell in the newly developed triple quadrupole ICP-MS (ICP-QQQ) for the determination of S, P, Si and Cl in the organic solvents*
Naoki Sugiyama, Tomoyuki Yamada

FP-2 *Common analyte internal standardization (CAIS) as a tool for mass discrimination correction in multi-collector ICP-MS*
Lara Lobo, Veerle Devulder, Karen Van Hoecke, Patrick Degryse, Frank Vanhaecke

FP-3 *Application of the damage-free multi-gas plasma jet to solution analysis*
Takahiro Iwai, Anastasia Albert, Kensuke Okumura, Hidekazu Miyahara, Akitoshi Okino, Carsten Engelhard

FP-4 *Mini colision cell for ICP-MS*
Iouri Kalinitchenko

FP-5 *Numerical simulation of droplet-plasma interactions in an inductively coupled plasma*
Sanaz Arabzadeh, Hamid Badiei, Kaveh Kahen, Javad Mostaghimi

FP-6 *Strategy for optimizing low-temperature plasma ambient ionization for high-resolution mass spectrometry: design of experiments*
Anastasia Albert, Carsten Engelhard

FP-7 *Low-temperature plasma ambient desorption/ionization high resolution mass spectrometry: fundamental study of the ionization characteristics compared to ESI and APCI*
Anastasia Albert, Carsten Engelhard

FP-8 *Detection of nano-sized organic aerosols by time-of-flight mass spectrometry with soft plasma ionization source*
Yoko Nunome, Kenji Kodama, Hyunkook Park, Yasuaki Ueki, Ryo Yoshiie, Sang Chun Lee, Kuniyuki Kitagawa, Ichiro Naruse

FP-9 *Novel approach to life science applications using triple quad ICP-MSMS (ICP-QQQ)*
Amir Liba

FP-10 *Problems in the determination of selenium by ICP-MS in biological material*
Marcin Wieczorek, Maciej Stafiński, Stanisław Walas, Paweł Kościelniak

FP-11 *Evaluation of the collision reaction interface (CRI) for analysis of soil treated with vinasse*
Silmara Bianchi, Joaquim Nóbrega, Ana Nogueira

FP-12 *Low volume injection autosampler for ICP-MS*
David Clarke, Bill Spence, Peter Winship, Damon Green

FP-13 *A specialized desolvating nebulizer and washout system for U-series dating with multicollector ICP-MS*
Fred G. Smith, Peter Winship, Bill Spence, Chad Paton

FP-14 *Intelligent, fully automated auto-dilution for high throughput multielemental analysis by ICP-Q-MS*
Jianfeng Cui, Julian Wills, Lothar Rottmann, Dan Wiederin

FP-15 *Spectral and spatio-temporal characterizations of an atmospheric DBD plasma jet*
Laura Chauvet, Cristina Muja, Bruno Caillier, Laurent Therese, Philippe Guillot

FP-16 *Portable automated separation system for routine purification and/or pre-concentration of radionuclides based on column chromatography*
Mechthild Burow

FP-17 *Ion Optics for ICP-MS*
Iouri Kalinitchenko, Andrew Gaal, XueDong Wang, Meike Hamester, Rene Scemnitzer, Andrew Toms

SECTION G SAMPLE PREPARATION AND INTRODUCTION

GP-1 *Introduction of a novel separation method for uranium and thorium by surface functionalized nanoparticles for uranium age determination*
Anastassiya Tchaikovsky, Andreas Limbeck

GP-2 *Passive sampling as a tool for time-integrated analysis of metal and metal species in marine waters using ICP-MS-MS*
Jördis Petersen, Daniel Pröfrock, José A.C. Broekaert, Andreas Prange

GP-3 *Determination of* ^{90}*Sr at ultratrace levels using an automated chromatographic system coupled to high resolution ICPMS*
Laura Aldave de las Heras, Miguel Sandow, Daniel Serrano-Purroy, Stefaan Van Winckel, Grzegorz Olszewski, Bodgan Skwarzec, Patrick Klemens

GP-4 *Batch and miniaturized column experiments as tools for the safety assessment of a clay based long term waste disposal site for high-level nuclear waste*
Jonas M. Sander, Christina Hein, Ralf Kautenburger, Horst P. Beck

GP-5 *Metal mobility in clay – from batch experiments to miniaturised column experiments with compacted clay*
Ralf Kautenburger, Christina Möser, Jonas Sander, Horst P. Beck

SECTION H APPLICATIONS OF PLASMA SPECTROMETRY

HP-1 *Inductively coupled plasma mass spectrometry (ICP-MS) linked immunoassay using gold nanoparticles (AUNPS) as element tag for chloramphenicol detection*
Purim Jarujamrus, Runglawan Chawengkirttikul, Juwadee Shiowatana, Atitaya Siripinyanond

HP-2 *As quantification in heavy distillates by ICP-MS*
Francesca Bazzano

HP-3 *Ultra-trace analysis of gold and platinum group elements in geological samples using ICP-MS with mixed gases*
Steven Wilbur, Craig Jones

HP-4 *Quantification of critical elements in ferro-chrome silicon/lead tetroxide based delay charge elements from millisecond electric detonators by inductively coupled plasma mass spectrometry*
Franky Puype

HP-5 *Determination of Hg in environmental waters using the Bruker aurora M90 in high sensitivity mode*
Peio Riss, Lionel Lumet

HP-6 *Using ICP-MS for research of hemodialysis procedure on state of blood in patients with Hepatitis C who are on replacement renal therapy*
Olesya Kovalenko, I.V. Boltina, E.O. Pisarev, M.Yu. Khil

HP-7 *Direct analysis of Cr, Ni, Pb and V in ethanol fuel by microwave-induced plasma optical emission spectrometry*
George L. Donati, Renata S. Amais, Daniela Shiavo, Joaquim A. Nóbrega, Shane Elliott

HP-8 *Development of method for trace elements screening in newborn babies blood by inductively coupled plasma mass spectrometry*
Veronique Vacchina, Jean-Marc Perini

HP-9 *Industrial and environmental applications of physicochemical nanometrology*
Mathieu Menta, Christine Glaeyzes, Damien Plaa, Jérôme Frayret

HP-10 *Cognac analysis using the Agilent 4100 microwave plasma-atomic emission spectrometer*
Maud Costedoat, Yolande Abdelnour, Jean-Pierre Lener

HP-11 *Characterisation of nanoparticles release from commercial products by A4F-ICP-MS*
Sara Totaro, Andrea Pigozzo, Laura Manodori, Riccardo Magarini, Enrico Sabbioni

HP-12 *Urinary chromium and nickel in the UK surface engineering industry*
Carmín Chávez, Jorge Guzmán, Aracely Hernández, Laura Hinojosa, Laura Ferrer, Elizabeth Leese, Emma Tan, Matthew Coldwell, Chris Keen, John McAlinden, Jackie Morton

HP-13 *Investigation of saliva as an alternative to blood samples for the biological monitoring of inorganic lead*
Jackie Morton, Kate Jones, James Staff, Erica Guice, Thom McCormick

HP-14 *Uranium measurement in urine with Agilent 7700x ICP-MS*
Sébastien Sannac

HP-15

HP-16 *Quantifying potassium in ultra high purity sodium salts by sector field ICP-MS*
Brad McKelvey

HP-17 *ICP-MS technology – a perfect solution for environmental challenges*
Ewa Pruszkowski, Cynthia Bosnak, Stan Smith

HP-18 *ICP-MS technology – clinical analysis made easy*
Ewa Pruszkowski

HP-19 *Determination of trace rare earth elements in high purity rare earth compounds by ICP-QQQ (ICP-MS/MS)*
Kazumi Nakano, Yasuyuki Shikamori, Naoki Sugiyama

HP-20 *Simultaneous determination of trace elements in high purity steel by triple quadrupole ICP-MSMS (ICP-QQQ)*
Yasuyuki Shikamori, Kazumi Nakano, Tetsuo Nishiyama, Naoki Sugiyama

HP-21 *The determination of major and trace elements in milk using ICP-Q-MS*
Shona McSheehy Ducos, Julian D. Wills, Lothar Rottmann

HP-22 *Determination of selected metals in clinical samples in connection with articular replacemen*
Martin Kuba, David Milde, Tomáš Pluháček, Jiří Gallo

HP-23 *Removal of Titanium based interferences on Nickel, Copper and Zink on ICP-QQQ with MS/MS based reaction technology*
Peter Planitz

HP-24 *ICP-MS detection of hemodialysis influence on trace elements content in whole blood*
M.G. Prodanchuk, Oleksii O. Makarov, E.O. Pisarev, B.S. Sheiman, E.G. Vasileva

HP-25 *ICP-MS trace elements concentration study in whole blood of hemodialysis children with chronic renal failure*
M.G. Prodanchuk, Oleksii O. Makarov, E.O. Pisarev, B.S. Sheiman, E.G. Vasileva

HP-26 *Determination of trace metallic impurities such as phosphorus and titanium in high purity silicon materials by ICP-MS/MS*
Junichi Takahashi, Noriyuki Yamada

HP-27 *ICP-MS analysis of engineered nanoparticles – fundamental characterization and sample preparation strategies*
Anne-Lena Fabricius, Björn Meermann, Lars Düster

HP-28 The determination of titanium in human serum by ICP-MS using dynamic reaction cell technology
David Price, Fadi Abou-Shakra

HP-29 Effect of storage temperature and packaging type on the trace metal analysis of wine
Jenny Nelson, L. Helene Hopfer, Susan E. Ebeler

HP-30 *Determination of selenium in bovine semen by ICP-MS using formic acid for sample preparation*
Silmara Bianchi, Clarice D.B. Amaral, Caroline S. Silva, Joaquim A. Nóbrega, Ana R.A. Nogueira

HP-31 *Attenuation of interferences in collision/reaction cell inductively coupled plasma mass spectrometry, using helium and hydrogen as cell gases – application to multi-element analysis in mastic gum*
Nikolaos Rousis, Paul Nisianakis, Nikolaos S. Thomaidis

HP-32 *Reduction of interferences in the determination of rare earth elements by an octopole collision/reaction cell inductively coupled plasma mass spectrometer – application to the analysis of chios mastic gum*
Nikolaos . Rousis, Paul Nisianakis, Nikolaos S. Thomaidis,

HP-33 *Elemental analysis of semiconductor gases using a gas exchange device coupled to high sensitivity ICP-Q-MS*
Tomoko Vincent, Kohei Nishiguchi, Keisuke Utani, Julian D. Wills, Lothar Rottmann

HP-34 *Investigations on the mechanism of manganese-induced injury of dopaminergic neurons*
Katharina Fernsebner, Bernhard Michalke

HP-35 *Essential metals profile in hair and nails of patients with laryngeal cancer*
Agnieszka Przybyłowicz, Małgorzata Herman, Magdalena Golasik,
Monika Seńczuk-Przybyłowska, Witold Szyfter, Wojciech Golusiński,
Zbigniew Krejpcio, Wojciech Gawęcki, Maksymilian Kulza, Stanisław Walas,
Ewa Florek, Wojciech Piekoszewski

HP-36 *Variation of concentration of selected essential and toxic metals in saliva of people with periodontal disease*
Małgorzata Herman, Magdalena Golasik, Agnieszka Przybyłowicz,
Anna Kurchańska-Flisykowska, Maksymilian Kulza, Paulina Chęsy,
Marzena Wyganowska-Witkowska, Anna Woniak, Monika Seńczuk-Przybyłowska,
Janina Stopa, Halina Mrowiec, Ewa Florek, Wojciech Piekoszewski

HP-37 *Comparison of results for manganese obtained by GF AAS and ICP-MS methods in urine collected from patients addicted from ephedrone and healthy volunteers*
Małgorzata Herman, Joanna Warchoł, Joanna Miąsik, Ewa Gomółka,
Wojciech Piekoszewski, Stanisław Walas

HP-38 *Human hair analysis in relation to similar environmental and occupational exposure*
Małgorzata Iwona Szynkowska, Aleksandra Pawlaczyk, Jadwiga Albińska,
Marta Marcinek, Tadeusz Paryjczak

HP-39 *The release of metal ions from silver-modified dental materials into artificial saliva medium*
Aleksandra Pawlaczyk, Małgorzata Iwona Szynkowska, Krzysztof Sokołowski,
Jerzy Sokołowski, Monika Łukomska-Szymańska, Tadeusz Paryjczak

HP-40 *Analytical problems of determination of rare earth elements in natural waters*
Irena Wysocka, Irena Jaroń, Jarosław Kucharzyk

HP-41 *Elemental analysis of human origin samples by ICP MS and HG AFS for medical diagnostics support*
Emilia Natalia Grygo, Halina Mrowiec, Stanisław Walas, Edyta Daniel,
Anna Stochel-Gaudyn, Krzysztof Fryderek, Paweł Kościelniak

HP-42 *Determination of ^{99}Tc in peat by FI-ICP MS with recovery evaluation on the base of ^{95m}Tc measurement*
Stanisław Walas, Krzysztof Kleszcz, Anna Tobiasz, Halina Mrowiec,
Jerzy Wojciech Mietelski

HP-43 *Triple quaad ICP-MSMS: illuminating the challenges in clinical analyses*
Amir Liba, Pierre Dumas

HP-44 *Trace metal determination in heavy and extra heavy crude oils by ICP MS: comparison of different methods for acid digestion*
Georgia Sanabria-Ortega, Christophe Pecheyran, Gernot Hudin, Edit Marosits,
Olivier F.X. Donard

HP-45 *Quantification of platinum group elements (Pt, Pd and Rh) in roadside soil with ICP MS*
Aleksander M. Schwan, T. Liebminger, Walter Goessler

SECTION C GLOW DISCHARGE

8:30 – 11:15 **SIGHTISEEING OF KRAKOW OLD TOWN**
Meeting place: Auditorium Maximum UJ, Krupnicza 33

11:15 – 11:45 Coffee break *Level -1*

11:45 – 13:00 **SESSION C1** ***Room A***
Chair: Ryszard Łobiński

11:45 CH *The story of the Journal of Analytical Atomic Spectrometry, JAAS, the chronicle of plasma spectrometry*
Les Ebdon

12:35 CK-1 *No joke! Hookah smoke might make you choke*
Joseph Caruso, Ryan Saadawi, Julio Landero-Figueroa, Matthew Winfough, Traci Hanley

13:05 – 14:30 Lunch *Level -1*

14:30 – 16:00 **POSTER SESSION (section: I, J, K, L) AND EXHIBITION** ***Level -1***

16:00 – 17:15 **SESSION C2** ***Room A***
Chair: Freddy Adams

16:00 CP *Pulsed radiofrequency glow discharge time-of-flight-mass spectrometry for gas and solids direct speciation*
Alfredo Sanz-Medel, José Manuel Costa, Beatriz Fernández, Lara Lobo, Auristela Solà; Jorge Pisonero, Nerea Bordel, Rosario Pereiro

16:45 CK-2 *New developments concerning analytical glow discharges*
Volker Hoffmann

17:20 – 18:05 **PARALLEL SESSION C3-a** ***Room A***
Chair: Koichi Chiba

17:20 C-a01 *Atomic emission spectrometry with an atmospheric pressure helium DC glow discharge using various ways of sample introduction*
José Broekaert, Katharina Moß, Klaus-Georg Reinsberg

17:35 C-a02 *Depth-profile analysis of thermoelectric layers on Si wafers by pulsed r.f. glow discharge time-of-flight mass spectrometry*
Klaus-Georg Reinsberg, Christian Schumacher, Agnes Tempez, Kornelius Nielsch, José A.C. Broekaert

17:50 C-a03 *Characterization of a He atmospheric pressure glow discharge for ambient desorption/ionization mass spectrometry*
Jaime Orejas, Jorge Pisonero, Nerea Bordel, Kevin P. Pfeuffer, Steven J. Ray, Gary Hieftje, Alfredo Sanz-Medel

17:20 – 18:05 PARALLEL SESSION B3-b *Room B*
Chair: Alfredo Sanz-Medel

17:20 C-b01 *Development of a new discharge source with a 4-cm cathode size for plasma imaging*
Maxim Voronov, Volker Hoffmann, Tobias Steingrobe, Wolfgang Buscher, Carsten Engelhard, Steven Ray, Gary Hieftje

17:35 C-b02 *New insigths in pulsed-RF-GD-OES: study of the spacial and temporal distributions of excited species and effect of an external magnetic field*
Nerea Bordel, Rebeca Valledor, Paola Vega, Thomas Nellis, Jorge Pisonero

17:50 C-b03 *Development and study of a plain cathode DC discharge source operated in pulse regime current controlled mode*
Olivér Bánhidi

18:30 VENDORS' EVENT

POSTER SESSION

SECTION I GLOW DISCHARGE

IP-1 *Development of imaging detection techniques in glow discharge optical emission spectroscopy*
Tobias Steingrobe, Wolfgang Buscher, Carsten Engelhard, Maxim Voronov, Volker Hoffmann, Steven J. Ray, Gary M. Hieftje

IP-2 *Glow discharge as a tool for the preparation of samples for electron microscopic measurements*
Varvara Efimova, Volker Hoffmann

IP-3 *Quantitative depth profile analysis of amorphous silicon thin film solar cells by pulsed radiofrequency glow discharge optical emission spectrometry*
Pascal Sanchez, Beatriz Fernandez, Armando Menéndez, David Gomez, Rosario Pereiro, Alfredo Sanz-Medel

IP-4 *The evaluation of the analytical performance of atmospheric pressure microdischarge generated between microjet and a liquid cathode*
Piotr Jamróz, Krzysztof Gręda, Paweł Pohl, Wiesław Żyrnicki

IP-5 *The effect of the addition of non-ionic surfactants to the solution on the analytical performance of the miniaturized atmospheric pressure glow-discharge generated in contact with a liguid cathode*
Krzysztof Gręda, Piotr Jamróz, Paweł Pohl

IP-6 *A new catalogue of glow discharge spectra – the current state*
Zdeněk Weiss, Edward Steers, Juliet Pickering, Volker Hoffmann

IP-7 *Matrix effects in glow discharge emission spectroscopy caused by hydrogen*
Zdeněk Weiss

IP-8 *Development of new ionization sources for DMA: comparative study of photoionization and APGD sources*
Marcos Bouza, Jaime Orejas, Silvia Lopez-Vidal, Eladio Montoya, Jorge Pisonero, Nerea Bordel, Rosario Pereiro, Alfredo Sanz-Medel

IP-9 *Application of pulsed GD-TOFMS as a powerful screening tool for conductive polymers chemical identification*
Claudia González de Vega, Beatriz Fernández, Nerea Bordel, Rosario Pereiro, Alfredo Sanz-Medel

IP-10 *Full survey chemical analysis of thin films with pulsed fast flow glow discharge mass spectrometry*
Joachim Hinrichs, Lothar Rottmann, Karol Putyera

SECTION J ATOMIC EMISSION SPECTROSCOPY

JP-1 *Ultrasound focused extraction and element quantification in middle light petroleum distillates by ICP-AES and ICP-MS*
Francesca Bazzano, Monica Angela Anelli

JP-2 *Silicon determination in diesel and biodiesel by microwave-induced plasma optical emission spectrometry*
Renata Amais, George Donati, Daniela Shiavo, Joaquim Nobrega, Shane Elliott

JP-3 *Determination of palladium content in valacyclovir hydrochloride using inductively coupled plasma – optical emission spectrometer with AGM-1 (Auxiliary Gas Module)*
Dharmendra Vummitti, Jean-Pierre Lener

JP-4 *Vegetable oil analysis for biodiesel production using the Agilent 4100 microwave plasma – atomic emission spectrometer*
Maud Costedoat, Yolande Abdelnour, Jean-Pierre Lener

JP-5 *Comparative study of different methodologies of transient signal processing for determination of chromium by SPME-TD-plasma-OES*
Krzysztof Jankowski, Stanisław Kuś

JP-6 *Properties of a KHz frequency nitrogen miniplasma for trace analysis by atomic spectroscopy*
Krzysztof Jankowski, Edward Reszke

JP-7 *Application of ICP OES to the examination of postmortem material in a case of poisoning with an iodine compound*
Teresa Lech

JP-8 *Mercury determination in biological materials by ICP OES in cases of metallic mercury intoxication*
Józefa Krystyna Sadlik

JP-9 *Real-time RF power monitoring of process chamber by self-plasma optical emission spectroscopy*
Go Eun Kim, Seol Gwak

JP-10 *Development of a tungsten boat furnace for the simultaneous determination of Ag, Bi, Pb, Te and Zn in nickel super alloys using ICP-OES*
Paul Tirk, Helmar Wiltsche

JP-11 *Determination of main metals and contaminating elements in various high performance passivates by microwave plasma atomic emission spectrometry*
Hans-Dieter Projahn, Josefine Hauk

JP-12 *Analysis of liquid foodstuffs and beverages by means of dried-droplet laser ablation ICP-OES*
Winfried Nischkauer, Frank Vanhaecke, Johann Lohninger, Andreas Limbeck

JP-13 *Matrix effect overcoming in ICP and DCP-ARC -atomic-emission environmental analysis*
Olga Shuvaeva

JP-14 *Advances in liquid sample introduction in ICP-OES: a new efficient prototype for reduced sample consumption*
Nikolay Kovachev, Montserrat Hidalgo, Terrance D. Hettipathirana, Jean-Pierre Lener, Antonio Canals

JP-15 *Determination of mercury in soils and sediments after preconcentration of mercury vapor by SPME followed by thermal desorption and OES detection*
Monika Truskolaska, Krzysztof Jankowski, Edward Reszke

JP-16 *Investigation of usefulness of different elements potentially applied as internal standards in ICP-OES measurements*
Weronika Bureć-Drewniak, Jarosław Kucharzyk, Irena Jaroń

JP-17 *Determination of selected elements in FAME by ICP OES technique using internal standard method performed in continuous flow system*
Marek Kozak, Joanna Kozak

JP-18 *Application ICP OES and ICP MS spectrometry for plant quality evaluation*
Anna Tobiasz, Maria Filek, Halina Mrowiec, Apolonia Sieprawska, Stanisław Walas, Helina Hartikainen

JP-19 *Determination of rare earth elements in electronic waste using ICP-OES spectrometry*
Uwe Oppermann, Jürgen Schram, Jan Knoop

SECTION K LASER ABLATION AND ELEMENTAL IMAGING

KP-1 *Imaging and quantification analysis of the elements in peanut seeds*
Yanbei Zhu, Akiharu Hioki, Koichi Chiba

KP-2 *Elemental mapping using the simultaneous DP-LIBS and LA-ICP-OES setup*
Karel Novotný, Kateřina Štěpánková, Lucie Krajcarová, Aleš Hrdlička, Jozef Kaiser, Viktor Kanický

KP-3 *Bioimaging techniques of metals by laser ablation inductively coupled plasma mass spectrometry for diagnosis of fibrotic liver disorders*
M-M. Pornwilard, Ralf Weiskirchen, Nikolaus Gassler, J. Sabine Becker

KP-4 *Challenging the spatial resolution limits of high-resolution mapping in laser ablation-inductively coupled plasma-mass spectrometry using active 2-volume cells.*
Dhinesh Asogan, Damon Green, Stephen Shuttleworth, John Roy, Bill Spence, Peter Winship

KP-5 *Bioimaging of rice tissue with the use of a laser ablation system coupled with to Agilent 7700x ICP-MS*
Sébastien Sannac

KP-6 *Examination of writing inks by LIBS technique for forensic purpose*
Agnieszka Kula, Katarzyna Pasionek, Renata Wietecha-Posłuszny, Małgorzata Król, Michał Woźniakiewicz, Paweł Kościelniak

KP-7 *Development of a polymer binder and a pellet presser for the analysis of powdered solid samples by LA-ICP-MS*
Yanbei Zhu, Akiharu Hioki, Koichi Chiba

KP-8 *Laser ablation ICP-MS study of prospective glass internal reference materials*
Monika Jarošova, David Milde, Petr Sulovský

KP-9 *Analysis of human kidney stones: elemental association, identification of various constituents and quantitative analysis by LA-ICP-MS*
Michaela Vasinova Galiova

KP-10 *Optimization and validation of a laser ablation inductively coupled plasma mass spectrometry method for determination of Cd, Cu, Pb and Zn in plants*
Anetta Hanć, Danuta Barałkiewicz

KP-11 *Development and application of metal-tagged antibodies for immuno-imaging by use of LA-ICP-MS*
Simone Hardt, Christian Scheler, Norbert Jakubowski, Larissa Waentig, Boris Neumann, Guido Sauter, Hartmut Schlueter, Michael Linscheid

KP-12 *Elemental analyses of soils and sediments fused with lithium borate using isotope dilution laser ablation ICP-MS*
Julien Malherbe, Fanny Claverie, Beatriz Fernandez, Aitor Alvarez, Rosario Pereiro, Alfredo Sanz-Medel, John L. Molloy

KP-13 *Effects of helium flow geometry on elemental fractionation in laser ablation ICP-MS*
Jay Thompson, Leonid Danyushevsky, Mike Shelly, Sarah Gilbert

KP-14 *A single software platform for LA-ICP-MS applications using a new high sensitivity ICP-Q-MS*
Julian Wills, Lothar Rottmann, Steve Shuttleworth

KP-15 *Advances in development of non denaturating gel electrophoresis technique for uranium-protein complexes quantitative analysis by LA-ICP MS*
Ming Xu, Sandrine Frelon, Olivier Simon, Ryszard Łobiński, Sandra Mounicou

KP-16 *Utilization of laser ablation inductively coupled plasma mass spectrometry for elemental mapping biological tissues*
Tomas Vaculovic, Pavlina Sobrova, Jan Strnadel, Vratislav Horak, Lenka Vyslouzilova, Viktor Kanický, Rene Kizek, Vojtech Adam

KP-17 *Aliasing effects in laser ablation ICP MS: sequential detection vs. low dispersion*
Urs Hartfelder, Bodo Hattendorf, Detlef Günther

KP-18 *Advantages of high sensitivity ICP-MS coupled to laser ablation*
Andrew Toms, René Chemnitzer, Meike Hamester

KP-19 *Silver nanoparticles toxicity studies by PAGE-LA-ICP-MS*
Maria S. Jimenez, Maria T. Gómez, Carmen Diez, Aurora Avellana, Lluis Arola, M. Josepa Salvadó, Cinta Bladé, Juan Ramón Castillo

KP-20 Study of elemental fractionation using 1030 nm and 257 nm high repetition rate FSLA/ICPMS
Ariane Donard, Fanny Claverie, Fabien Pointurier, Christophe Pécheyran

KP-21 *Development of fast quantitative analysis for biological samples using LA-ICP-MS technique*
Eva Kovacs-Szeles

KP-22 *Elemental analysis by a miniature laser ablation/ionisation mass spectrometer, LMS*
Marek Tulej, Andreas Riedo, Maike Neuland, Stefan Meyer, Peter Wurz

KP-23 *Evaluation of ^{87}Sr/^{86}Sr isotopic ratios in fish scale hydroxyapatite by femtosecond laser ablation coupled to an MC –ICPMS*
Ariane Donard, Christophe Pécheyran, Sylvain Bérail, Marc Pouilly

KP-24 *Laser ablation ICP-MS of cell lysates after silver nanoparticle treatment: Is quantification possible?*
Frank S. Bierkandt, Philipp Reichardt, Andrea Haase, Harald Jungnickel, Jutta Tentschert, Andreas Luch, Norbert Jakubowski

KP-25 *Multivariate optimization of extraction parameters in single-drop microextraction followed by laser-induced breakdown spectrometry for trace elemental analysis of water samples*
Miguel Ángel Aguirre, Hristina Nikolova, Montserrat Hidalgo, Antonio Canals

KP-26 *Particles produced by laser ablation for profiling titanium nitride coated silica*
Jin Sook Lee, Heung Bin. Lim

KP-27 *Method development for a minimal invasive investigation of ancient copper alloys and formated corrosion layers using laser ablation inductively coupled plasma mass spectrometry*
Damian Walaszek, Adrian Wichser, Markus Faller, Marianne Senn, Laetitia Phillipe, Barbara Wagner, Ewa Bulska, Andrea Ulrich

KP-28 *LA-ICP-MS and PIXE-PIGE studies of glass beads – new insight into the fingerprinting of museum objects*
Malgorzata Iwona Szynkowska, Aleksandra Pawlaczyk, Stanisław Sypniewski, Geoffrey Grime, Michael Merchand, Melanie Bailey, Wojciech Chudziak, Małgorzata Markiewicz

KP-29 *LA-ICP-TOF-MS investigations of papers*
Małgorzata Iwona Szynkowska, Aleksandra Pawlaczyk, Katarzyna Palińska, Marcin Kunicki, Andrzej Parczewski

KP-30 *Analysis of paper and gel inks by LA-ICP-MS and SEM techniques using chemometric approach*
Małgorzata Iwona Szynkowska, Paulina Chęsy, Aleksandra Pawlaczyk, Marcin Kunicki, Andrzej Parczewski

KP-31 *Application of LA-ICP-TOF-MS technique in forensic ink studies*
Małgorzata Iwona Szynkowska, Aleksandra Pawlaczyk, Katarzyna Palińska, Marcin Kunicki, Andrzej Parczewski

KP-32 *Characterization and quantification of tio2 nano particles in sunscreen lotion using laser diffraction and ICP- OES spectrometry*
Uwe Oppermann, Jürgen Schram, Jan Knoop

KP-33 *Diode laser thermal vaporization inductively coupled plasma mass spectrometry for analysis of biological microsamples*
Pavla Foltynová, Viktor Kanický, Jan Preisler

KP-34 *Extracting oil inclusions by femtosecond laser ablation for GC-MS analysis*
Fanny Claverie, Sebastien Dreyfus, Robert Pottorf, Ngami Phan, Marlene Madincea, Christophe Pecheyran

KP-35 *Short-range remote LIBS through a shielding window for monitoring nuclear waste materials*
Daewoong Choi, Yongdeuk Gong, Yonghoon Lee, Bo-Young Han, Heesung Shin

KP-36 *Utilization of laser-induced breakdown spectroscopy (LIBS) for fast online determination of elements of interest in minerals*
David Prochazka, Jan Novotný, Radomír Malina, Jindřich Kynický, Karel Novotný, Petr Babula, Vojtech Adam, René Kizek, Jozef Kaiser

KP-37 *High spatial resolution elemental mapping using fs-LA-ICP-MS and fs-LIBS*
Jhanis .J. Gonzalez, V. Zorba, D. Oropeza, X. Mao, R.E. Russo

KP-38 *Development of the mobile stand-off laser-induced breakdown spectroscopy setup*
Jan Novotny, Michal Brada, Jozef Kaiser, Karel Novotný, Aleš Hrdlička, Radomír Malina, David Prochazka, Michal Petrilak

KP-39 *Analytical benefits of a rotating XY shutter and an infinitely variable aperture for laser ablation sampling*
Ciaran O’Connor, Katherine McLachlin, Rob Hutchinson

KP-40 *Analysis of high-purity cu using high-sensitivity LA-ICP-MS*
K. Warnken, J.D. Wills, L. Rottman, Ciaran O’Connor, R. W. Hutchinson

KP-41 *High throughput analysis of industrial grade nimonic alloys using LA-ICP-OES*
Katherine McLachlin, Jayme Curet, Rob Hutchinson, Ciaran O’Connor

SECTION L ISOTOPIC ANALYSIS

LP-1 *Lead isotope analysis: removal of* ^{204}*Hg isobaric interference from* ^{204}*Pb using a quadrupole ICP-MS equipped with MS/MS technology*
Glenn Woods

LP-2 *Application of Sr isotope ratios for the determination of origin of prehistoric wood*
Monika Horsky, Johannes Tintner, Michael Grabner, Kerstin Kowarik, Hans Reschreiter, Anton Kern, Thomas Prohaska

LP-3 *Measuring* ^{26}*Mg/*^{24}*Mg and* ^{44}*Ca/*^{40}*Ca isotope ratios in environmental samples by Q-ICP-MS*
Gregory Van Der Heijden, Benoît Pollier, Etienne Dambrine, Peio Riss, Arnaud Legout

LP-4 *Strontium isotopic analysis of human skeletal tissue in a present-day forensic context*
Kris Latruwe, Patrick Degryse, Frank Vanhaecke

LP-5 *Isotope dilution analysis for foraminiferal Mg/Ca paleothermometry*
Marco Roman, Patrizia Ferretti, Clara Turetta, Warren Cairns, Carlo Barbante

LP-6 *Determination of* ^{129}*I/*^{127}*I in Fukushima soil samples by ICP-MS*
Takeshi Ohno, Yasuyuki Muramatsu, Chiaki Toyama, Hiroyuki Matsuzaki

LP-7 *Determination of isotopic ratios of uranium (*^{235}*U/*^{238}*U) for the different origins in Barcelona's tap water distribution system in order to determine the source of a water leak*
Alfredo Diaz, Ricard Devesa, Jordi Martin-Alonso

LP-8 *Alternative method for fast and precise Pb isotope ratio determination in crude oil, asphaltenes kerogen and sedimentary rocks by GC-MC-ICPMS*
Georgia Sanabria, Christophe Pécheyran, Sylvain Berail, Olivier F.X. Donard

LP-9 *Challenges for mass fraction measurements of* ^{166m}*Ho using ion-counting multi-collector ICP-MS and isotope dilution*
Geerke Floor, Florence Guéguen, Hélène Isnard, Christophe Quétel

LP-10 *Isotope dilution mass spectrometry as a new strategy for quantitative elemental analysis of soils and sediments by pulsed glow discharge time of flight mass spectrometry*
Beatriz Fernandez, Aitor Alvarez, Julien Malherbe, Fanny Claverie, John L. Molloy, Rosario Pereiro, Alfredo Sanz-Medel

LP-11 *Accurate quantification of mercury in marine samples by using isotope dilution high resolution inductively coupled plasma mass spectrometry*
Emiliya Vassileva

LP-12 *Elimination of isobaric interferences in lead isotopic ratio determination of ancient gold samples using reaction cell mode for ICPMS*
Andrea Ulrich, Adrian Wichser, Glenn Woods, Uwe Nötzel

LP-13 *Determination of Pu atom ratio in settling particles using isotope dilution HR-ICP-MS*
Masatoshi Yamada, Jian Zheng

LP-14 *A comparative study of iron isotopic ratios in transgenic and non transgenic soybean by ICP-MS*
Silvana Oliveira, Amauri Menegário, Marco Aurélio Zezzi Arruda

LP-15 *Bromine isotope analysis-a tool for investigating biogeochemical cycle of bromine-containing organic and inorganic compounds in the environment*
Faina Gelman, Anat Bersnstein, Elena Levin, Ludwik Halicz, Zeev Ronen

SECTION D ELEMENTAL SPECIATION

8:30 – 10:30 **SESSION D1** ***Room A***
Chair: Norbert Jakubowski

8:30 DH *Fifty years of plasma analysis and imaging, personal recollections*
Freddy Adams

9:15 DP *Are we studying the important element species or only those we can measure?*
Jörg Feldmann, Eva M. Krupp, Andrea Raab, Dagmar S. Urgast

10:00 DK-1 *Field-flow fractionation with atomic spectrometric detection for characterization of engineered nanoparticles*
Atitaya Siripinyanond, Kanchana Songsilawat, Atitaya Samontha, Supharart Sangsawong, Wilaiwan Somchue, Pornwilard M-M, Panida Wimuktiwan, Jakarwan Yostawonkul, Ju-Wadee Shiowatana

10:30 – 11:00 Coffee break *Level -1*

11:00 – 12:00 **SESSION D2** ***Room A***
Chair: Gunda Koellensperger

11:00 DE *Association of ICP MS and high resolution ESI MS for speciation analysis: a powerful tool for developing novel analytical methods*
Laurent Ouerdane, Ryszard Łobiński

11:30 DK-2 *Size fractionated chemical analysis of engineered nanoparticles using plasma mass spectrometry*
Andrea Ulrich, Sabrina Losert, Nina Bendixen, Adrian Hess

12:05 – 13:05 **PARALLEL SESSION D3-a** ***Room A***
Chair: Francesco Cubadda

12:05 D-a01 *Titanium monitoring in biological fluids of patients with metallic implants: from ions to nanoparticles*
Maria Montes-Bayón, Yoana Nuevo-Ordoñez, Juan Soto-Alvaredo, Joerg Bettmer, Elisa Blanco-González, Alfredo Sanz-Medel

12:20 D-a02 *Am I working with a nanomaterial? How to get the answer by single particle ICP-MS*
Francisco Laborda, Javier Jimenez-Lamana, Eduardo Bolea, Juan R. Castillo

12:35 D-a03 *Zinc speciation in the cereal grain*
Daniel Persson, Thomas Hesselhøj Hansen, Jan K. Schjoerring, Søren Husted

12:50 D-a04 *ICP-MS determination of metals/metalloids and analytical speciation of arsenic in a stream that receives drainages of abandoned silver mines in Guanajuato, central Mexico*
Katarzyna Wróbel, Yann René Ramos Arroyo, Iraís Rodríguez Huerta, Eunice Yañez Barrientos, Alma Hortensia Serafin Muñoz, Kazimierz Wróbel

12:05 – 13:05 PARALLEL SESSION D3-b ***Room B***
Chair: José Luis Gómez-Ariza

12:05 D-b01 *Size-based element speciation of nanomaterials in food: the potential of combining asymmetric flow FFF with ICP-MS, light scattering and electron microscopy*
Heidi Goenaga Infante, Julien Heroult, Dorota Bartczak, Volker Nischwitz

12:20 D-b02 *Method development for toxicokinetics and tissue distribution of nano-TiO_2 by high resolution inductively coupled plasma mass spectrometry (HR-ICPMS)*
Petra Krystek, Willem den Otter, Henny Verharen, Esther Brandon, Wim de Jong

12:35 D-b03 *Characterization and stability studies of silver ion and silver nanoparticles. Bioconcentration by zebrafish larvae*
Ana López Serrano, Jon Sanz Landaluze, Riansares Muñoz-Olivas, Carmen Cámara

12:50 D-b04 *Chemistry of silver nanoparticles in burns healing: from in vitro to in vivo by ICP-MS*
Chiara Rigo, Warren Cairns, Letizia Ferroni, Barbara Zavan, Marco Roman,
Carlo Barbante, Vincenzo Vindigni, Ivan Munivrana, Bruno Azzena

13:05 – 14:30 Lunch *Level -1*

14:30 – 16:00 POSTER SESSION (section: M) AND EXHIBITION ***Level -1***

16:00 – 17:45 PARALLEL SESSION D4-a ***Room A***
Chair: Maria Montes-Bayón

16:00 D-a05 *Determination of Ti from TiO_2 manufactured nanoparticles in biological materials by Q-ICP-MS: optimization and validation*
Yacine Nia, Sandrine Millour, Laurent Noël, Thierry Guerin

16:15 D-a06 *Metallomic and metabolomic study of antagonistic metal interactions in mice mus musculus under controlled exposure*
Miguel-Angel Garcia-Sevillano, Rocio Jara-Biedma, Tamara Garcia-Barrera,
José Luis Gómez-Ariza

16:30 D-a07 *Determination of silver nanoparticles in foodstuff using AF4-UV-Vis/ICP-MS and TEM*
Karim Ramos, M. Milagros Gómez-Gómez, Lourdes Ramos, Carmen Cámara

16:45 D-a08 *Plasma-based instrumentation for ambient mass spectrometry and nanoparticle characterization*
Carsten Engelhard, Anastasia Albert, Britta Vortmann, Bastian Franze,
Jacob T. Shelley, Ingo Strenge

17:00 D-a09 *Comparison of different methods for investigation of metallic engineered nanoparticles*
Sabrina Gschwind, Harald Hagendorfer, Olga Borovinskaya, Detlef Günther

17:15 D-a10 *Development of LC-ICP-MS based immunoassays for targeted analysis of biological samples*
Daniela Kretschy, Gunda Koellensperger, Stephan Hann

17:30 D-a11 *Determination of selenomethionine in ambient waters*
Kelly Lynn LeBlanc, Dirk Wallschläger

16:00 – 17:30 PARALLEL SESSION D4-b *Room B*
Chair: Heidi Goenaga Infante

16:00 D-b05 *Future prospective of spectrochemical analysis in bioinorganic trace and speciation analysis: from macro to microanalytics*
Henryk Matusiewicz

16:15 D-b06 *SeMeSeCys metabolism in rats fed with ^{77}Se-enriched sauerkraut*
Maria Sánchez Martínez, Teresa Pérez Corona, Cristina Martín Villaluenga, Juana Frías, Concepción Vidal Valverde, Jesús Porres, Gloria Urbano, Carmen Cámara, Yolanda Madrid

16:30 D-b07 *Challenges in nanotoxicological studies of silicon and titanium dioxide using an analytical platform based on reaction cell ICP-MS as elemental detector*
Federica Aureli, Angela Sorbo, Marilena D'Amato, Gabriele Moracci, Andrea Raggi, Anna Chiara Turco, Francesco Cubadda

16:45 D-b08 *Hyphenated techniques using plasma mass spectrometry to study the transport, distribution and metabolism of metallodrugs*
Michael Sperling, Christine Brauckmann, Miriam Schwarzer, Olga Reifschneider, Christoph A. Wehe, Uwe Karst

17:00 D-b09 *Quantitative determination of arsenic metabolite-protein interaction by elemental speciation analysis*
Gerrit Hermann, Petra Heffeter, Walter Berger, Stephan Hann, Gunda Koellensperger

17:15 D-b10 *The use of CCT mode with the iCAP Q ICP-MS: Sensitivity improvement by collisional focusing and effective reaction chemistry in challenging IC-ICP-MS based speciation applications*
Daniel Kutscher, Julian D. Wills, Lothar Rottmann

18:45 GALA DINNER IN WIELICZKA SALT MINE – optional
Meeting place: Auditorium Maximum UJ, Krupnicza 33

POSTER SESSION

SECTION M SPECIATION ANALYSIS METALLOMICS AND NANOPARTICLE ANALYSIS

MP-1 *Metallothiolomics – investigation of thiol peptide regulated metal homeostasis in algae by LC-ESI MS, LC-ICP MS and element imaging techniques*
Dirk Schaumlöeffel, Marie-Pierre Isaure, Gerd-Joachim Krauss, Dirk Dobritzsch

MP-2 *Analysis of lanthanide labelled protein digests via RP-IP-nanoHPLC coupled to ICP-MS and MALDI-MS*
Angela Holste, Andreas Tholey, Dirk Schaumlöffel

MP-3 *Silver nanoparticle characterization and stability assessment thereof in cell culture media by ICP-MS in single particle mode*
Bastian Franze, Ingo Strenge, Christoph A. Wehe, Carsten Engelhard

MP-4 *Study of arsenic species occurrence in Spanish daily food consumption*
Maria Pérez-Vizcaya, Macarena González-Fernandez, Tamara García-Barrera,
José Luis Gómez-Ariza

MP-5 *Combined techniques: LC-ICP MS and LC-ESI-LTQ Orbitrap MS as a powerful tool to investigate elements speciation in plants*
Paulina Flis, Laurent Ouerdane, Ryszard Łobiński

MP-6 *Phytochelatins production in microalgae chlorella sorokiniana in response to metals*
Veronica Gómez-Jacinto, Tamara García-Barrera, Inés Garbayo-Nores,
Carlos Vilchez-Lobato, José Luis Gómez-Ariza

MP-7 *Characterization of metals bound to marine dissolved organic matter by size exclusion and anion exchange HPLC hyphenated with ICP-MS*
Antonio Moreda-Piñeiro, Pilar Bermejo-Barrera, Natalia García-Otero

MP-8 *Water soluble halides speciation in atmospheric particulate matter by anion exchange HPLC-ICP-MS after pressurized hot water extraction*
Antonio Moreda-Piñeiro, Pilar Bermejo-Barrera, Jorge Moreda-Piñeiro,
Elia Alonso-Rodríguez, Purificación López-Mahía, Soledad Muniategui-Lorenzo,
Darío Prada-Rodríguez

MP-9 *Speciation analysis of chromium in drinking water samples based on ion-pair reserved-phase HPLC-ICP-MS: full validation of the analytical method*
Barbara Pikosz, Magdalena Belter, Monika Marcinkowska, Danuta Barałkiewicz

MP-10 *Species stability – speciation analysis of chromium: A case study of water samples from surroundings of Radom*
Barbara Pikosz, Monika Marcinkowska, Danuta Barałkiewicz

MP-11 *Speciation analysis of sugar phosphates via anion exchange chromatography combined with ICP-DRC MS*
Chu Dinh Binh, Kristaps Klavins, Stephan Hann, Gunda Koellensperger

MP-12 *Phosphorus-tagged metabolomics for analysis of phospholipids in Alzheimer's disease*
Raúl González-Dominguez, Tamara Garcia-Barrera, José Luis Gómez-Ariza

MP-13 *Combination of metabolomics and metallomics in P. clarkii tissues to assess the pollution in Doñana National Park*
Amanda Gago-Tinoco, Raúl González-Domínguez, Tamara García-Barrera,
Julian Blasco-Moreno, José Luis Gómez-Ariza

MP-14 *Characterization of metallothioneins in mouse liver under cadmium exposure*
Rocio Jara-Biedma, Raúl González-Domínguez, Tamara García-Barrera,
José Luis Gómez-Ariza

MP-15 *Speciation analysis of mercury, tin and lead based on a novel microwave-induced plasma excitation source as detector in gas chromatography*
Wolfgang Buscher, Rasmus Janzen, Michael Sperling, Joerg Ehlbeck, Andre Bösel, Susanne Lischka, Christian Piechotta

MP-16 *Mass spectrometry techniques (CE-ICP-MS, ESI-MS) in probing of ruthenium anticancer drug mechanism of action under conditions simulating human blood and cancer cytosol environments*
Magdalena Matczuk, Xifeng Lu, Katarzyna Pawlak, Svietlana Aleksenko, Lidia Foteeva,
Andrei Timerbaev, Maciej Jarosz

MP-17 *Size exclusion chromatography and size migration capillary electrophoresis coupled with ICP MS for separation of phytochelatins complexes*
Agata Miszczak, Magdalena Matczuk, Magdalena Rosłon, Katarzyna Brama,
Katarzyna Pawlak

MP-18 *Speciation analysis of cobalt and manganese in various diet supplements*
Justyna Wojcieszek, Magdalena Matczuk, Lena Ruzik

MP-19 *Metallomic and metabolomic study of laboratory mouse mus musculus under experiment exposure to evaluate arsenic/cadmium interactions*
Miguel-Ángel García-Sevillano, Tamara García-Barrera, José Luis Gómez-Ariza

MP-20 *Speciation and metabolism of organotin compounds in zebrafish larvae*
Ana López-Serrano Oliver, Aline Rocha Borges, Mercedes Gallego-Gallegosa,
Riansares Muñoz-Olivas, Carmen Cámara

MP-21 *Use of metallomics, metabolomics and redox proteomics in environmental metal pollution assessment using mus spretus mice from Doñana National Park as bioindicator*
Miguel Ángel García-Sevillano, Tamara García-Barrera, Francisco Navarro-Roldán,
José Luis Gómez-Ariza

MP-22 *Trace-level speciated analysis of chromium(III) and chromium(VI) using LC-ICP-MS*
Miao Jing, Juane Song, Zhi-xu Zhang, Yan Dong

MP-23 *Automated multiple extraction procedure coupled on-line to ICP-OES for assessment of bio-accessible trace metal fractions in airborne particulate matter*
Victoria Mohr, Manuel Miró, Andreas Limbeck

MP-24 *Natural reactions to naturally high selenium availability: complexity of Se-metabolites in lecythidaceae nuts*
Anikó Németh, Juan Francisco García-Reyes, Judit Kosáry, Mihály Dernovics

MP-25 *Chromium speciation in feed samples*
Véronique Vacchina, Fabienne Seby

MP-26 *SEC (DAD) ICP-MS for the metal-proteins interaction studies*
Warren R.L. Cairns, Sara Crotti, Carlo Barbante

MP-27 *Anion exchange HPLC–ICP-MS for the speciation of bioavailable selenium from seafood*
Antonio Moreda-Piñeiro, Vanessa Romarís-Hortas, Raquel Domínguez-González,
Pilar Bermejo-Barrera, Jorge Moreda-Piñeiro, Elia Alonso-Rodríguez,
Puificación López-Mahía, Soledad Muniategui-Lorenzo, Darío Prada-Rodríguez

MP-28 *Multielemental determination of arsenic(III), arsenic(V) and chromium(VI) in water by high performance liquid chromatography inductively coupled plasma mass spectrometry*
Magdalena Belter, Danuta Barałkiewicz

MP-29 *Study of arsenic speciation in raw wakame, cooked wakame and urine excreted after wakame seaweed ingestion*
Pilar Bermejo-Barrera, Cristina García-Sartal, María del Carmen Barciela-Alonso

MP-30 *Metrological approach in species analysis*
Claudia Swart, Claudia Frank, Olaf Rienitz

MP-31 *Indirect Se-metabolomics: complexity of influenced non-Se pathways*
József Lénárt, Attila Hegedűs, Júlia Győrfi, Mihály Dernovics

MP-32 *Quantification of iron containing blood proteins by means of LC/ICP-MS*
Claudia Frank, Christine Brauckmann, Claudia Swart, Detlef Schiel

MP-33 *Cr(VI) determination in soil solution by speciated isotope dilution ICP-MS*
Tea Zuliani, Janez Ščančar, Radmila Milačič

MP-34 *Use of stable isotope-enriched selenite tracer to differentiate and determine native and spiked selenium behavior in soils*
Pamela Di Tullo, Maite Bueno, Yves Thiry, Florence Pannier

MP-35 *The use of HPLC-ICP-MS and stable isotopes in the investigation of Cr speciation in tea infusions and bread samples*
Breda Novotnik, Tea Zuliani, Janez Ščančar, Radmila Milačič

MP-36 *Quantification of proteins with non-covalently bound metalloenzymes*
Julia Gleitzmann, Andrea Raab, Claudia Swart, Detlef Schiel, Jörg Feldmann

MP-37 *Arsenic speciation in urine using micro liquid chromatography-ICP-MS for routine biological monitoring*
Elizabeth Leese, Jackie Morton, Vikki Carolan

MP-38 *Relationship between diet and urinary arsenic species in two ethnic groups from Leicester, UK*
Essam Talha, Elizabeth Leese, Jackie Morton, Richard Jenkins, Vikki Carolan, Parvez I. Haris

MP-39 *Development of analytical strategy to study selenoprotein expression in human cell lines*
Juliusz Bianga, Zahia Touat-Hamici, Sandra Mounicou, Stéphane Duhieu, Ryszard Łobiński, Joanna Szpunar, Laurent Chavatte

MP-40 *Selenium metabolomics in yeast using bimodal (reversed-phase/hydrophilic ion interaction) liquid chromatography – ICP MS and electrospray hybrid quadrupole trap/orbital mass spectrometry*
Carine Arnaudguilhem, Katarzyna Bierla, Laurent Ouerdane, Hugues Preud’homme, Ryszard Łobiński

MP-41 *RNA analysis utilizing size-exclusion chromatography hyphenated with ICP-MS*
Shin-Ichiro Fujii, Keisuke Nagasawa, Groombridge Alex, Kazumi Inagaki, Koichi Chiba, Akiko Takatsu

MP-42 *In vitro nanotoxicity of silver nanoparticles: characterization of silver forms by AsFlFFF–UV-Vis–ICPMS*
Javier Jimenez-Lamana, Francisco Laborda, Eduardo Bolea, Lluis Arola, M. Josepa Salvado, Cinta Blade, Juan R. Castillo

MP-43 *Nanoparticle characterisation using FFF-ICP-Q-MS and FFF-SP-ICP-Q-MS*
Shona McSheehy Ducos, Christoph Johann, Ulrich Roesch, Daniel Kutscher, Lothar Rottmann

MP-44 *Comparison of GC-MS and GC-ICP-MS for the determination of PBDEs in marine samples from a food safety monitoring program*
Helge Hove, Stig Valdersnes, Daniel Fliegel

MP-45 *Determination of the brominated flame retardant HBCD by RP-HPLC-ICP-MS and its application to environmental monitoring*
Veronika Sele, Stig Valdersnes, Daniel Fliegel

MP-46 *Hericium erinaceus: a mushroom with yeast-like Se-metabolism*
Orsolya Egressy-Molnár, József Lénárt, Júlia Győrfi, Mihaly Dernovics

MP-47 *Vanadium speciation in soil and slag leachates by anion exchange HPLC-ICP-MS after EDTA complexation: the importance of sample preparation*
Marilena D’Amato, Maja Larsson, Federica Aureli, Andrea Raggi, Jon Petter Gustafsson, Francesco Cubadda

MP-48 *Off-line MALDI and ICP MS detection of a single record of metallothionein separation*
Iva Tomalová, Ondřej Polanský, Pavla Foltynová, Radka Millionová, Jan Preisler

MP-49 *On-line quantification strategies combined with AF4/SF-ICP-MS for speciation analysis of ENMs*
Björn Meermann, Anne-Lena Fabricius, Frank Vanhaecke, Lars Düster

MP-50 *Pilot study about nanoparticles in mouthwashes regarding to size and elemental composition*
Petra Krystek, Patrick Bauerlein, Pascal Kooij, Markus J. Spallek

MP-51 *Sn speciation in oyster’s organs: use of stable isotopic tracers to track metabolic pathways*
Zoyne Pedrero, Romain Bridou, Sylvain Bouchet, Hugues Bijoux, Monica Fernandez, Sandra Mounicou, Mathilde Monperrus, Patrice Gonzalez, David Amouroux

MP-52 *2D-UPLC (heart cutting / comprehensive) in real time and spectral accuracy improvement for speciation of complex samples by ICPMS: an original mass spectrometry strategy*
Hugues Preud'homme, Ryszard Łobiński

MP-53 *Investigations on organotin compounds reactivity using enriched isotopic tracers in polluted coastal sediments from the eastern Adriatic, Croatia*
Martina Furdek, Joana Cavalheiro, Mathilde Monperrus, Maité Bueno, Emmanuel Tessier, Nevenka Mikac

MP-54 *Novel strategy for the accurate quantification and identification of chromium species in food supplements*
John Entwisle, Volker Nischwitz, Heidi Goenaga-Infante

MP-55 *Elemental labeling and isotope dilution analysis for the quantification of the peptide hepcidin-25 in serum samples by HPLC-ICP-MS*
Tobias Konz, María Montes-Bayón, Alfredo Sanz-Medel

MP-56 *Using AsFLFFF-ICP-MS and XAS for the study of colloidal arsenic speciation in mine soils*
Miguel Ángel Gómez-González, Francisco Laborda, Eduardo Bolea, Susana Serrano, Peggy A. O'day, Fernando Garrido, Juan R. Castillo

MP-57 *Mass spectrometry based methodologies for studying the DNA binding properties of new cytostatic ruthenium complexes*
Elisa Blanco-González, Mario Corte, Maria Montes-Bayón, Elena Lastra, M. Pilar Gamasa

MP-58 *Study of absorption/bioavailability and distribution of ^{57}Fe from supplemented ^{57}Fe-lactoferrin formula milk by IPD-ICP-MS*
Sonia Fernández-Menéndez, María Luisa Fernández-Sánchez, Belén Fernández Colomer, Jose López-Sastre, Alfredo Sanz-Medel

MP-59 *Speciation of metal complexes in soil and plant related samples with elemental and molecular mass spectrometry*
Yvonne Schindlegger, Walter D.C. Schenkeveld, Stephan M. Kraemer, Eva Oburger, Barbara Gruber, Markus Puschenreiter, Angela Sessitsch, Gunda Koellensperger, Stephan Hann

MP-60 *Gold as an activity-based probe to address the active thioredoxin reductase concentration in cell culture by HPLC-ICP-MS*
Juan Gómez-Espina, María Montes-Bayón, Elisa Blanco-González, Alfredo Sanz-Medel

MP-61 *New strategies for the measurement of global DNA methylation in cisplatin sensitive and resistant cell lines using ICP-MS*
Tamara Iglesias González, María Montes-Bayón, Luisa María Sierra Zapico, Elisa Blanco González

MP-62 *Glutathione peroxidase levels in biological fluids: a potential biomarker for glaucoma*
Raquel González De Vega, Maria Luisa Fernández Sánchez, Héctor González Iglesias, Miguel Coca, Alfredo Sanz-Medel

MP-63 *An isotope dilution strategy for the quantification of platinum-gg adducts in cancer lung cells exposed to carboplatin*
Susana Cuello, Julien Heroult, Christian Dietrich, Volker Nischwitz, Heidi Goenaga-Infante

MP-64 *Evaluation of new pre-concentration techniques for organotin compounds analysis in water samples*
Joana Cavalheiro, David Amouroux, Hugues Preud'homme, Mathilde Monperrus

MP-65 *Quantification of the major arsenolipids in certified algal reference material NMIJ CRM 7405 (Hijiki)*
Kevin Francesconi, Josef Ehgartner, Georg Raber

MP-66 *Development of an easy-to-use analytical method for the determination of inorganic arsenic in food of animal origin*
Angela Sorbo, Francesco Cubadda, Federica Aureli, Marilena D'Amato, Andrea Raggi, Anna Chiara Turco, Laura Ciaralli

MP-67 *Novel SMPS-ICPMS coupling allows simultaneous analysis of size distribution and elemental composition of airborne nanoparticles*
Adrian Hess, Christian Ludwig, Andrea Ulrich

MP-68 *In-vitro studies with gold nanoparticles monitored by HPLC-ICP-MS*
Juan Soto Alvaredo, Carlos Lopez Chavez, Cristina Sanchez Gonzalez, Juan Llopis Gonzalez, Maria Montes-Bayón, Joerg Bettmer

MP-69 *The role of ICP-MS and ESI-MS in production of intact protein standards for quantitative proteomics*
Anna Konopka, Martin E. Boehm, Dominic Winter, Wolf D. Lehmann

MP-70 *Flow field-flow fractionation coupled with inductively coupled plasma mass spectrometry (FLFFF-ICP-MS) for study of Pt(II) and hen egg white protein binding*
Atitaya Samontha, Wilaiwan Somchue, Juwadee Shiowatana, Atitaya Siripinyanond

MP-71 *Asymmetrical flow field-flow fractionation coupled with ICP-MS for multi element analysis of plasma proteins*
Soheyl Tadjiki, Trevor Havard, Heidi Goenaga Infante

Friday, 15th February 2013

SECTION E LASER ABLATION

8:30 – 10:30 **SESSION E1 *Room A***
Chair: Joerg Feldmann

8:30 EH *A 45-year journey in ICP-AES: from academic research to industrial problem solving*
Jean-Michel Mermet

9:15 EP *Fundamentals and applications in laser ablation-inductively coupled plasma mass spectrometry*
Detlef Günther

10:00 EK-1 *Laser plasma spectrochemistry: LIBS and LAMIS*
Rick Russo, Xianglei Mao, Jhanis Gonzalez, Vassilia Zorba, Inhee Choi, Jong Yoo

10:30 – 11:00 Coffee break *Level -1*

11:00 – 12:00 **SESSION E2 *Room A***
Chair: Detlef Günther

11:00 EE *Analysis and thickness determination of ultra-thin layers by two complementary techniques: LA-ICP-MS and RF-GD-TOFMS*
Jorge Pisonero, Bodo Hattendorf, Cristina Gonzalez, Nicole Tibbetts,
Katharine Dovidenko, Denise Anderson, Dustin Ellis, Detlef Günther,
Alfredo Sanz-Medel, Nerea Bordel

11:30 EK-2 *Calibration strategies for laser ablation inductively coupled plasma mass spectrometry – possibilities and limitations*
Ewa Bulska, Barbara Wagner

12:05 – 13:05 **PARALLEL SESSION E3-a *Room A***
Chair: Barry Sharp

12:05 E-a01 *Development and applications of laser-assisted plasma spectrometry techniques*
Viktor Kanicky

12:20 E-a02 *High-resolution elemental bio-imaging of Ca, Mn, Fe, Co, Cu and Zn employing LA-ICP-MS and hydrogen reaction gas*
Jessica Lear, Dominic Hare, David Bishop, Fred Fryer, Paul Adlard,
David Finkelstein, Philip Doble

12:35 E-a03 *Laser ablation ICP MS for direct elemental and isotopic analysis of dried urine spots*
Martin Resano, Maite Aramendía, Luis Rello, Sylvain Bérail,Christophe Pécheyran,
Frank Vanhaecke

12:50 E-a04 *Multiplexed quantification of selected plant proteins using lanthanide labelled antibodies and LA-ICP-MS*
Thomas de Bang, Pai Pedas, Poul Erik Jensen, Søren Husted

12:05 – 13:05 PARALLEL SESSION E3-b *Room B*
Chair: Christophe Peycheran

12:05 E-b01 *Development and application of new metal-based diagnosis methods*
Larissa Waentig, Simone Hardt, Sandra Techritz, Norbert Jakubowski, Peter H. Roos

12:20 E-b02 *New strategy for the quantitative analysis of solid materials by on-line isotope dilution laser ablation ICP-MS*
Beatriz Fernandez, Pablo Rodriguez-Gonzalez, J. Ignacio Garcia-Alonso,
Rosario Pereiro, Alfredo Sanz-Medel, Julien Malherbe, Julio Rodriguez-Fernandez

12:35 E-b03 *Red stoneware analysis towards authentication of the real historic objects by SEM-EDS and LA-ICP MS*
Barbara Wagner, Karolina Malinowska, Mikolaj Donten, Irma Fuks,
Barbara Szelegejd

12:50 E-b04 *Cassiterite fingerprinting by LA-ICP-MS*
Hans-Eike Gäbler, Sönke Rehder, Andreas Bahr, Frank Melcher,
Simon Goldmann

13:05 – 14:30 Lunch *Level -1*

14:30 – 16:30 PARALLEL SESSION E4-a *Room A*
Chair: Martin Resano

14:30 E-a05 *New laser desorption sample introduction techniques for inductively coupled plasma mass spectrometry*
Jan Preisler, Pavla Foltynová, Tomáš Vaculovič, Viktor Kanický

14:45 E-a06 *Investigation of sulphur isotope fractionation and signal smoothing during the analysis of sulphides by LA-ICP-MS*
Sarah Gilbert, Leonid Danyushevsky, Ross Large, Sebastien Meffre,David Death

15:00 E-a07 *Effects of small amount of* N_2 *on the drift in relative sensitivities in laser ablation ICP-MS for geological and biological applications*
Leonid Danyushevsky, Mike Shelley, Jay Thompson, Sarah Gilbert

15:15 E-a08 *Use of Zr xerogel for elemental analysis of crude oil by LIBS*
Mauro Martinez, Manuel Caetano, Jose Chirinos, Vincent Piscitelli,
Brice Bouyssiere, Ryszard Łobiński

15:30 E-a09 *Better imaging analysis by LA-ICP-MS – an analyst's toolkit*
Rob Hutchinson, Katherine McLachlin, Ciaran O'Connor

15:45 E-a10 *Use of the jet interface for improved performance of laser ablation with sector-field ICP-MS*
Torsten Lindemann, Julian Wills, Lothar Rottmann, Stephen Shuttleworth

16:00 E-a11 *Results from the Elemental Analysis Working Group (EAWG): Improving forensic glass comparison analysis using LA-ICP-MS*
Jose Almirall, Stefan Becker, Marc Duecking, Tatiana Trejos, Peter Weis

16:15 E-a12 *Effect of laser wavelength and pulse width on laser produced aerosols: Implications to fs-LA-ICP-MS*
Prasoon Diwakar, Nicole LaHaye, Sivanandan Harilal, Ahmed Hassanein

14:30 – 16:30 PARALLEL SESSION E4-b *Room B*
Chair: Ewa Bulska

14:30 E-b05 *A high speed interface for coupling laser ablation to ICP-MS*
Barry Sharp, David Douglas, Amy Managh, Helen Reid

14:45 E-b06 *Evaluation of internal standards for quantitative tissue imaging*
Daniel A. Frick, Charlotte Giesen, Teresa Hemmerle, Dario Neri, Bernd Bodenmiller, Detlef Günther

15:00 E-b07 *Measuring calcium concentrations of fluid inclusions by microthermometry and LA-ICP-MS*
Markus Waelle, Tobias U. Schlegel,. Christoph A. Heinrich

15:15 E-b08 *LA-ICPMS: laser ablation sampling with combined ICP-Q-MS and MC-ICP-MS detection for simultaneous trace elemental and isotope ratio analyses*
Julian Wills, Nicholas Lloyd, Lothar Rottmann, Claudia Bouman, Steve Shuttleworth

15:30 E-b09 *Quantitave analysis of phosphorylates proteins by LA-ICP-MS*
Frank Bierkandt, Norbert Jakubowski, Peter H. Roos, Michael Linscheid

15:45 E-b10 *Laser-induced breakdown spectroscopy for investigational purposes in the pharmaceutical industry*
Lydia Breckenridge

16:00 E-b11 *TruLine™ – a novel, high-performance sample cell for laser ablation*
Katherine McLachlin, Ciaran O'Connor, Rob Hutchinson

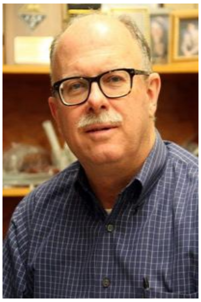
16:15 E-b12 *Sr isotope ratios in calcium-rich matrices by (LA)-MC-ICPMS: an ongoing challenge*
Johanna Irrgeher, Patrick Galler, Andreas Zitek, Maria Teschler-Nicola, Thomas Prohaska

16:30 – 16:45 CLOSING CEREMONY

European Winter Conference
on Plasma Spectrochemistry
10-15 February 2013, Krakow, Poland

short courses

Introduction to ICP-MS



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Robert Samuel Houk, received his undergraduate training at Slippery Rock University of Pennsylvania (B.S. 1974) and completed his doctoral work at Iowa State University (Ph.D. 1980). Following postdoctoral work at Ames Laboratory, he joined the Iowa State faculty in 1981.

His awards include the Lester W. Strock Award, 1986; Maurice F. Hasler Award, 1993; ACS Award in Chemical Instrumentation, 1993; Wilkinson Teaching Award, 1993, the Anachem Award, 2000 and the ACS award for Spectrochemical Analysis in 2012.

ISOTOPIC ANALYSIS VIA ICP – MASS SPECTROMETRY: WHAT, HOW AND WHY.

Frank Vanhaecke
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Frank Vanhaecke (1966) is Professor in Analytical Chemistry at Ghent University (Belgium), where he leads the 'Atomic & Mass Spectrometry – A&MS' research unit that focuses on the determination, speciation and isotopic analysis of (trace) elements via ICP – mass spectrometry (ICP-MS). One of the specific topics studied, is isotope ratio determination using single- and multi-collector ICP-MS in the context of elemental assay via isotope dilution, tracer experiments with stable isotopes and the use of small natural variations in the isotopic composition of metals and metalloids for provenance determination and for obtaining better insight into biological, environmental and geological problems.

Frank is (co-)author of some 200 scientific papers in international journals, 15 book chapters and more than 350 conference presentations and is a Fellow of the Royal Society of Chemistry RSC.

In 2011, he received a 'European Award for Plasma Spectrochemistry' for his contributions to the field.

Abstract

The course starts with a general introduction and reviews the various origins of natural variations in the isotopic composition of elements. The capabilities and limitations of various types of ICP-MS instrumentation for isotope ratio measurements are discussed. Attention is also devoted to instrumental bias caused by detector dead time and mass discrimination and approaches for correction for these biases are covered.

A next section focuses on applications relying on the quantification of induced changes in isotope ratios and includes elemental assay using isotope dilution and tracer experiments with stable isotopes to obtain a more profound insight into (bio)chemical reactions or physical processes.

Next, attention will be devoted to applications based on the natural variation in the isotopic composition of metallic and metalloid elements as a result of (i) the presence of radiogenic isotopes and (ii) isotope fractionation effects.

Isotopic analysis of elements with one (e.g., Sr) or more (e.g., Pb) radiogenic isotopes can be relied on for dating purposes (geochronology) as the parent radionuclide decays into the corresponding daughter nuclide with a characteristic half-life. The quite pronounced variation in the isotopic composition of the elements containing the radiogenic daughter can also be relied on in the context of provenancing – i.e. the determination of the geographical origin of, e.g., agricultural products, human remains or the raw products used in the manufacturing of objects of art.

It is now accepted that the isotopic composition of all elements with two or more isotopes can show natural variation as a result of isotope fractionation effects, i.e. the isotopes of an element do not take part with exactly the same efficiency to physical processes or (bio)chemical reactions. Both kinetic and thermodynamic isotope fractionation can occur and this leads to typically very small differences in the isotopic composition of the target elements. One area of application is the provenancing referred to above. As the extent of isotope fractionation is affected by the conditions prevailing when the physicochemical process is occurring, isotope ratios “stored” in historical archives (e.g., sediments, speleothems or ice cores) can also be used as paleoproxies, providing insight into the variation of conditions such as temperature, pH or atmospheric CO2 levels over geological times.

Throughout the course, the basic principles and theoretical background of isotope ratio applications will be discussed and real-life examples will be used to illustrate their capabilities and limitations.

QUALITY IN ANALYTICAL SCIENCES:
TrainMiC® connects people

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Graduated at the Faculty of Chemistry, Warsaw University. Presently Head of the Theoretical Aspects of Analytical Chemistry Group. Member of the Committee of Analytical Chemistry of Polish Academy of Sciences Head of the Commission of Atomic Spectrometry of the Committee of Analytical Chemistry of Polish Academy of Sciences Working out-side of home university in Germany, Sweden, France and Belgium.

Author or co-authors of over 140 scientific publications, co-author of several chapters, author of a book “Metrology in chemistry”, and co-authors of a number of papers focused on the metrology in chemistry. Awarded with Bunsen-Kirchoff Award (Gesellschaft Deutscher Chemiker); Wiktor Kemula Medal (Polish Chemical Society); W. Świętosławski Award (University of Warsaw) Topics of interest: analytical chemistry: inorganic and bioinorganic trace analysis; environmental, clinical and food samples; archeometry; atomic spectrometry (AAS, OES, MS); atom formation process in graphite furnace and in plasmas; mechanism of matrix interferences; hydride generation with AAS, ICP and MIP OES; Investigation of speciation with GC MIP-OES, HPLC ICP-MS or solid sorbents with AAS (mercury, antimony, selenium and aluminium). Flow and flow injection system for AAS, OES and MS; The use of EPMA, SIMS, XANES and LA ICP-MS for the investigation of surface and sub-surface domain of various solids (graphite, archeological samples, plants); Isotopic dilution in ICP-MS; chemical isotope effects of Ga, In and Ge; metrology in chemistry: validation of analytical techniques; traceability in chemical measurements; uncertainty evaluation; quality system in chemical laboratories.

Members of the Editorial Board of TrainMiC® programme and the Team Leader of PL TrainMiC® team.

Abstract

Quality of chemical measurements is an important issue in today’s world influencing quality of life, border-cross trade and commerce. On an international scale, the world of chemical measurements is undergoing major changes. Since a decade initiatives have been taken at an international level and across the measurement sectors to ensure that the measurement science issues are applied in a systematic way. This is done to improve the quality of chemical measurement results and thus make them acceptable everywhere. Only in recent years have the principles of measurement science (metrology) in chemistry received the attention they should. This does not replace the need for many aspects of quality assurance, but compliments this, i.e. bringing a solid foundation to build on.

The course is organised under the responsibility of TrainMiC® European Programme, European Commission funded training platform to foster advanced professional training on generic issues related to the quality of measurement results (Metrology in Chemistry). The aim of the overall TrainMiC® course is to give a comprehensive overview on the importance of the use of metrological principles when performing chemical measurements of various kind. This is of great relevance for routine laboratories, which are driven by the requirements of the ISO/IEC 17025 standard, but also for research laboratories, that may benefit from the implementation of the metrological approaches into their measurements practice. TrainMiC® is about how to interpret the metrological requirements of ISO/IEC-17025 for chemical and bioanalytical measurements in many different sectors (environment, food, consumer protection, etc.).

AGENDA AND TOPICS:

- Traceability of measurement results
- Single laboratory validation of measurement procedures
- Uncertainty of measurement: Principles and Approaches to evaluation
- Selection and use of reference materials
- Quality control

This TrainMiC® course is designed for the analytical chemistry students at the PhD and PostDoc level as well as senior researchers. Several examples related to the mass spectrometry measurements will be given.

QUANTIFICATION STRATEGIES FOR METALLOMICS: POSSIBILITIES AND TRENDS

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Maria Montes Bayón holds a permanent position as Senior Lecturer in the Analytical Chemistry Area of the Department of Physical and Analytical Chemistry at the University of Oviedo since April 2008. In September 1993 she joined the Analytical Spectrometry Group leaded by Prof. Sanz-Medel and started with a research stay at the University de Plymouth (UK) under the ERASMUS program supervised by Dr. Hywel Evans. The results obtained during a year of research in the UK were included in her Master of Science presented in Oviedo (November 1994). Right after, she started PhD studies in Oviedo and in July 1999 she defended her Doctoral Thesis awarded with the Extraordinary Prize in the Area of Analytical Chemistry within the University of Oviedo. In April 2000, she joined the research group of Prof. Joseph A. Caruso in the Department of Chemistry at the University of Cincinnati, Ohio (USA) as Postdoctoral Fulbright Fellow until July 2002. In August of the same year she gets back to the University of Oviedo as Ramón y Cajal Researcher (Tenure) in the Spectroscopy Group until 2007. Finally, in 2008 she obtained the position of Senior Lecturer. She is co-author of more than 80 original research publications and reviews, as well as several book chapters. She participates in different research projects (national and regional) through which the research in funded. She is member of the Advisory Board of Journal of Analytical Atomic Spectrometry and Metallomics, both from the Royal Society of Chemistry. She is also coordinator of several ERASMUS agreements within the research Group with five European Institutions (Gdansk, Plymouth, Graz, Pau y Aberdeen).

RESEARCH INTERESTS:The research studies she is conducting nowadays are focused on the development of analytical strategies based on mass spectrometry (elemental and molecular) for the determination of important clinical biomarkers related to:1. The study of alterations in Fe metabolism related to Fe-containing proteins and its importance in prevalent diseases such as dibetes mellitus, glaucome or chronic alcoholism.2.- The development of individualized chemotherapeutic treatments based on the use of Pt-drugs through selective monitoring of Pt-adducts with DNA nucleobases.3.- The oxidative stress generated by the presence of trace metals released from prosthesis and implants (e.g. Ti), by the development of associated complications in diabetes mellitus (e.g. rethinopaty) or in chemotherapeutic treatments (e.g. cisplatin).

Abstract

The quantification of the metallome in a given biological compartment is still a remaining challenge in the analytical community. Since the metallome, by definition, includes the entirety

of metal- and metalloid species present in a biological system, the need for development of strategies to tackle the quantitative aspect of, at least, a little part of the metallome are urgently demanded. In this regard, the course will revise the ICP-MS based strategies used for bio-inorganic speciation analysis that can be then adapted to the metallomics studies and will be critically compared with other quantitative possibilities including those based on molecular MS techniques or in immunoassays. Special attention will be given to the quantification methodologies based on the use of generic standards (a unique feature of ICP-MS) and isotope dilution analysis (essential to conduct highly precise and accurate determinations).

Different scenarios will be addressed: when the aim of the metallomic study is to obtain quantitative information just on the presence of a given element/s in a biomolecule or biological fluid and when then information required is the concentration of a specific biomolecule carrying a specific metal/metalloid. The different approaches to tackle these two problems will be highlighted. Finally, some of the actual trends regarding the use of element-tagged results via ICP-MS to extract biologically relevant information such as enzymatic activities, enzymes inhibitors or DNA integrity etc. will be also illustrated.

LASER ABLATION ICP MS

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Detlef Günther obtained a Diploma degree in Chemistry in 1987 and a Ph.D. degree in Analytical Chemistry from the Martin-Luther-University Halle-Wittenberg under supervision of L. Moenke-Blankenburg in 1990. His postdoctoral work in the Institute of Plant Biochemistry Halle was focused on development of analytical methods to characterize heavy metal-binding proteins using HPLC-ICP-MS. Next, he joined the group of H.P. Longerich at the Memorial University of Newfoundland, Canada. In 1995 he start working at the Institute of Isotope Geology and Mineral Resources at ETH Zürich, where in 1998 he was appointed as Assistant professor in the Laboratory of Inorganic Chemistry, in 2003 was promoted to Associate professor for Trace Element and Micro Analysis and became Full professor in 2008. Since August 2010 he is Chair of the Department of Chemistry and Applied Biosciences at ETH Zurich. He is recipient of the Ruzicka Award (2002), the European Award for Plasma Spectrochemistry (2003), the Fresenius Award (2007) and the Lester Strock Award (2007). His research is focused on fundamentals and application of Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS), which includes studies on laser-sample interaction, aerosol transport and plasma-related excitation processes. Fundamental processes of UV-ns and UV-fs laser ablation in combination with Q-ICP-MS, SF-ICP-MS, ICP-TOFMS and MC-ICP-MS as well as alternative excitation sources, such as Glow discharge are currently under investigation. The trace element, micro analysis and isotope ratio determinations have been demonstrated on a wide variety of applications.

European Winter Conference on Plasma Spectrochemistry

10-15 February 2013, Krakow, Poland

abstracts

opening session

WINTER CONFERENCE ON PLASMA SPECTROCHEMISTRY: THE BACKGROUND

Ramon BARNES
ICP Information Newsletter, Hadley, USA

The popularity of plasma sources for atomization and excitation in atomic spectroscopy and ionization in mass spectrometry and the need to discuss recent developments of these discharges in spectrochemical analysis stimulated the organization of the first Winter Conference on Plasma Spectrochemistry in 1980. Over the years since the Winter Conference has brought together many international scientists experienced in applications, instrumentation, and theory in an informal setting to examine recent progress in the field.

Previous meetings were held in San Juan, Puerto Rico (1980); Orlando, Florida (1982); San Diego, California (1984, 1988, 1992, 1994); Kailua-Kona, Hawaii (1986), St. Petersburg, Florida (1990), Fort Lauderdale, Florida (1996, 2000, 2004), Fort Myers, Florida (2010), Scottsdale, Arizona (1998, 2002), Tucson, Arizona (2006, 2012), and Temecula, California (2008). Attendance has grown from 170 in 1980 to approximately 600 with worldwide scientific participation representing 30 countries. Technical sessions comprise lectures and posters describing application, fundamental, and instrumentation developments with popular electrical plasma sources. The inductively coupled plasma (ICP), glow discharge sources, microwave induced plasma, direct current plasma, and laser-assisted plasma spectrochemistry are featured. New spectrometric instrumentation, novel sample introduction systems, plasma system automation, sample preparation approaches, elemental speciation, spectroscopic standards, quality assurance, new diagnostic characteristics, and theoretical treatments are highlighted. Plasma applications in agricultural, biological, clinical, environmental, forensic, geo- and marine sciences, and advanced and nano materials are growing.

More than 300 technical papers are presented, and selected papers have been published together as the Conference proceedings in Spectrochimica Acta, Part B (1981, 1983, 1985, and 1987), Journal of Analytical Atomic Spectrometry (1988, 1990, 1992, 1994, 1996, 1998, 2000, 2002, 2004, 2006, 2008, 2010, 2012), and Journal of Analytical Bioanalytical Chemistry (1998, 2000, 2002, 2004, 2006). This meeting is sponsored biennially by the ICP Information Newsletter, Inc., a nonprofit, philanthropic research organization located in Hadley, Massachusetts and Lehigh Acres, Florida, and organized by Dr. Ramon Barnes of the University Research Institute for Analytical Chemistry.

Some in the field consider the Winter Conference one of the technically most significant meetings convened on these topics. Fourteen European Winter Conferences have been held as well in Leysin, Switzerland (1985), Lyon, France (1987), Reutte, Austria (1989), Dortmund, Germany (1991), Granada, Spain (1993), Cambridge, England (1995), Gent, Belgium (1997), Pau, France (1999), Lillehammer, Norway (2001), Garmisch-Partenkirchen, Germany (2003), Budapest, Hungary (2005), Taormina, Italy (2007), Graz, Austria (2009), and Zaragoza, Spain (2011). The 2013 conference is planned for Krakow, Poland, February 10-15, 2013. Four Asia-Pacific Winter Conferences have been held in Chiang Mai, Thailand (2005), Bangkok, Thailand (2006), Tsukuba, Japan (2008), and Chengdu, China (2010). The fifth Asia-Pacific meeting planned for August 26-30, 2012 for Jeju Island, Republic of Korea continues the expansion of the meeting objectives.

The 2014 Winter Conference on Plasma Spectrochemistry, eighteenth in this series of biennial meetings sponsored by the ICP Information Newsletter (http://icpinformation.org), will be held Monday, January 6 through Saturday, January 11, 2014, on Amelia Island near Fernandina Beach, Florida (www.ameliaisland.com) at the Omni Amelia Island Plantation resort (www.omniameliaislandplantation.com). Continuing education short courses at introductory and advanced levels and manufacturers' seminars, which have been presented since the first Winter Conference, also will be offered January 3 - 6. An exhibition of spectroscopic instrumentation and accessories has always been a major part of the Winter Conference and has grown to more than 50 participating companies and organizations. Many new plasma systems have debuted during this exhibition. Renowned senior researchers will give Heritage Lectures, and the 2014 Winter Conference Award in Plasma Spectrochemistry will be presented.

This lecture will describe some of the Winter Conference innovations and milestones during the past 30 years.

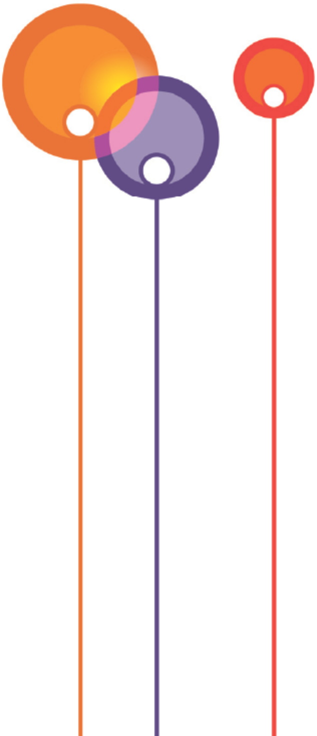
LECTURE OF THE PLASMA AWARD LAUREATE

Norbert JAKUBOWSKI
BAM Federal Institute for Materials Research and Testing, Division 1.1
Inorganic Chemical Analysis, Berlin, Germany

The 2013 Plasma Award winner, Norbert Jakubowski, studied physics at the University of Duisburg/Essen and completed his PhD in physics at the University of Hohenheim. He was a senior scientist at the Institute for Analytical Sciences, Dortmund and Berlin (from 1983 to 2009) and is now Head of BAM's Division I.1 Inorganic Chemical Analysis and Reference Materials (since July 2009). His research interests include inorganic trace and ultra trace analysis of liquids and solids by use of ICP-MS and GD-MS, elemental speciation analysis and development of elemental tags for quantitative detection of biomolecules. He has received awards including the Alan Date Memorial Award from VG Elemental, Surrey, GB (1990), Zimmer International Scholar from University of Cincinnati, USA (2005) and a Waters Symposium Award for Pioneers in ICP-MS (2006).

section A

Fundamentals and instrumentation



HISTORICAL DEVELOPMENT AND RECENT ADVANCES IN ICP MASS SPECTROMETRY

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Interesting aspects of the development of ICP-MS will be surveyed. These include:

a) initial origins of the idea,
b) first successful experiments,
c) analytical capabilities and applications of early commercial versions.

Further research and development that have resulted in modern ICP-MS instruments will be surveyed. For example, initial experiments in collision cells and in diagnostics of the ion extraction process will be described. Finally new scientific uses from the literature and developments from the author's group will be discussed, including the fate of laser ablated particles in the ICP.

NOVEL MODELS AND METHODS FOR PLASMA SPECTROCHEMISTRY

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In this presentation, two new tools for spectrochemistry will be described and assessed. The first is intended to evaluate and improve the accuracy of ICP emission measurements and the other to simplify calibration procedures in elemental analysis. Without doubt, most realistic analysts are more concerned about matrix interferences than about any other aspect of ICP-AES. Regrettably, there is at present no commercially available strategy to indicate when matrix interferences are present or, if they are, how to alleviate them. As a result, a prudent user of ICP-AES must resort to time-consuming and troublesome methods such as standard additions, internal standardization, and matrix matching. It will be shown here how the spatial pattern of emission can be used as a reliable indicator to flag the presence of interferences. Importantly, the method is applicable to both conventional radial emission measurements and axial ones, where interferences are even stronger and more likely. Further, when radial emission is viewed, the method is capable of directing the operator to the proper spatial zone in the ICP where interferences are either reduced or eliminated. The technique to simplify calibration is based upon the stoichiometric conversion of all elements to a common one that can be detected more sensitively. Because all elements are then represented by the “replacement” ion, they can all be quantified by means of the same calibration curve. In this way, only a single set of standards is needed for an entire calibration. Further, this form of universal calibration enables all species in the sample to be determined, whether they are anions or cations, and even when their identity is unknown.

AK-1

DEVELOPMENT OF HIGH PERFORMANCE TRIPLE TUBE CONCENTRIC NEBULIZER FOR PLASMA SPECTROMETRY

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A nebulizer is one of the most important components in plasma spectrometers such as ICP-OES and ICP-MS. A nebulizer that can generate fine aerosols results in a stable and highly intense signal in ICP-OES and ICP-MS, since the ICP exhibits severe constrains in terms of the droplet diameter of the aerosols and the amount of solvent loading to the plasma. If droplets larger than 10 μm are introduced into the plasma, they have a severe effect on measurements in their vicinity from the increased time taken for their desolvation and vaporization; this gives large localized differences in temperatures, affecting emission stability and sensitivities. Recently, a high tolerance for total dissolved solids (TDS) has also been required as a nebulizer function, because more problematic samples with complicated matrices or high concentrations of salts have been routinely analyzed by ICP-OES and ICP-MS, especially in material, clinical, biological and environmental research fields. However, fine nebulization and high TDS tolerance are incompatible functions for conventional nebulizers.

We developed a high performance concentric nebulizer (HPCN) for ICP-OES [1] and ICP-MS [2]. The HPCN has a unique triple tube concentric structure. It shows an excellent performance for the following three points; a fine aerosol generation, high tolerance for total dissolved solids (TDS), easy designing for various flow rates of solution. In the nebulization of the HPCN, a microthread liquid flow is formed inside the nebulizer nozzle by a flow focusing effect. This phenomenon gives both the fine aerosol generation and the high TDS tolerance. The HPCN can generate fine aerosol; over 90% of the primary aerosols are below the diameter of 10 μm. It also showed a good tolerance to high total dissolved solids (TDS) using 20% NaCl solution at the liquid flow rate of 0.8 mL min^{-1}.

In this presentation, we will show the analytical performance of the HPCN and its application for seawater analysis, small volume sample analysis, speciation analysis coupling with micro flow separation techniques, and single yeast cell analysis by time-resolved ICP-MS.

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SELECTING PLASMA SOURCE BASED ON MULTI-ELECTRODE SYSTEMS

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During the last decades, there has been a steady increase in the use of RF and microwave (MW) discharges that serve as efficient sources of ionized and excited atoms and molecules for plasma spectrochemistry. Dealing with many MWP constructions we attempted to make a classification of frames from which one should be able to describe chosen cavity and say what performance it can be expected [1]. The classification has helped to forecast a renaissance of capacitive microwave plasma technique and the development of MW driven micro-discharges. It has also showed the ways how to provide symmetry and stability of the plasma by the application of energy splitting with a plurality of electrodes surrounding the plasma. Additionally, the application of a rotating field originating from splitting the same power source or combined from a number of synchronized individual power sources can generate a field with the minimum energy at the axis [2,3]. Such discharges are, as a rule, axially symmetrical.

Here, the present state of multi-electrode plasma sources is reviewed, with special emphasis placed on the strengths and weaknesses of currently developed systems. Attention is then directed towards basic and applied studies that are underway to extend the range of operating parameters and reduce the remaining shortcomings of the technique. Such efforts include the design and evaluation of novel sources, attempts to understand and overcome limitations, techniques of sample introduction, and methods for improving precision in routine analysis. The first part of the study was concerned with the selecting RF and MW discharges sustained by the rotating field [2]. Four MWP sources operating with three, five, six or eight phases have been developed which differ in shape and volume. The performance of the multi-electrode plasma could be improved by changing of the electrode arrangement and the use of higher power levels as well as by the use of the pulsed discharge and the water-cooled electrodes.

Next, a highly flexible technology has been developed for constructing plasma sources based on the multi-phase rotating field concept and the digitally controlled modulation of plasma heating at audio and ultrasonic frequency [4]. The essence of this approach lies in the fact that a non-stationary plasma discharge sustained by a rotating electric field is attached between at least two electrodes positioned in the plane around the axis, and the electrodes are supplied with pulsed power generator equipped with a semiconductor logic controlled by a digital processor, wherein at least a fraction of each electrode cycle, passes through the state in which it is detached from the power source. Therefore, the excitation power of the source may be controlled by variations of the pulse width, frequency, commutation mode and gas flow rate for maintaining a tunable source driven by rectangular waves and digital signal processing. The DSP offers high performance and advanced software capabilities that enable both randomized pulse generation adjustments of the slopes as well as variable pulse width modulation, control of repetition frequency, change of the commutation modes, etc. It is argued that plasma sources of the future might be simpler and less expensive yet more powerful than those now in use.

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CHARACTERIZATION AND APPLICATION OF THE THERMAL INKJET-BASED AEROSOL GENERATOR AS AN ALTERNATIVE TOOL FOR SAMPLE INTRODUCTION IN PLASMA SPECTROMETRY

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The introduction of liquid samples into plasma excitation and ionization sources in the field of inorganic trace analysis is commonly established through the continuous generation of aerosols via pneumatic nebulization. It is well known that such aerosols not only show a relatively broad particle size distribution but mostly also result in a too high load for the plasma source (ICP) and thus are not suitable for direct introduction. Various spray chamber designs – e.g. optimized for maximum sensitivity or minimum dead volume and wash-out times – serve to overcome this problem, allowing only the small-sized droplets to pass to the plasma source. However, this might also result in an unfavourable loss of sensitivity.

Therefore, the accurate handling of small reagent and sample volumes is of particular importance, not only in the field of hyphenated techniques, based e.g. on the combination of capillary electrophoresis (CE) and plasma source mass spectrometry. Commonly, an additional make-up solvent flow has to be added to the eluent flow to meet the specifications of conventional nebulization systems for sample introduction into the plasma source. A new strategy for direct and flexible introduction of liquid samples is desired, preferably on the basis of small and monodisperse droplets, to minimize the risk of contamination and degradation of chromatographic resolution.

The recently introduced approach for the generation of individual ultralow-volume droplets and aerosols from liquid samples by applying the developed drop-on-demand droplet and aerosol generator based on thermal-inkjet technology [1] will be presented and characterized and further developments will be outlined. Advantages, drawbacks and also its potential for couplings with HPLC and CE will be discussed. A novel calibration strategy [2] based on the dosing frequency-dependant transfer of sample mass into the ICP and its application for the analysis of real samples will be outlined.

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A-a01

IMPROVEMENT OF ANALYTICAL PERFORMANCE OF DROPLET DIRECT INJECTION ICP-TOFMS USING DESOLVATION SYSTEM AND HIGH SPEED DATA ACQUISITION

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In recent years, there is growing interested in trace element analysis for single cell or nano-particles. Because cause of cancer or Alzheimer disease is hoped to be figure out by analyzing trace element in single cell [1]. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has been widely used for trace element analysis because of analytical figure of merit. However, conventional sample introduction system for ICP-MS consumes large amount of sample solution and so it is difficult to realize individual single cell analysis. In our previous research, droplet direct injection nebulizer (D-DIN) system was developed for single cell analysis. By including cells in a droplet, this system enables to measure trace elements containing in individual cell.

We applied D-DIN system to ICP Time of Flight Mass Spectrometry (ICP-TOFMS) for achieving simultaneous multi-element analysis in a single cell. The absolute detection limits of ^{65}Cu and ^{66}Zn using D-DIN ICP-TOFMS were 7.5 pg (10^{-12} g) and 17 pg, respectively. To achieve trace elements analysis in a single cell, analytical sensitivity of ag (10^{-18} g) level is required.

We thought two way of increasing analytical sensitivity. One is developed desolvation system for droplet, because the droplet volume was too large for ICP to ionize sufficiently. Schematic of the system [2] is shown in Fig. 1. Droplet has heated before introducing ICP, and the temperature of this heating system was changed from 25 to 260 °C. To investigate ionization process in detail in the plasma, we applied desolvation system to D-DIN-ICP-Atomic Emission Spectrometry (AES). With the droplet desolvation system, emission intensity of Ca ion line enhanced about 10 times compare with normal system. This result was shown effectiveness of droplet desolvation system. Another one is developed high speed data acquisition, because signal integration time is so long for transient signal of droplet in usual ICP-MS. To realize fast signal measurement, ion current from the detector was directly measured using a high-speed digital oscilloscope. Mass signal can be obtained from only signal without integrating unnecessary noise by using this way. As a result, absolute detection limit of 36 fg was obtained. The mass spectrum is shown in Fig. 2. The absolute detection limit was achieved approximately 100 times compared with the previous results. In addition, to improve more sensitivity, we think a new signal processing method, too. These results will be presented.

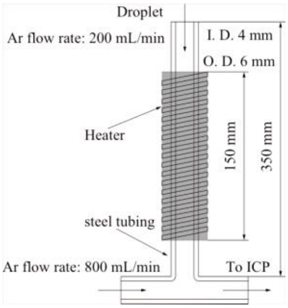

Fig. 1. Schematic of droplet desolvation system

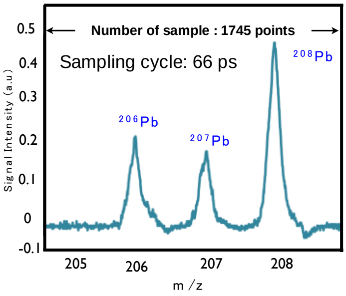

Fig. 2. Pb spectrum by high speed ion counting

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ORGANIC SOLVENT ANALYSIS USING A ICP-QQQ-MS (MS/MS CAPABLE) INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETER

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The elemental analysis of organic solvent-based samples is of importance to a great number of industries including petrochemical, pharmaceutical, semiconductor and research. With the requirement to measure ever lower limits either for regulatory or product quality reasons Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is being frequently utilised due to its sensitivity.

Organic solvents in ICP-MS present their own unique problems in terms of plasma stability and spectral interferences. Plasma stability problems can be easily overcome by intelligently selecting the appropriate sample introduction hardware allied to robust generator designs but the problems of plasma, carbon and oxygen-based spectral interferences remain.

Many collision-reaction cell designs have been employed to improve the measurement of key elements in solvents but until now some elements are still troublesome especially if isotopic information is required (e.g. for isotope analysis). This paper demonstrates some applications of an ICP-MS instrument capable of MS/MS mode of analysis (with a quadrupole preselecting target masses before the collision/reaction cell) for several key elements.

A-a03

SINGLE-PARTICLE ANALYSIS USING ULTRA-FAST QUADRUPOLE ICP-MS

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The application of engineered nanoparticles (ENP) in industrial and consumer products is gaining steady momentum. This is countered by an increasing concern regarding the fate of nanoparticles in the environment and health risks associated with human exposure to such materials.

Inductively coupled plasma mass spectrometry (ICP-MS) is considered a viable metrology tool for ENP quantitation and characterization due to its high specificity, sensitivity, and wide dynamic range. More recently, ICP-MS has been used in “single particle” mode to capture analyte signal pulses originating from individual nanoparticles in the ICP and relate the recorded data to information such as particle count, size distribution and analyte mass [1].

For single-particle applications, quadrupole-based ICP-MS systems have been known to be limited by the dwell and settling time of the scanning electronics as well as the speed of the detection electronics [2]. In addition, allowing shorter dwell times directly increases the upper limit of the dynamic range for nanoparticle analyses [3]. This also reduces the possibility of more than one nanoparticle generating the signal during a given dwell time.

In our laboratory, we have explored the possibility of a fast scanning mode with NexION 300 for dwell times as short as 1 μs, and with no settling time, for single mass determinations. Figure 1 shows a typical example of such measurements with a gold nanoparticle sample. The results show that the fast temporal behavior of the signal can be recorded in the pulse counting mode with sufficient number of data points to properly represent the pulse from a single nanoparticle. This also enables fundamental studies such as the effect of plasma operating conditions (e.g., nebulizer gas flow rate and sampling depth) on the nanoparticle signal.

In this presentation, the latest results of our research work on the fast scanning mode for single-particle ICP-MS will be discussed in detail.

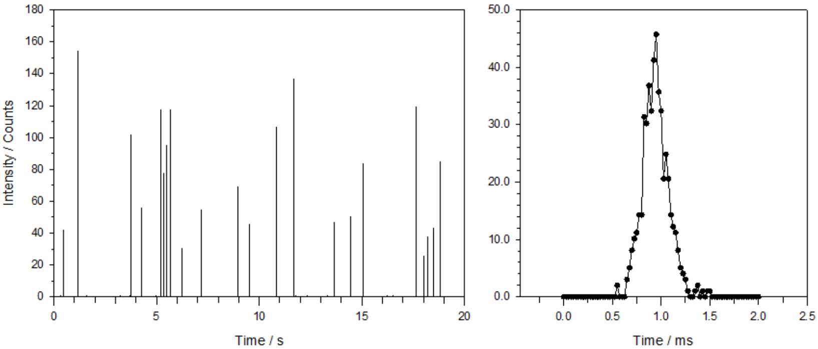

Fig. 1 a) Example of single-particle signals from 100 nm Au nanoparticles (50 ng.L-1) monitored by a NexION 300 operating in fast scanning mode (Dwell time: 0.025 ms; no settling time between measurements), b) example of a magnified pulse in the time axis.

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A-a04

AUTOMATIC SAMPLE PRETREATMENT INSTRUMENT FOR SOLID PHASE EXTRACTION OF TRACE ELEMENTS PRIOR TO THE DETERMINATION BY ICP-MS

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Solid phase extraction (SPE) techniques using chelating resins are effective for the preconcentration of trace elements and separating them from the alkali metals, alkaline earth metals, and most anions in a solution [1-3]. In most cases, the adsorptions of the trace elements to the chelating resins were carried out at a relatively neutral pH condition close to pH 6. Therefore, adjustment of the pH condition of the sample is required to ensure the recoveries of trace elements and the reproducibilities of the results.

In this presentation, the authors present an automatic pH adjustment instrument for the SPE of trace elements. The automation of the pH adjustment instrument was realized with a contactless pH monitoring system and an aqua ammonia solution adding system, along with an automatic controlling program based on the LabVIEW® programming software.

The contactless monitoring of the pH was carried out by measuring the intensity of a transmitted light at 550 nm that passed through a sample solution to which methyl red had been added as a pH-indicator. Addition of the aqua ammonia solution as a reagent to adjust the pH was sprayed to the sample solution using a nebulizer which permitted the addition of a small amount of the reagent and the precise adjustment of the pH. The pH value of the sample was monitored by measuring the intensity of the transmitted light using a spectrometer, while the open-time of the valve controlling the quantity of an aqua ammonia solution was automatically controlled simultaneously with the measurement of the transmitted light. The precision of the pH adjustment was tested and confirmed by using a seawater sample.

A typical pretreatment of 100 mL of seawater sample in 0.1 mol L^{-1} HNO3 could be carried out in 5 min, while the automatic addition of a proper quantity of an aqua ammonia solution could shorten the pretreatment time to less than 1 min.

The blank values obtained with the present instrument were compared with those obtained with the assist of a glass pH electrode and with those obtained with the assist of a plastic pH electrode. The results showed that the blank values obtained with the present instrument were significantly lower than those obtained with the assists of the pH electrodes. The blank values and detection limits of trace elements were given as the analytical figures of merits. The usefulness of the present method was confirmed by analyzing a sample of coastal seawater.

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DETECTION OF CANCER MARKERS USING SURFACE MODFIED METAL/DYE-DOPED MAGNETIC SILICA NANOPARTICLES IN ICP-MS

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Carbohydrate antigen (CA19-9) was a biomarker developed to detect colorectal cancer, but it is more often used for pancreatic cancer. In a very early stage the level of CA19-1 is often normal, so it is not a good cancer marker for a screening test. Normal blood levels of CA 19-9 are below 37 U/mL (units/milliliter). For the detection of CA19-9 and similar cancer markers, metal/dye-doped magnetic silica nanoparticles (MDM-SNPs) were synthesized for particle tagging using inductively coupled plasma-mass spectrometry (ICP-MS). The doped metals/dyes/magnetic particles in silica nanoparticles were sufficiently stable for extended storage in aqueous media owing to the protection offered by the silica shell. The plot of metal signal obtained by ICP-MS vs. the number of particles showed excellent linearity. In addition, fluorescence from the doped dyes is useful to monitor particle loss during inevitable treatment procedures and to determine the binding ratio of target material. The presence of magnetic nanoparticles at the core was confirmed by TEM, of which the magnetic property was useful for collection and separation during sample treatment.

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3D ION OPTICS FOR ICP-MS

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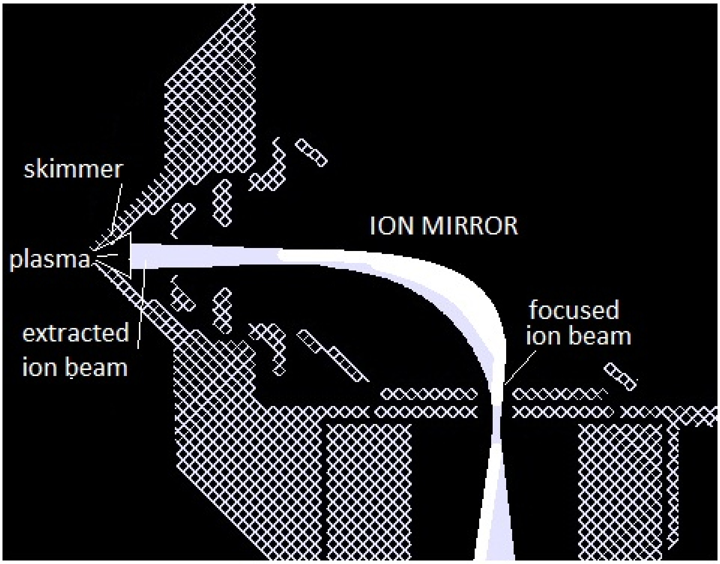
Ion optics is one of the most important elements of modern ICPMS. Ion optics are supposed to extract the ion beam from the plasma, while separating the ion beam from neutrals, electrons, photons, solid particles and droplets which are usually present in the plasma. Ion optics is also supposed to efficiently focus extracted ions into a tightly focused ion beam. The challenge is that ICPMS ions have considerable initial energy spread and significant spatial distribution preventing the efficient ion beam extraction and focusing. Traditionally, ICPMS ion optics used designs such as Bessel Box, Photon Stop, Shadow Stop, Omega lens, Off-Axis lens and Q-deflector, which are all based on transmitting principles and are not capable of focusing an ion beam efficiently. This happens due to fundamental physical limitations: chromatic and spherical aberrations associated with the initial ion beam condition and transmitting ion optics properties.

Ion Mirror – the reflective ion optics concept utilized by Bruker ICPMS, is free of those chromatic and spherical aberrations and provides 3D - 1mm diameter focusing of the ion beam [1]. The Ion Mirror is many times more efficient in focusing ions into quadrupole mass-analyzer resulting in significant sensitivity improvement compared to traditional transmitting ion optics. This is achieved without sacrificing other important characteristics of the Bruker ICPMS – such as low oxides, doubly charged, reduced matrix effects, memory effects.

3D Ion Mirror optics, development logic, SIMION modeling, calculations and other technical details will be presented. Further improvements in sensitivity by optimizing the operating conditions will be demonstrated.



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A-a07

COMBINATION OF THE INDUCTIVELY COUPLED PLASMA AND DISTANCE-OF-FLIGHT MASS SPECTROMETRY: EXPLORING A NEW CHAPTER IN ATOMIC MASS SPECTROMETRY

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Over the last 35 years, the inductively coupled plasma (ICP) has proven to be a robust ion source for atomic mass spectrometry (MS). Broadly, ICPMS offers both the high sensitivity and wide dynamic range necessary for a range of challenging analytical problems such as metallo-protein identification, chemical speciation, geochronology, and nuclear forensics.

Though the ICP is itself a robust ion source, the type of mass analyzer employed in an ICPMS instrument significantly impacts analytical performance. In the past, the ICP has been coupled to scanning analyzers such as quadrupole mass filters and double-focusing mass spectrometers, spatially dispersive systems such as the Mattauch-Herzog mass spectrograph (MHMS) and multi-collector instruments, and time-of-flight mass spectrometers. Each of these mass analyzers has its own distinctive performance characteristics sensitivity, precision, duty cycle, mass-spectral coverage, mass bias, mass resolution, and abundance sensitivity all dictate its potential analytical applications. Here, we expand the field of atomic mass spectrometry with the first results of an ICP – distance-of-flight mass spectrometer.

Distance-of-flight mass spectrometry (DOFMS) is an offshoot of time-of-flight mass spectrometry (TOFMS). In DOFMS, ions are accelerated to mass-dependent velocities, allowed to traverse a field-free region where they separate based on these velocity differences, and then are all detected at a single instant, so that positions of ion strikes across the length of a spatially selective detector correlate to mass-to charge (*m/z*) value. As such, DOFMS spatially disperses ions according to *m/z* value, while maintaining advantages of TOFMS such as high speed, high ion throughput, complete spectral coverage, unlimited mass range, and simple instrument design. Additionally, DOFMS presents an opportunity to incorporate state-of-the-art charge-sensitive array detectors into a velocity-based MS platform. The use of these detectors is pivotal to the development of the ICP-DOFMS because they offer broad dynamic range, direct readout, multichannel advantages, and improved isotope-ratio precision through simultaneous collection.

In the Hieftje lab, we have constructed and begun to characterize an ICP-DOFMS instrument fitted with a focal-plane camera detector. In this presentation, the fundamental characteristics of our ICP-DOFMS instrument will be explored. Also, ICP-DOFMS will be compared to ICP-TOFMS and ICP-MHMS to clarify the position of this new analyzer within the range of atomic mass spectrometers and to define the future prospects of ICP-DOFMS.

DETERMINATION OF CHALLENGING ELEMENTS IN THE CONTEXT OF MARINE ENVIRONMENTAL ANALYSIS: EXPLORING THE POTENTIAL OF ICP-MS-MS

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The continuous and still growing anthropogenic impact on marine ecosystems recently results in a rising number of international agreements and new legislative requirements, which demand the monitoring of a wide range of both priority and new substances of concern steadily released into the aquatic environment. The quantification of pollution levels of different environmental compartments with either organic or inorganic contaminants as well as the measurement of individual body burdens of selected organisms at different trophic levels represents the "standard procedure" used, to derive information with respect to environmental assessment or for the status description of an ecosystems.

Quantitative analysis of elements and element species in marine environmental samples is in particular challenging due to the complex matrix of such samples, which often results in strong interferences when using ICP-MS as detector. A further challenge originates from new legislations, which demands on the development of new more sensitive methods for the determination of already defined priority compounds or newly emerging contaminants at lowest concentration levels as well as the parallel inclusion of biological effect orientated investigations related with the measured contamination levels.

Especially the on-going methodological and instrumental developments in analytical chemistry in particular the recent introduction of ICP-MS-MS helps to improve the accurate quantification of contaminants at trace levels in complex matrix, but it also offers some interesting possibilities with respect to the quantification of selected biological effect markers in the marine environmental samples.

This contribution will show some first results dealing with the characterization and optimization of a recently introduced ICP-MS-MS system as well as its application for the analysis of different complex marine environmental samples after digestion or via using hyphenated techniques such as capillary LC. Compared to results obtained via conventional collision cell ICP-MS improved recoveries as well as drastically improved detection limits for interfered elements such as P, S, Ti, Cr, V, As or Se have been obtained, opening new possibilities for metal quantification but also for the heteroatom based quantification of potential biological effect markers.

A-a09

NOVEL METHODOLOGICAL APPROACHES FOR THE ACCURATE AND RAPID ANALYSIS OF ELEMENTAL IMPURITIES IN PHARMACEUTICAL PRODUCTS ACCORDING TO USP 232/233.

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Jessica KOVAC[2], Cornel VENZAGO[2], Stephan HANN[1]**
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New guidelines of the United States Pharmacopeia (USP) regulating elemental impurity limits in pharmaceuticals seal the end of unspecific and inaccurate analysis of (heavy) metal(oid)s as outlined in USP <231>. Chapter <232> specifies both, daily doses and concentration limits, respectively of metallic impurities in pharmaceutical final products as well as in active pharmaceutical ingredients (API) and excipients. In chapter <233> method implementation, method validation and quality control during the analytical process are described. By contrast with the – by now – applied methods, substance specific quantitative analysis features new basic requirements, further, significantly lower detection limits ask for the necessity of a general changeover of the methodology towards multi element analysis by ICP-AES and ICP-MS, respectively.

We present a novel methodological approach based on flow injection analysis and ICP-SFMS/ICP-QMS for the quick and accurate analysis of Cd, Pb, As, Hg, Ir, Os, Pd, Pt, Rh, Ru, Cr, Mo, Ni, Mn and Fe in drug products by prior microwave assisted acid digestion according to the regulation. In comparison to the acquisition of continuous signals, this method is advantageous with respect to the unprecedented high sample throughput (total analysis time <40 s) and low sample consumption (<50 µL) while meeting the strict demands on detection/quantification limits, precision and accuracy.

ULTRA-FAST ICP-OES DETERMINATIONS OF MAJOR, MINOR AND TRACE ELEMENTS IN SEAWATER USING NEXT GENERATION SAMPLE INTRODUCTION TECHNOLOGY

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Agilent Technologies, Australia

Major, minor and trace elements in seawater samples have been determined by axial ICP-OES using the novel OneNeb nebulizer and productivity enhancing Switching Valve System (SVS 2) accessory. Samples were prepared and analysed as per the US EPA 6010C method with excellent recoveries being obtained for certified reference materials. A robust analytical method was used for these challenging samples with a reduced plasma flow and featured IECs to correct for the various spectral interferences that can occur when analysing samples with complex matrices. The OneNeb was found to be the ideal nebulizer for handling the challenging sample matrix with excellent results being obtained. Significant improvements in sample throughput were achieved by using the SVS 2 sample introduction accessory, which had the added benefit of reducing the need to perform routine maintenance on the torch and sample introduction components.

A-a11

FAST SEMI-QUANTITATIVE AND QUANTITATIVE DIRECT SOLIDS ANALYSIS USING A FULLY SIMULTANEOUS MATTAUCH-HERZOG ICP-MS AND TRANSIENT SIGNAL ACQUISITION

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The fast determination of the elemental composition of solid materials is often hindered by time-consuming digestion procedures necessary for analytical methods typically requiring liquid samples, e.g. ICP-OES or ICP-MS. Consequently, to overcome this challenge, direct solid sampling methods have been developed and coupled to ICP-OES and ICP-MS, most notably laser ablation or electro-thermal vaporization. While these methods can convert a solid sample directly into a suitable sample aerosol, compared to the introduction of a liquid sample, several additional challenges arise for a fast semi-quantitative and, to a somewhat lesser extent, for a 'fully-quantitative' direct solid sample analysis.

Among minor issues like plasma stability and a different optimization with a dry aerosol, the major challenges are the requirements to measure fast transient signals and the design of a suitable calibration strategy, especially where no matrix-adapted solid standards might be available. If semi-quantitative analysis is regarded as 'calibration-less' (as e.g. in ICP-MS based on a response factor model), the demand for a suitable robust evaluation strategy becomes even more difficult to fulfill.

The fully simultaneous measurement of the complete inorganic mass spectrum should offer a uitable approach to overcome the aforementioned challenges. With all isotope signals measured at the same time, and at a sufficiently high repetition frequency, all elemental information from the sample can be retrieved, even with relatively fast transient signal generating sample introduction systems like ETV or few-/single-pulse laser ablation.

While the benefits of fast fully simultaneous measurement of complete spectra are obvious for transient signals, it is less obvious that this capability also drastically improves semi-quantitative analytical capabilities (not only for transient signal acquisition), as well as the efficient use of correction algorithms, e.g. for interferences, again improving data quality. Using laser ablation and ETV as examples, the presentation examines how semi-quantitative analysis based on a response function model and subsequent iterative data processing in combination with a fully simultaneous ICP-MS allows for a fast and direct analysis of solid samples. Analytical figures of merit, especially for accuracy, shall be presented and compared to traditional, calibration-based, evaluation methods for different sample matrices.

DETERMINATION OF BORON IN HIGH-TEMPERATURE ALLOY STEEL USING NON-LINEAR INTER-ELEMENT CORRECTION AND MICROWAVE PLASMA – ATOMIC EMISSION SPECTROMETRY

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The determination of B in high-temperature alloy steel using the innovative microwave plasma – atomic emission spectrometry (MP-AES) is presented. This new technology runs entirely on air, eliminating the need for expensive and flammable gases, while providing analytical performance that exceeds Flame Atomic Absorption.

Boron in steel, generally considered an analytically difficult element in a highly impacted matrix, was determined using HNO3-HCl digested steel solutions and 249.773 nm B emission line. Iron spectral interferences on this B emission line were corrected using a non-linear inter-element correction method. Steel matrix effects on B recovery were alleviated using the method of standard addition. The amount of B in NBS 348a steel is found to be 58±1 mg kg^{-1} and the certified amount of B is 55±4 mg kg^{-1}.

BACKGROUND LEVELS OF METALS IN URINE SAMPLES TO ASSIST WITH EXPOSURE ASSESSMENTS.

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Introduction

Biological samples such as urine and blood provide matrices where the endogenous status of elements can be determined. These measurements aid the assessment of systemic exposure to elements in both workers and non-exposed persons. Determining background levels of metals in urine samples from non-exposed people allows for normal levels in a population to be established. This provides a baseline for a direct comparison (and interpretation) of biological monitoring (BM) results from workers exposed to metals. There is a need to establish current background levels of elements in urine both for commonly monitored elements and for rarer elements being increasingly utilised in new technologies.

In this project urine sample were collected from unexposed persons and the samples were analysed by ICP-MS for a wide range of metals including rare and unusual metals.

Method

Background levels of more than 40 elements in urine from a UK population are presented here from 137 people. The samples were analysed by ICP-MS in different diluents and matrices depending on the elements. It has been possible to assign 95th percentile data to most of these elements (the rest are all below the LOQ of the method).

Results

The limits of quantification (based on the dilution factor of the sample multiplied by the background equivalent concentration from the standard calibration of each element) and the quality control data were established for each element. Summary statistics, including 95th percentile reference levels were determined for each element. Results show that it has been possible to establish 95th percentile background levels for most of the elements. The overall compares well with German and American results, however there are differences for some elements.

Mixed effect analysis was carried out on the elements, however, based on the high percentage of results <LOQ, the analysis was not carried out for the following elements: Zr, Sb, Bi, Ag, Os, Ir, Pt, Mn, and Sn. The mixed effect analysis showed that, for all of the remaining elements, creatinine correcting the data in all cases gave a reduction in variability or no significant difference in variability. It was also shown that smokers have elevated cadmium and lower boron and selenium levels than non-smokers.

Conclusions

Reference levels based on 95th percentiles for many elements have been established for a UK population. From the data presented here it would suggest that elemental concentrations in urine should be creatinine corrected. This data also shows that there have been no major changes in the unexposed levels of 'routine' metals used in everyday biological monitoring at HSL.

Comparison with HSL routine biological monitoring data shows that most (>70%) workers are within 95th percentile reference values for the elements presented here.

This data will be very useful and help to interpret results and assess exposure.

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A-a14

DETERMINATION OF TRACE-LEVEL AMOUNTS OF LANTHANIDES, THORIUM, PLUTONIUM AND AMERICIUM FROM URANIUM SAMPLES

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Impurities are present in nuclear materials as residuals of the initial source material and/or the chemical process used. The distribution and isotopic comosition of these contaminants are characteristic to the feed material, producing facility and location, which is of vital importance in nuclear forensics and safeguards. However, since these impurities are at very low concentration in nuclear-grade samples (typically below 5-50 $\mu g \cdot g^{-1}$ for common elements), the measurement can be cumbersome for several analytes or parameters, such as for lanthanides or when high precision isotope analysis of the impurities is to be performed (e.g. Pb, Sr or Nd analysis).

The separation and measurement of lanthanides (Ln), Th, Pu, Am from large size (400-500 mg) nuclear grade samples by inductively coupled plasma mass spectrometry is presented. Our method involves a simple co-precipitation of the analytes with Fe(III) or Al(III) carrier under well-defined pH. The distribution of U, Th, Pu, Am and Ln was followed by gamma spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) during the separation process.

The procedure is an effective preconcentration step for the forthcoming extraction chromatographic separation. The limits of detection for different elements in question are in the low pg/g range, the achievable cumulative U decontamination factor is in the magnitude of 107 - 108. The procedure was validated by the measurement of reference material (Cetama, Morille). The applicability of the method was demonstrated by the measurement of lanthanides in high purity uranium samples. The method can also be extended for the trace-level isotopic analysis of neodymium measured by multicollector ICP-MS. By the combination of the lanthanide pattern with the isotopic information, the uranium deposit type and the origin of an unknown nuclear material can be assessed with high reliability.

DETERMINATION OF LIGHT ELEMENTS IN STEEL BY OPTICAL EMISSION SPECTROSCOPY

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In general combustion analysis is the preferred and most common technique to quantitatively determine light elements such as C, N and O in steel. The major reason is that it is very difficult to analyze low concentrations of those elements with optical emission spectroscopy due to many possible contamination sources. Recently improvements have been made to spark source optical emission spectroscopy which makes it possible to determine oxygen and nitrogen with SS-OES and also lowering detection limits and improving accuracy for C and S measurements.

The main advantage of those improvements is that the full chemical composition of a sample can be determined with one instrument. This could significantly reduce cost in the sense of reduced analysis time and less consumption of consumables.

Depending on the concentration range and general chemical composition however, in some cases combustion analysis will still be required.

In this presentation results from combustion analysis will be compared to those of Spark Source Optical Emission Spectroscopy, resulting in guidelines concerning the applicability of SS-OES as an alternative to combustion analysis for steel materials.

OPTIMIZATION OF GEOMETRICAL AND OPERATING PARAMETERS OF AN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER: A COMPUTATIONAL STUDY

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An inductively coupled plasma connected to a sampling cone is computationally investigated. It is studied how and to what extent the plasma characteristics upstream in the ICP are affected by changes in geometrical and operating parameters. By changing the position of sampling cone above the load coil (7 – 17 mm) as well as the diameter of the sampler orifice (1, 1.5, 2 mm), the optimum range of geometrical parameters is investigated. Moreover, the role of pressure behind the sampler for each different geometrical setup is studied. Finally, also the effect of injector flow rate, auxiliary flow rate and applied power are examined. The optimum range of injector flow rate for a certain setup, which guaranties the presence and also a proper length of the central channel in the torch, is obtained. Our results show that depending on the purpose, it is possible to control that only the injector gas passes through the sampler orifice or it is accompanied by the auxiliary flow. Using a proper applied power can increase the efficiency of the system. Indeed, by changing the gas path lines, it can control which flow (i.e., central or intermediate) goes to the sampler orifice. By changing the plasma temperature, it results in changes in the ionization rate in the coil region and by changing the length of the cool central channel it affects the process of transferring the droplets to the sampler.

EXPANDING THE DIRECT ANALYSIS CAPABILITIES OF PLASMA-BASED AMBIENT MASS SPECTROMETRY SOURCES

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A variety of discharge ion sources have been developed to desorb/ionize molecules directly from surfaces in the ambient environment lending them to the field of ambient mass spectrometry. Essentially, the goal of this field is to use the selectivity and sensitivity of the mass spectrometer to resolve components in complex mixtures, obviating the need for sample pretreatment or separation. These plasma sources, which include direct analysis in real time (DART), the flowing atmospheric-pressure afterglow (FAPA), and the low-temperature plasma (LTP), yield high desorption/ionization efficiencies and simple mass spectra. While numerous discharge designs and applications have been introduced, little work has focused on fundamentally examining these discharges in the context of molecular mass-spectrometric analyses. Such information is important to improve the weaknesses of plasma-based ambient MS methods which include desorption and ionization matrix effects, inability to quantify analytes without an internal standard, and online identification of analytes in a complex system.

Here, mass-spectrometric experiments, in conjunction with other established analytical methods, were used to understand the desorption and ionization pathways for the FAPA and LTP sources. These studies have revealed desorption and ionization pathways that differ from those theorized in the literature. For instance, some species are liberated into the gas phase through mechanisms other than thermal desorption, which is often believed to be the main desorption pathway for these plasma-based sources. Current data suggests that certain analytes can undergo a chemical-sputtering process where a reaction with excited plasma species leads to liberation of molecules from a surface.

These fundamental findings were then used to develop different source designs and/or operating modes, which enhance identification and quantification of analytes. One example that will be presented is altering the ionization chemistry of the discharge such that different analyte ions can be formed with varying operating conditions, which increases the range of detectable analytes. Furthermore, this type of system can be made switchable such that a number of analytes can be directly identified during a single analysis.

A-b03

TECHNOLOGICAL PROGRESS IN CONSTRUCTION OF ROTATING PLASMA SOURCES

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Rotating microwave and pulse (“digital”) plasma sources exhibit some limitations of their important physical parameters – in particular electron density number and excitation temperatures. It is due to the fact, that above a certain power level (about 50 W per electrode), analytical lines from the electrode material are becoming visible in the spectra. Ways of safe power increasing are described in the presentation, such as intensive cooling of the electrodes and optimization of some of the operating parameters.

A-b04

DISPERSED PARTICLE EXTRACTION – A NOVEL APPROACH FOR ANALYTE ENRICHMENT AND MATRIX REMOVAL

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“Conventional” Solid Phase Extraction (SPE) is a well-established technique and undisputedly a onvenient tool for sample pre-treatment. However, in certain cases, it suffers from problematic elution procedures, since quantitative recoveries can only be obtained by using concentrated acids, organic solvents and/or noxious eluting agents. Besides concerns about operational safety, the obtained solutions are usually not adequate for ICP analysis since they may cause corrosion and exhibit adverse effects on the plasma.

Therefore, a novel approach for SPE-based sample pre-treatment is introduced to the field of inorganic trace analysis. Here, the analyte-resin adduct is analyzed directly with no elution required. The proposed Dispersed Particle Extraction is based on the state-of-the-art principle of “on-bead detection” which is frequently used in bio-analytical chemistry. There, analyte-loaded beads with diameters in the order of 50 to 100 µm are analyzed using flow-through cells in combination with photometric, fluorescence and chemiluminescence detection [1-4].

Sorbent beads of this size are not compatible with standard sample introduction devices for ICP techniques. Therefore, we use sub-µm silica particles equipped with a nano-porous surface which is chemically modified to obtain Strong Anionic and Strong Cationic Exchanger functionalities (SAX and SCX, respectively). By dispersing these particles in a liquid sample (“Dispersed Particle Extraction”), the analytes are retained on the particle surface. Thus, the analytes can be separated from the sample by removing the particles from the surrounding solution. After chemical decomposition of the nano-particles, the obtained clear solution can be analyzed via conventional ICP-MS instrumentation. Due to the small particle diameter and the porous structure, extremely low amounts of the material are sufficient for quantitative recoveries. Another benefit of the Dispersed Particle Extraction is the implementation of the “renewable surfaces principle” where fresh sorbent material is used for each analysis. This completely eliminates memory-effects or analyte losses usually observed when repeatedly using SPE columns.

In order to highlight the advantages of Dispersed Particle Extraction we present an overview of the following applications:

a) determination of rare earth elements in saline waters,
b) separation of uranium and thorium for improved age-determination of nuclear material,
c) determination of platinum group elements in urban roadside-dust.

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A-b05

INVESTIGATION OF CORROSION PRODUCT DEPOSITS ON NUCLEAR FUEL RODS BY MEANS OF ICP-MS AND ELECTRON MICROSCOPY

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Dissolved and suspended solid corrosion products from structural elements in light-water reactors (so called crud) are of concern to the nuclear power operators: a) large fraction of these corrosion products deposit on the outer surface of fuel rods, where they can compromise the thermal efficiency of the rods and lead to increased cladding corrosion and potential fuel failure; b) crud particles can migrate away from the cladding surface and can cause radioactive contamination in cooling-water systems and spent-fuel storage areas. While the conditions leading to rod failure are not always fully understood, the failures are generally attributed to a combination of water chemistry, fuel duty, and cladding materials.

Fuel crud mainly consists of iron, nickel, manganese, and chromium oxides. Investigations of the structure revealed that the main phases for boiling water reactor crud are normally hematite and non-stoichiometric nickel ferrite spinels, whereas for pressurized water reactor crud the main phases are shown to be non-stoichiometric nickel ferrite and nickel metal or oxide.

The structural characterization of dispersed crud has in resent years been expanded towards the characterization of Pt nanosize particles which are added to the boiling water reactor (BWR) feed water. The method developed by GE Hitachi, called “Online NobleChemTM”, is intended to prevent irradiation assisted stress corrosion cracking of structural components in the pressure vessel of a WR. Pt acts as a catalyst in order to achieve reducing conditions on the surface of the reactor internals while adding low amounts of hydrogen during normal operation. Therefore, knowledge about the Pt distribution is essential for proving the efficiency of the protection method.

The characterization of the chemical composition of crud collected on filter holders and of the Pt distribution in crud by means of inductively coupled plasma mass spectrometry (ICP-MS), scanning (SEM) and transmission electron microscopy (TEM) will be discussed in the presentation.

A-b06

SPECTROMETRIC TECHNIQUES APPLIED TO THE OPTIMIZATION AND PROCESS CONTROL OF A PILOT PLANT FOR THE RECOVERY OF RARE EARTHS FROM RED MUD

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Red mud (RM), the bauxite residue of the Bayer process for the production of alumina, is an insoluble, highly alkaline (pH 10-13), fine grained waste. In Greece about 600,000 tons of RM are produced per year. It consists mainly of oxides and compounds of the major elements Fe, Al, Ca, Na, Si, Ti, as well as of various minor and trace elements, such as V, Cr, Zr, Nb, Rare Earth Elements (REEs) and more. Due to its characteristics it can be used in industrial and construction applications, in water and waste treatment as well as for the recovery of valuable elements such as Ti, Zr, REEs (Sc, Y, lanthanides). The rare earth elements are of high techno-economical interest due to their use in high and green technology applications such as catalysts, super-alloys, permanent magnets, superconductors, ceramics, batteries, fuel-cells. Their numerous uses in advanced materials combined with their high commercial value especially in high purity have led to international efforts for their separation from the matrix (minerals, byproducts) and their recovery as individual elements. The REEs content of the Greek RM was found to be about 1000g·ton^{-1} with a scandium (Sc) content about 130g·ton^{-1} comparable to its main economically exploitable deposits [1].

An innovative method for the separation and recovery of REEs and especially of Sc from RM was developed in lab scale and up scaled to a pilot plant [2,3]. This includes selective acid leaching, ion exchange and extraction/back-stripping processes resulting in a high purity Sc final product. For the process control (recovery, purity of the products) and the optimization of the several steps of the pilot plant procedure, various modern spectrometric techniques have been used. The mineralogical and chemical composition of different RM batches were studied by XRD, SEM-EDAX, FT-IR and XRF [4]. Plasma techniques as ICP-OES and ICP-MS were used for the determination of REEs in RM after appropriate digestion, in the liquid mixtures in the various stages of the pilot plant and for the control of the purity of the final products. AAS was used for the determination of main and minor elements, respectively. The efficiency of the techniques used for the determination of REEs was investigated due to the high matrix content of RM. The spectral interferences especially from the high Fe concentration of the RM were studied and the appropriate wavelengths of REEs as well as the optimized operating parameters were proposed. The validity of the methods used was tested with appropriate reference materials and the obtained precision, accuracy and detection limits for the above techniques were compared. The optimization of the pilot plant method for high recoveries along with the production of high purity products is of great importance especially for the elaboration of a feasibility study for the recovery of REEs and mainly scandium oxide from red mud in industrial scale.

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A-b07

INORGANIC ARSENIC IN SEAFOOD: DOES THE EXTRACTION METHOD MATTER?

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Seafood products have naturally high concentration of total arsenic, however, a large portion of the arsenic in seafood is present in the form of the benign organic compound arsenobetaine (AB). Other arsenic species, including the most toxic inorganic arsenic (iAs) species, are generally present in lower concentrations [1]. Determining the iAs in seafood can pose an analytical challenge since it only constitutes a small portion of the total arsenic concentration among a large variety of other organoarsenic species. Today, EU legislation for maximum levels of iAs in foodstuff are on the horizon, therefore reliable methods for the determination of iAs in foodstuff are needed.

High-performance liquid chromatography (HPLC) with online detection by inductively coupled plasma-mass spectrometry (ICP-MS) is a very common method for separation of arsenic species [2], but to do so beyond doubt of co-elution with any other As compound is often difficult to achieve. The addition of an extra step of hydride generation (HG) to HPLC-ICP-MS for arsenic speciation was shown to be an excellent option [3]. There has been an on-going debate within the scientific community whether the iAs concentration determined in food commodities is dependent on the analytical procedure (extraction/instrumental setup)[4].

To test whether the concentration of iAs determined in seafood is dependent on the extraction method, nine different extraction methods were evaluated for three seafood samples: Certified reference materials (CRM) DOLT-4 (Dogfish Liver) and TORT-2 (Lobster Hepatopancreas), and a commercial herring fish meal. All experimental work was carried out by the same operator using the same instrumentation (including HPLC-HG-ICP-MS), thus eliminating possible differences in results caused by lab related factors.

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DISSOLUTION MADE EASY FOR CHROMITE ORES, FERROCHROMES AND CHROMIUM SLAGS BY PEROXIDE FUSIONS FOR ICP ANALYSES

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Introduction

Although more than 10 chromium minerals are known, only one is of commercial importance as a source of chromium. This mineral is known as chromite and has the theoretical composition $Fe.Cr_2O_4$ containing 68 percent chromic oxide (Cr_2O_3). The main product generated by chromite is ferrochrome which is a major player in the steel industries. Ferrochrome for the stainless steel industries uses more than 90% of the world's chromite output.

Mining and Steel industries must assess the quality of the chromite ore to optimize the production of good quality stainless steel so the chemical analyses of the chromite ore as well as its final and waste products are mandatory. Metal analysis traditionally uses AA or ICP-OES to measure the metal contents in the ores and industrial products. However, the traditional dissolution method for chromite and ferrochrome is a multi-step, multi-acid digestion which requires the use of HNO_3, HF and $HClO_4$ and can take anywhere from 1 to 3 hours.

Knowing the risks associated with the use of HF and $HClO_4$, many laboratories look for alternative methods for obtaining full dissolution of their samples while optimizing the uptime and productivity.

The proposed method describes an easy way to determine the concentration of elements of interest contained in chromite ores, ferrochromes as well as ferrochrome slags using peroxide fusions for ICP-OES determination.

Materials and Methods

Three reference materials were tested: CRM NIST 64c – (FeCr), CRM Mintek SARM8 (Chromite Ore) and Mintek SARM77 (FeCr slag) as well as 3 different samples.

All fusions were performed on a Claisse Peroxide six position automated Fluxer using a sodium peroxide and sodium carbonate flux mixture.

Quantitative analyses were performed using an ICP-OES fitted with a cross flow nebulizer, a Scott spray chamber, and an alumina injector. All calibration standards were matrix matched using the same sodium peroxide/carbonate flux used for the fusion of the samples. Acids were of the trace metal grade.

Background corrections (BGC), multi-component spectral fitting (MSF), and inter-element spectral corrections (IEC) were performed to deal with the multiple interferences. ICP-OES parameters were adjusted to minimize torch effects with the RF Power adjusted at 1500 W, argon flow at $16\ L\cdot min^{-1}$, and sample flow below $1.0\ mL\cdot min^{-1}$.

Significance

The significance of this research resides in the simplicity of the method, its speed (complete sample dissolution in less than 12 min), automation and the absence of harsh acids. Furthermore, this technique does not require highly skilled operators.

A-b09

DYNAMIC EXTRACTION OF SOLUBLE SURFACE LAYERS WITH ON-LINE ICP-OES DETECTION – A NOVEL APPROACH FOR DETERMINATION OF DEPTH PROFILES

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Over the past decades a global search for new materials and technologies improving energy storage and transformation has started in order to provide a sustainable solution for the world's continuously increasing demand of energy. One of the most promising candidates for future energy conversion is the solid oxide fuel cell (SOFC) [1] using mixed ionic and electronic conducting (MIEC) perovskite oxides such as La0.6Sr0.4CoO3-δ (LSC) [2] with comparatively fast oxygen exchange kinetics even at intermediate temperatures. However during operation degradation effects of the electrochemical kinetics can occur that are most likely correlated to changes of the electrode surface of LSC, impeding the commercial use [3].

To achieve a better understanding of the underlying physical and chemical phenomena mechanistic studies with thin LSC films (200 nm) deposited via pulsed-laser-deposition on yttria-stabilized zirconia (YSZ) electrolyte substrates were performed. The effect of different deposition parameters or annealing times was investigated using a special set-up for in situ etching of the sample surface and on-line analysis of the eluate composition by inductively coupled plasma – optical emission spectrometry (ICP-OES). With this approach chemical etching depth profiles of the investigated samples could be determined, which provide in contrast to classic batch-wise extraction time resolved information about the etching process. Owing to the continuous optimization of this method, highly reproducible measurements became possible showing cation composition changes even in the first two nmol, corresponding to 0.1 to 2 nm depth depending on thin film surface accessibility. Investigations were supported by electrochemical impedance spectroscopy (EIS) and time of flight - secondary ion mass spectrometry (ToF-SIMS), indicating the formation of a Sr rich phase at the surface which increases with annealing time.

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MICROWAVE ASSISTED HIGH PRESSURE FLOW DIGESTION: NEW APPROACHES TO SOLVE OLD PROBLEMS

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Microwave assisted sample digestion using pressurized closed vessels is a well-established and widely used technique for sample mineralization. The main drawbacks of this batch type approach are the inherent difficulties of automation and direct coupling capabilities to the analyte quantification instrument. Flow digestion on the other hand can circumvent these problems.

In this contribution we will present a novel continuous flow, high pressure flow digestion system for liquid samples and slurries. The sample mineralization was performed in a PFTE tube located in the radiation field of a commercial microwave sample digestion system (Multiwave 3000, Anton Paar, Austria). To attain the desired high digestion temperature of up to 230°C (the acids boiling temperature is a function of the pressure within the PTFE tube), the PTFE tube was placed inside a pressurized autoclave formed by a multi turn glass coil. This coil was pressurized with up to 40 bar nitrogen supporting the PTFE tube and preventing tube rupture. A new gas liquid separator integrated in the presented flow digestion system circumvented many of the problems and shortcomings of previously reported gas liquid separators. The flow digestion system was fully automated and computer controlled and allowed unattended sample decomposition of large numbers of samples.

As the entire flow path of the presented high pressure flow digestion system was made of inert, fluorinated polymers the selection of the used acid cocktails for sample mineralization was not constrained by potential corrosion problems. 12 certified reference materials (plant materials, food, sewage sludge) were digested using nitric acid (30% v/v) or mixtures of nitric acid with hydrochloric acid (3% v/v), hydrofluoric acid (3% v/v), or hydrogen peroxide. The results were in very good agreement with the certified values.

Other characteristics of the presented high pressure flow system are very low blank values even for contamination prone elements like Zn and the absence of element- specific losses, that were observed in other high pressure flow digestion systems [1].

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ELEMENTAL IMPURITY COMPLIANCE STRATEGY FOR A LARGE VOLUME PARENTERAL MANUFACTURER

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Elemental impurities may be introduced into drug products from excipients, active ingredients, product packaging or from the manufacturing process. Traditionally, heavy metals have been assessed in drug products by a general screening test that indicates metallic impurities by colored sulfide precipitation and more recently by ICP-AES. Several studies have been conducted to evaluate the toxicity of potential elemental impurities in drug products and establish a permitted daily exposure for individual elements. Due to the potential toxicity of certain elements, drug product manufacturers will need to develop a strategy to control individual element impurity levels within acceptable limits. Our site compliance strategy has been premised on using ICP-MS technology over the less sensitive technique of ICP-AES because the permissible daily exposures for elemental impurities in large volume parenterals (LVP: defined as a daily dose of an injection greater that 100 mL) are the lowest of any class of drug presentation. A pharmaceutical strategy will be presented to consider all aspects of implementation of ICP-MS product release in a cGMP manufacturing environment including partnership and qualification of vendors, a survey of finished product manufacturing processes, ICP-MS laboratory design and integration of on-going control testing into existing CFR Part 11 compliant information management systems. System suitability for daily instrument usage along with sample preparation scenarios were evaluated. Air and water purification systems were evaluated to ensure minimal elemental contamination appropriate for sub part-per-billion level quantitation.

ICP-MS STUDY OF ROLE OF MICROELEMENTS IN THE BLOOD OF ONCOLOGIC PATIENTS

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The problem of oncological diseases develops a significant meaning nowadays. Cytogenetic studies with oncological subjects have been performed for long and rather successfully. However, these studies cannot fully explain the reason of origination and define a forecast for disease. One of the factors that would help to find a necessary explanation could be a study of microelements' pool. Their impact on immune system and body as a whole is ambiguous and has so far been explored insufficiently.

The purpose of our study is to define the content of microelements in healthy patients compared to those with a compromised medical history (oncologic pathology) and brain tumors (meningioma of different malignancy grades). Bruker 820 ICP-MS equipped with Ion Mirror optics and CRI mini-Collision Cell technology was used for microelements quantitative and qualitative determination due to extra sensitivity and excellent interference reduction. ICP-MS collected data were compared to parallel cytogenetic study of peripheral blood lymphocytes in these groups of patients. Lymphocytes cultivation and chromosome specimen preparation was carried out by a standard semi-micromethod [1].

During the experiment the blood samples were obtained: 21 samples with benign meningioma (malignancy stage I-II) and 29 samples with malignant meningioma (malignancy stage III-IV). As a control group, the following samples were examined: patients with somatic pathology presenting no family history of oncologic diseases (13 samples) and with family history of oncologic diseases (14 samples), as well as a group of healthy patients (20 samples presenting no family history of oncologic diseases and 11 samples with family history of oncologic diseases).

Cytogenetic studies showed that the presence of oncologic pathology in a family has proven increased risk of oncological diseases, however more detailed forecasting about body condition has not been provided so far.

According to the references, patients with tumors have increased iron levels in their blood, which is comprehensively reported in our studies. It is worthy of note that patients with family history of oncologic diseases have higher values than those in analogous groups, i.e. depending on the amount of iron in the blood it is possible to calculate a hypothetical risk of disease origination. According to a number of authors [2] patients with malignancies have either iron deficiency or redundancy. Samples from the group represented with somatic pathology compromised by family history of oncologic diseases had decreased iron levels; and those with tumors had increased iron levels. Pretty similar picture is observed with regard to selenium also. Elevated levels of zinc and nickel were also noted in oncologic patients.

Therefore, the retrieved data on detection of microelement level in the blood can be used as additional criteria while forecasting origination and development of tumor masses in groups of people presenting with family history of oncologic diseases.

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OPTIMISATION OF OPERATIVE CONDITIONS FOR THE DETERMINATION OF SILICON CONCENTRATIONS IN VITRO AND EX VIVO BIOLOGICAL MATRICES BY DRC-ICP-MS

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Silicon (Si) appears to play an important role in connective tissue health (e.g. blood vessels, skin and hair). However its analysis is hampered by number of issues: a) its low biological levels compared to environmental ubiquity, b) its formation of thermally refractory oxides and c) in case of quadrupole ICP-MS, by the presence of various polyatomic interferences such as N_2 and CO. Thus ICP-OES has been the preferred analytical technique as it outperformed quadrupole ICP-MS for this particular analyte and most novel analytical approaches for in vitro and ex vivo biological matrices have been left in the domain of high resolution MC ICP-MS or have been limited to alternative approaches, such as the use of tracer (e.g. Ge) in transport studies.

DRC-ICP-MS offers the possibility to remove selectively polyatomic interferences - however in the case of silicon not everybody seemed to succeed leading to much controversy regarding the analysis of silicon by DRC-ICPMS [1-3]. Thus in this study a thorough investigation into the applicability and reliability of the dynamic reaction cell used with various gases for removing N_2 and CO interferences was undertaken. We have succeeded in developing a new method for the analysis of ^{28}Si and ^{29}Si by DRC-ICP-MS in biological matrices capable of achieving analytical LODs < 1 ppb under standard non-clean room laboratory conditions and in original sample volumes of 50 µL. To help us achieve this, we used an inert sample introduction system, the flow injection sample introduction technique and a DRC-ICP-MS with ammonia as reaction gas in DRC mode only. We will report results of analysis of silicon in serum samples and in vitro transport studies in oocytes as examples of application of this new method.

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ICP-MS AS MONITORING TOOL TO ENSURE THE QUALITY AND SAFETY OF NORWEGIAN MARINE FISH

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Fisheries and aquaculture are growing global sources of protein for the human diet. At the same time these marine ecosystems act as ultimate sinks for globally emitted inorganic pollutants of anthropogenic and natural origin. Some of these pollutants such as Cd, As, Hg and Pb may pose a health risk for consumers and thus some have maximum limits in fish and seafood laid down in EU regulations (e.g. Cd Hg and Pb) while for others such as arsenic and inorganic arsenic legal limits in seafood have not been established yet.

Safe and healthy food is of growing concern for consumers and regulative bodies, especially taking the global food trade in account. Therefore, since fisheries and aquaculture are key industries and export sectors of Norway, the National Institute of Seafood and Nutrition Research (NIFES) monitors the quality and safety of Norwegian seafood for the Norwegian Food Safety Authority.

In addition to ongoing monitoring of aquacultured seafood, large baseline studies have been initiated over the last years with the aim of documenting the current reference level of the pollutants in different marine fish over the entire Norwegian coast and economical zone.

NIFES has so far completed baseline studies for six species: Norwegian spring spawning herring (800 fish), North Sea herring (1000 fish), Mackerel (850 fish), Greenland halibut (1300 fish), Atlantic cod (2200 fish) and Northeast arctic saithe (950 fish). The fish were collected from the entire distribution area of each species within Norwegian waters and analyzed individually for a wide range of heavy metals and other elements as well as for the persistent organic pollutants dioxins, PCBs and polybrominated diphenyl ethers. To cope with this large scale biomonitoring, NIFES has established a method based on microwave assisted digestion of marine tissue and subsequent determination of trace metals by Q-ICP-MS. The method is now an NMKL method, CEN method and AOAC method. The baseline studies of marine fish show in general, with few exceptions, low levels of contaminants, below the legal limits. Apart from discussing the food safety aspect of the baseline studies we also show the potential for scientific collaborations based on our large current and future samples set of marine species from the North Sea, Skagerrak, Norwegian sea, Barents Sea and Norwegian fjords.

A-b15

COMBINING HIGHEST SENSITIVITY WITH SELECTIVITY FOR QUADRUPOLE ICP-MS

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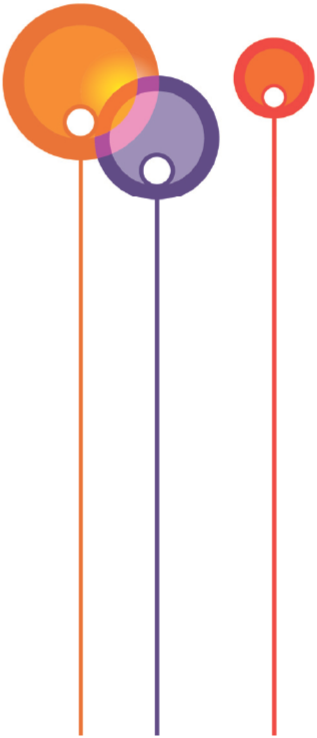
The applications for trace elemental analysis are steadily increasing: beside the classical fields such as environmental and semiconductor analysis more and more interest for trace elemental analysis in food, pharmaceutical, clinical analysis and material characterization can be observed, not to forget hot topics such as analysis of nano-particles. At the same time the requirements for lower detection limits, sample throughput, matrix robustness, and not to forget easy to use instruments are increasing.

ICP-MS plays meanwhile a major role in the trace elemental laboratory and is faced with this increasing interest for analysis of different sample types. An important performance characteristic for ICP-MS is the sensitivity or betters the signal to noise ratio. High sensitivity is not just important to reach low detection limits but offers a range of side benefits, such as the ability to use higher dilution factors for complex, e.g. high TDS (total dissolved solids) samples, without sacrificing detection limits, faster scan speed due to shorter integration times, and when coupled to laser ablation devices high sensitivity is mandatory to detect signals derived from small spot-sizes. The presentation will describe the layout of an ICP-MS designed for highest sensitivity not just in standard mode (> 106 cps/ppb) but also in collision / reaction mode (> 105 cps/ppb). Furthermore applications examples which benefit from this performance characteristic will be shown.

B section

Stable isotope analysis & HR ICP MS



ISOTOPE DILUTION MASS SPECTROMETRY – AN EXHAUSTING WAY FROM AN EXOTIC TO A GENERALLY ACCEPTED METHOD IN ELEMENTAL TRACE AND ELEMENTAL SPECIES DETERMINATION

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Until 1990 the isotope dilution mass spectrometric (IDMS) technique was more or less exclusively used in connection with thermal ionization mass spectrometry (TIMS). Until this time, TI-IDMS elemental trace analyses were preferably carried out for geological purposes, in nuclear technology and for the certification of standard reference materials. In 1965 I started with this analytical technique and, in the following, an important part of my research activities was connected to this method. Our greatest success in TIMS was the development of an extremely sensitive and precise method for measuring osmium isotopes by negative thermal ionization mass spectrometry [1]. This opened the door to apply the Re/Os clock to geological samples, which was not possible before using other mass spectrometric techniques like RIMS.

In 1989 our group published the first species-specific TI-IDMS results on selenium species using off-line separation prior to TIMS measurements [2]. However, an important step forward in species-specific IDMS was the first use of a HPLC/ICP-MS hyphenated system in 1994 to determine lead and iodine species by the group of Les Ebdon and our group, respectively [3,4]. The great advantage of ICP-MS was its relatively easy on-line coupling with separation techniques. In the following, the species-specific technique was preferably used for accurate determination of environmentally important species like methyl mercury or the butyl tin compounds. The species-specific method was also applied to identify species transformations and multi-species methods were developed in this connection.

However, a really extensive application of hyphenated ICP-IDMS methods for elemental species was not possible until the species-unspecific ICP-IDMS technique was established in 1994 by Rottmann and Heumann [5]. This method allows multi-species determinations without the use of a species-specific spike. Nowadays, hyphenated species-unspecific ICP-IDMS determinations of heteroatoms like sulphur became a common and world-wide used quantification technique, for example in proteomics. Some comments will also be given on IUPAC's recommendation that the atomic weight is no longer a fixed value for ten important elements [6]. Finally, an example of elemental speciation in a spectacular environment, which was one of our most exciting research projects, will be presented.

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HIGH PRECISION ISOTOPE RATIO MULTIPLE COLLECTOR ICP MS FROM PLANET FORMATION TO MEDICINE

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Multiple collector ICPMS has provided new opportunities to explore at high precision and in small samples the innate isotopic diversity of the periodic table, in a fashion that was only being imagined two decades ago. Isotopic systems that offered great potential for understanding the natural world, but were extremely hard to develop and exploit, became tractable. The geochemical applications have been varied. For example, measuring the decay products of short-lived nuclides such as 182Hf in the early Solar System has yielded the age of planet Mars, and confirmation of the Giant Impact theory for the origin of the Moon. Measuring nucleosynthetic Ti isotopic diversity in meteorites has provided powerful evidence that the Moon formed from atoms derived from Earth, not the impacting planet Theia. Mass dependent fractionation has allowed identification of Si as one of the hotly debated light elements in Earth's metallic core. Applications to recent Earth history are no less broad. Small mass dependent isotopic fractionations in elements as different as Li, Mg, Si, V, Fe, Ni, Ge, Mo and U are being used to explore the history and nature of weathering, sedimentary processes, biological productivity and ocean chemistry and how these are affected by climatic change. While there is much still to do in geochemistry the field is diversifying still further and a key area that is being explored now is the natural isotopic fractionation associated with specific compounds and processes in the biological and medical realm.

UNLEASHING THE FULL POWER OF ICP-MS BY EXPLOITING ISOTOPIC INFORMATION

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There is no doubt that ICP – mass spectrometry is a very versatile and powerful technique for (ultra)trace element analysis, but its forces are really unleashed when also relying on its capability to provide information on the isotopic composition of target elements [1,2].

Although single-collector ICP-MS instruments only offer a relatively modest isotope ratio precision, they fulfill the requirements for the majority of work involving quantification of induced changes in the isotopic composition of the target element(s), e.g., in the context of elemental assay or elemental speciation relying on the use of isotope dilution or of tracer experiments using stable isotopes. It will be discussed how introduction of more novel types of ICP-MS instrumentation, such as ICP-MS/MS and Mattauch-Herzog ICP-MS allow to further extend the application range and/or improve the figures of merit in various ways.

Of course, for isotope ratio determination, multi-collector sector field ICP-MS instrumentation is the *nec-plus-ultra* equipment. It provides the superior isotope ratio precision required to detect, quantify and exploit the typically modest natural variation in the isotopic composition of elements, resulting from isotope fractionation processes. While obtaining high precision is easy, assuring high accuracy is much more demanding and brings the ICP-MS scientist back to the lab for isolation of the target element from the concomitant matrix.

It will be demonstrated that not only elements with radiogenic nuclides, such as Sr and Pb [3], but also elements that show much smaller natural variation in their isotopic composition as a result of isotope fractionation seem promising as a source of information required to unravel the origin of the raw material an archaeological or historical object is manufactured of. Also in the field of biomedicine, the concept of natural variation in the isotopic composition of metals is being realized and efforts to see whether and how the corresponding measurements can be exploited in a diagnostic context will be discussed.

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BK-2

MASS-INDEPENDENT FRACTIONATION OCCURRING IN MC-ICPMS: A COMMON PHENOMENON? AND ITS IMPLICATION FOR ACCURATE ISOTOPE AMOUNT RATIO MEASUREMENTS

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Since its commercialization in 1992, the multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) has quickly become a powerful research tool for the determination of isotope amount ratios for its applications in a wide range of fields and disciplines [1-2]. Attributed to its inherited high sample throughput, a simple sample introduction and the ability of the ICP source to ionize nearly all elements in the periodic table, publications of MC-ICPMS have grown exponentially over the last twenty years. It has reached a total of 4,810 by March 2012, with 960 publications in the year of 2011 alone [2]. This deluge, however, has also created significant confusion and inconsistencies in how to obtain highly accurate and precise isotope amount ratios measurements by MC-ICPMS. compared to the conventional thermal ionization mass spectrometry (TIMS), MC-ICPMS suffers much larger mass bias. The mass bias in MC-ICPMS is generally considered to be mass-dependent fractionation (MDF), and is corrected by various mass-dependent correction models such as the most widely used Russell's law (Eq. 1).

$$r_{i,j} = R_{i,j} \cdot \left(\frac{m_i}{m_j}\right)^f \quad (1)$$

Here $R_{i,j} = n(^{i}E)/n(^{j}E)$ is true or mass bias corrected ratio, $r_{i,j}$ is the measured (uncorrected) isotope ratio and E is the element of interest, f is the fractionation function and m_i, m_j are the nuclide masses. However, mass-independent fractionation (MIF) in MC-ICPMS was reported for elements such as Ge, Cd, Nd, Hg, Pb and W [5-7]. Until recently MIF in MC-ICPMS has been perceived as a rare phenomenon that occurs in operations in dry plasma mode and with the use of high sensitivity X skimmer cone. In our most recent study, significant MIF in MC-ICPMS is observed for a wide range of multi-isotopic elements such as Si, Ca, Cr, Fe, Zn, Sr, Mo, Cd, Ba, Ce, Sm, Hf, Nd and W under normal operation conditions and with the use of standard cones. These findings suggest that MIF is a common phenomenon within MC-ICPMS, and consequently has serious implications on the absolute isotope amount ratio measurements. The application of the traditional mass-dependent correction models in MC-ICPMS, including Russell's law and the double spike model that was once perceived as most accurate, need to be reconsidered, since the use of mass-dependent models to correct for instrumental bias for isotopes that display mass-independent discrimination can result in inaccurate isotope amount ratios. In this talk, research results on MIF observed in MC-MCP in our group and its implication for isotope amount ratio measurements will be presented and discussed in details.

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THE POTENTIAL OF ISOTOPIC RESEARCH IN ANALYTICAL ECOGEOCHEMISTRY

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Analytical Ecogeochemistry deals with the development and application of analytical methods for the advanced, highly sensitive and reliable measurement of elements and isotopes in abiotic and biological media and its application to fundamental questions of ecosystem ecology following a holistic approach, including the human sphere. Selected isotopic systems (e.g. H, C, N, O, S, Sr) are in use to study these processes. Nonetheless, new isotopic systems are increasingly investigated (e.g. B, Mg, Ca, Zn, Cu, Cd, Hg). The analytical process is still challenging due to small fractionations and potential interferences. The development and application of isoscapes represents in this context a crucial pre-requisite for many applications, pointing out the strong spatial relation of this ecosystem based scientific approach.

This paper will focus on the development and use of isoscapes (isotopic landscapes), which reflect spatially depicted distributions of isotopic compositions usually produced by using Geographic Information Systems. In this context, isoscapes are used to predict the provenance of agricultural goods or the interpretation of mobility and migration in biological systems. A comprehensive approach for the use of isoscapes in terrestrial and aquatic ecosystems will be discussed on the example of the Sr isotopic system together with the need for accurate and reliable data and limits arising from measurement uncertainties.

These considerations will be expanded to the discussion of a novel approach for the identification of mixed isotopic ratios as a result from different sources available in the same entity on the example of mixed uranium isotopes in single particles.

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ACCURATE PLUTONIUM ISOTOPE ANALYSIS USING SF-ICP-MS PROVIDED EVIDENCE FOR THE RELEASE OF PLUTONIUM FROM THE FUKUSHIMA DAIICHI NUCLEAR POWER PLANT ACCIDENT

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After the nuclear accident at the Fukushima Daiichi Nuclear Power Plant (DNPP) in March 2011, hydrogen explosions and reactor building explosion resulted in releases of a large amount of radionuclides into the atmosphere and ocean. The released high volatility fission products including ^{129m}Te, ^{131}I, ^{134}Cs, ^{136}Cs and ^{137}Cs were carried together with the air parcel, and subsequent wet and dry depositions, caused accumulation of them on the ground. For the non-volatile actinides, Pu isotopes attracted great public attention because Pu isotopes present a large risk for internal radiation exposure via ingestions of contaminated agricultural crops, in particular for ^{241}Pu (a beta-emitter, $T_{1/2} = 14.4$ years), with its decay, the ingrowth of ^{241}Am (alpha and gamma-emitter, $T_{1/2} = 432.7$ years) will present a new radiation risk. The accurate determination of Pu isotopic composition may provide important information for the estimation of reactor damage, considering the fact that high radiation levels make it impossible to directly measure damage to the melted reactor cores. Therefore, the release of Pu isotopes into the environment from the Fukushima DNPP accident needs to be clarified.

We report a study on the accurate determination of Pu isotopic composition (atom ratios of ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu, and the ^{241}Pu/$^{239+240}$Pu activity ratio) using a sector field ICP-MS in surface soil, litter samples and marine sediments. Surface soil samples in Chiba, Kamagaya, and Mito cities in the Kanto Plain, and in the Evacuation-Prepared Area and the Deliberate Evacuation Area (DEA), and litter samples in DEA were collected. Marine sediments were collected in the Pacific 30 km off Fukushima. The results provided isotopic evidence for release of Pu into the atmosphere and deposition on the ground in northwest and south of the Fukushima DNPP in the 20-30 km zones, and shed light in understanding the release process and sources in the FDNPP. The high activity ratio of ^{241}Pu/$^{239+240}$Pu (> 100) from the Fukushima DNPP accident highlights the need for long-term ^{241}Pu dose assessment, and the ingrowth of ^{241}Am. We estimated that the total amounts of Pu isotopes released into the atmosphere were ca. four orders of magnitude lower than those of the Chernobyl accident. The Pu contamination from the Fukushima DNPP accident was not observed in marine sediments outside the 30 km zone.

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B-a02

CALIBRATION OF ABSOLUTE $^{13}C/^{12}C$ ISOTOPE AMOUNT RATIO MEASUREMENTS BY MC-ICPMS USING SYNTHETIC ISOTOPE MIXTURES

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Methodology based on using synthetic isotope mixtures for calibration of multiple collector (MC) ICPMS has been adapted for measurements of absolute $^{13}C/^{12}C$ isotope amount ratios of natural glycine – an amino acid of relevance to food security applications.

Ten synthetic isotope mixtures of accurately known and different $n(^{13}C)/n(^{12}C)$ isotope abundance ratios were prepared by gravimetric weighing and mixing of two well-characterised glycine materials, each highly enriched in either ^{12}C or ^{13}C isotopes. These mixtures were used to calibrate $^{13}C/^{12}C$ isotope amount ratio measurements by MC ICP-MS; the calculated calibration factors enabled determination of absolute $^{13}C/^{12}C$ isotope amount ratios of a candidate glycine reference material with natural C isotopic composition. To achieve this, an improved measurement protocol for $^{13}C/^{12}C$ isotope ratios by MC-ICPMS, which employed high resolution mode to completely avoid spectral interference of $^{12}C^{1}H+$ ions on $^{13}C+$ ion current, was developed. Non-linearity between measured ion currents and magnitudes of $^{13}C/^{12}C$ isotope ratios was observed for carbon isotopes. This needs to be accounted for in order to obtain more accurate values of $^{13}C/^{12}C$ isotope ratios for parent isotopically enriched materials, in which abundances of ^{13}C and ^{12}C isotopes differ by several orders of magnitude. We will discuss possible ways to account for this effect as well as indicate the main factors contributing to the measurement uncertainty budget. Confirmatory C isotope ratio data as obtained using elemental analyser (EA) IRMS for the candidate glycine reference material will also be presented.

B-a03

PRECISE Hg ISOTOPIC COMPOSITION MEASUREMENTS AT ULTRA-TRACE LEVEL: DOUBLE STAGE GOLD-TRAP / MC-ICP-MS COUPLING

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Stable Hg isotope ratio analysis is widely used in environmental sciences, essentially for discriminating Hg sources. Up to now, the analytical technique of reference for these measurements is the coupling of a Cold Vapour Generator (CVG) and a MC-ICPMS. The principal limitations of this technique are the high Hg concentrations needed (typically [Hg] = 2 $\mu g \cdot L^{-1}$) and the potential matrix effects.

The objective of this work was the development of a new approach for measuring Hg isotopic compositions based on the coupling of double stage gold trap pre-concentration mercury analyser (Tekran2600) with a Nu plasma MC-ICP-MS. The main difficulty was to deal with very short transient signals (15 s) and was solved using a suitable data treatment strategy. The mentioned coupling was successfully validated by the simultaneous analyses of seven certified reference materials (CRMs) with heterogenic matrices (Biological tissues, lichens, ores) by classical CVG / MC-ICP-MS. In addition, small single marine organisms (Glass eels) were also tested.

The main advantage of the proposed method is the noticeable decrease of the needed Hg concentrations, opening the possibility of Hg isotopic characterization of new environmental samples at natural Hg levels. Hg concentrations in analysed solutions actually ranged between 50 and 5 $ng \cdot L^{-1}$, showing good accuracy and precision for δ^{202}Hg ranging from 0.09 to 0.46‰ as external 2SD. Both mass dependent (MDF) and mass independent fractionation (MIF) were observed and fitted with theoretical predictions.

ISOTOPE RATIO DETERMINATIONS: HIGH SENSITIVITY FOR HIGHEST PRECISION

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Scientific disciplines like Food Chemistry, Geochemistry, environmental sciences and Paleontology are not only interested in the total concentration of an element but also in the isotope ratio of either two or more isotopes of the same element or isotopes of different elements. Researchers are interested in isotope ratios of elements such as Selenium, Strontium/Rubidium, Lead and Uranium. The knowledge of the isotope ratio $^{10}B/^{11}B$ is e.g. essential for nuclear power plants, or to elucidate geochemical questions.

ICP-MS is a powerful technique for the determination of trace elements in various matrices. Beyond that ICP-MS is able to determine isotope ratios with high accuracy and precision. The sensitivity of an ICP-MS is an indispensable performance characteristic and will enable the instrument to achieve highest isotope ratio precisions even at low, down to single digit ppt levels. High sensitivity is on one hand important to measure isotope ratios with high precision despite of low concentrations, and/or to measure large isotope ratios to achieve high precision for low abundant isotopes. On the other hand high sensitivity is important for single collector instrumentation to enable short integration times without sacrificing precision due to counting statistical limitations.

An additional challenge is the isotope ratio measurement of spectrally interfered isotopes. Effective interference management with high sensitivity in interference mode is required to ensure precision and accuracy of spectrally interfered isotope ratios.

The presentation will illustrate the layout of a high sensitive ICP-MS instrumentation (Bruker Daltonics). With a 90° reflecting ion optic and an optimized ion extraction the instrument is capable to obtain sensitivities of $> 10^6$ cps/ppb - without plasma shielding, and $> 10^5$ cps/ppb in collision mode for spectrally interfered isotopes.

The key parameters to improve the precision for isotope ratio analysis with ICP-QMS are discussed. Different examples for low and high mass element isotope ratios are presented.

SULPHUR METABOLISM STUDIES WITH ENRICHED STABLE ISOTOPES USING HPLC COUPLED TO MULTICOLLECTOR ICP-MS

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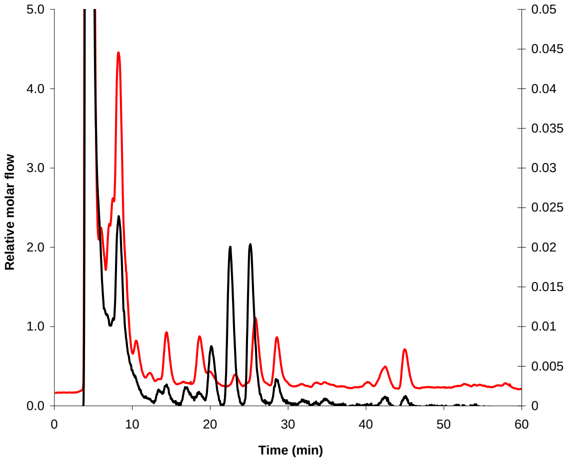
Enriched stable isotopes are increasingly employed for tracer and metabolism studies. For the study of sulphur metabolism we have prepared and characterized yeast labelled with ^{34}S [1,2]. Additionally, the combination of post-column IDMS using ^{33}S and the oral administration of ^{34}S-labelled yeast has been used to study in vivo sulphur metabolism by measuring the isotopic composition of sulphur in serum and/or urine of Wistar rats using Liquid Chromatography coupled to single collector sector field ICP-MS [3]. The methodology is extended here to new metabolic studies in healthy and diseased laboratory animals using a multiple collector ICP-MS as chromatographic detector. The use of a multicollector instrument is justified as the variations in the isotope enrichment of ^{34}S expected in the samples is very small requiring high precision measurements. For example, the figure on the left shows the relative molar flow chromatogram for a sample of rat urine after 6 hours of ^{34}S administration measured by multicollector ICP-MS. The red line corresponds to molar flow of natural abundance sulphur, left axis, while the black line corresponds to ^{34}S enriched sulphur (right axis). As can be observed, several peaks enriched in ^{34}S are detected and their isotope enrichment depends on the time after the oral administration of ^{34}S.



The capabilities of this double isotopic metabolic procedure for the development of a clinical test using ^{34}S-labelled yeast will be discussed.

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TRANSGENERATIONAL ISOTOPIC MARKING OF CARP *CYPRINUS CARPIO, L.* USING A ^{86}Sr/^{84}Sr DOUBLE SPIKE

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Transgenerational isotopic marking has recently been recognized as an effective tool for mass marking and tracking of individual fish to their original source. Compared to other conventional marking techniques, transgenerational marking offers several advantages. Most importantly, it is possible to mark all offspring of one individual female without the necessity of handling eggs or larval fish. Furthermore it is possible, to vary the concentrations of individual isotopes to specific marks for individual female fish [1]. An enriched isotopic spike solution is usually applied to gravid female spawners by injection into the body cavity [2-4] for transgenerational marking. The isotope is then incorporated into the central otolith region of the offspring which is known to be built up by maternally derived material [5,6].

Within this study transgenerational marking of a typical cyprinid fish species, *Cyprinus carpio*, L., was tested using a ^{84}Sr/^{86}Sr double spike. Buffered solutions with different isotopic composition and concentrations were administered to 4 female individuals by intraperitoneal injection 5 days before spawning, while one female was injected a neutral solution. After spawning, otoliths (Lapilli) from juvenile fish were sampled at the age of about 5 months at fish sizes between 3 and 4 cm and analyzed for their isotopic composition by LA-ICPMS by cross sectional line scans. Central otolith regions of the progeny showed a shift in the natural isotope ratios for the administered isotopes. Deconvolution of the blank corrected measurement data of the Sr isotopes was done to trace back the original spike ratio. The different spike ratios could be well distinguished reflecting the original composition of the spike solution. This study proved that it is possible to create batch-specific unique transgenerational marks in otolith cores by varying the concentrations of two naturally occurring Sr isotopes. This method has high potential to reduce the marking effort for any application in aquaculture and management where the tracking of high numbers of offspring is needed.

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B-a07

ASSESMENT OF IRON ISOTOPIC COMPOSITION AS A PARAMETER FOR IRON STATUS

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Iron deficiency has important consequences for human health and child development. Since humans have no means of active iron excretion, also iron overload can cause serious problems. In fact, disorders of iron homeostasis are among the most common human diseases. Hence, the iron status of an individual is an important measure for health. However, the determination of iron status is not straightforward. Several parameters such as transferrin concentration, ferritin concentration and iron saturation, need to be investigated and carefully compared to each other.

Scientists investigating the isotopic composition of iron in biomedical applications have shown repeatedly that the iron isotope ratios in blood are influenced by the metabolism. The iron isotopic composition changes when a person has an aberrant metabolism for iron (e.g., hemochromatosis [1,2]) and there is a difference in isotopic composition of iron between the blood of men and of women [3,4].

In this study, the parameters normally analyzed to determine the iron status were compared with the isotopic composition of iron in whole blood as determined using multi-collector ICP – mass spectrometry. Besides samples from healthy individuals, also samples from people with iron deficiency, iron overload, hemochromatosis or anemia of chronic disease were included. Significant relations were found between the iron isotopic composition of whole blood and the conventional parameters for iron status.

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METHOD DEVELOPMENT FOR THE DETERMINATION OF PBDEs IN WATER SAMPLES BY IDA-GC-ICP-MS: A NEW APPROACH TO MEET THE REQUIREMENTS OF THE EU-WFD?

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Polybrominated Diphenyl Ethers (PBDEs) have been widespread all around the world due to their intensive use as flame retardants. The adverse effects observed in living organisms and the environment after exposure to these substances have led to their classification as priority pollutants according to the Water Framework Directive (WFD), which sets Environmental Quality Standards (EQS), equivalent to the maximum allowable concentrations of 0.5 ng L^{-1} for the sum of the six most important congeners (28, 47, 99, 100, 153 and 154) in surface waters. Analytical methods devoted to the monitoring of priority substances must meet certain minimum performance criteria in terms of uncertainty ($\leq$ 50% at EQS, 95% confidence) and limits of quantification (LOQ $\leq$ 30% of EQS) with the aim to provide reliable measurements in complex environmental water matrix at the EQS level. The overall low concentrations of PBDEs in water, together with the challenging requirements defined by the WFD require the development of new methodologies which combine sensitive detection approaches with accurate and precise analytical techniques.

Inductively Coupled Plasma (ICP) can be a good alternative to the Electron Impact (EI) or Negative Chemical Ionisation (NCI) sources, more commonly used for the determination of PBDEs by Mass Spectrometry (MS), as it shows good selectivity towards brominated compounds and high sensitivity in the detection of bromine [1]. Furthermore, ICP-MS has been used in combination with Isotope Dilution Analysis (IDA) for the determination of other priority pollutants showing highly accurate and precise analytical results [2], which is very suitable to meet the challenging requirements of the WFD.

According to this, a methodology for the determination of PBDEs in water samples, based on IDA-GC-ICP-MS, has been developed. First, the GC-ICP-MS instrumental settings were optimised to achieve a good sensitivity for the detection of bromine followed by the development of a species specific IDA based quantification strategy using ^{81}Br-labelled standards. The proposed IDA methodology was applied to the evaluation of the enrichment factors obtained by different sample preparation procedures. Finally the optimised methodology was applied to the determination of PBDEs in water samples.

This work has been performed within the scope of an EMRP Researcher Grant for the development of a traceable measurement approach for monitoring PBDEs in coastal water, awarded in accordance with the EURAMET process to complement the JRP “Traceable measurements for monitoring critical pollutants under the European Water Framework Directive”.

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B-a09

ON THE DETERMINATION OF TRACE ELEMENTS IN LEAD-BISMUTH EUTECTIC BY MEANS OF ICP-SFMS

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The efforts of the Belgian nuclear research centre (SCK•CEN) towards developing Gen IV nuclear reactors are consolidated in the MYRRHA project (multi-purpose hybrid research reactor for high-tech applications) [1]. Once operational, the MYRRHA research reactor will employ a eutectic mixture of lead (45 wt%) and bismuth (55 wt%) as its primary coolant. Several challenges will undoubtedly accompany the use of such a heavy liquid metal. These problems could include (i) the corrosion of structural materials and (ii) the presence of potentially problematic impurities in the heavy liquid metal. Accurate and precise determination of such impurities and corrosion products is a necessity.

In this work, the capability of double-focusing sector-field inductively coupled plasma mass spectrometry (ICP-SFMS) for the determination of a wide variety of trace elements in a lead-bismuth eutectic (LBE) matrix is investigated. Due to particular instrumental limitations inherent to this technique, e.g., the occurrence of matrix effects, the lead and bismuth comprising the LBE matrix must be removed from the dissolved samples prior to analysis. A chemical separation procedure, based on both extraction chromatography [2] and anion-exchange chromatography [3], was developed to this end.

In the column chromatographic analyte/matrix separation procedure proposed, one column is suspended above the other, the upper 2 ml column being loaded with a lead-selective extraction chromatographic resin (Pb Spec, Triskem International) and the lower 5 ml column being loaded with an anion-exchange resin (AG 1x4, Eichrom Technologies). It was demonstrated that it is possible to quantitatively separate the lead-bismuth matrix from the majority of the target elements (i.e. Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ag, Cd, Ce, Re, Tl, Th), using dilute nitric and hydrofluoric acid as eluents. It was also shown that as little as 1% of the original lead-bismuth matrix remains with some of the other target elements (i.e. Nb, Mo, U), thereby greatly reducing matrix effects observed during ICP-SFMS measurements as well as minimizing memory effects in the instrument.

Validation of the separation procedure is accomplished by measuring both lead-matrix certified reference materials as well as semi-synthetic samples (i.e. dissolved Pb and Bi powders, subsequently spiked with small amounts of the target elements). Although the validation of the procedure is still ongoing, initial results prove promising. Analyses of lead-matrix CRMs generally yield recoveries between ca. 95% and ca. 105% for the five target elements that are present in these samples (i.e. Ni, Cu, Ag, Cd, Tl).

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ISOTOPE RATIO MAPPING BY MEANS OF LA-SINGLE COLLECTOR-ICPMS: Zn TRACER STUDIES IN THIN SECTIONS OF *DAPHNIA MAGNA*

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The use of Laser Ablation – Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) for obtaining elemental images of biological tissues has become increasingly popular over the last few years. This growing interest can be explained by the high sensitivity of this technique, its low detection limits, good spatial (lateral and in-depth) resolution as well as its ability to directly sample a wide variety of materials with minimum sample preparation [1]. Moreover, when compared to other competing techniques such as X-Ray based analytical techniques, LA-ICPMS shows the additional advantage of providing isotopic information, which could be of use for carrying out tracer studies in biological systems without the necessity of using radioactive nuclides. However, and although the possibility for obtaining isotope ratio maps is often reported to justify research efforts in the field of bioimaging with LA-ICPMS, there are few papers to date exploring this possibility and, by no means, is this application thoroughly characterized.

In this work, the possibilities of LA-single collector-ICPMS for obtaining Zn isotope ratio maps in thin sections of Daphnia Magna were evaluated. Zn was selected for the study considering the importance of this element for ecotoxicological studies. All aspects of the analytical methodology deployed were carefully studied and optimized for the best isotope ratio precision and accuracy. In this regard, acquisition parameters and correction of potential spectroscopic interferences received special attention, and the performance of two different mass resolution slits was evaluated: one providing a mass resolution power of $\Delta m/m=4000$ and peaks of triangular shape, and another one offering lower resolution power ($\Delta m/m=2000$) but providing enhanced ion transmission and flat-topped peaks. With the methodology developed, Zn isotope ratio images showing differences at the micrometer scale were obtained for exposed and unexposed Daphnia Magna individuals, demonstrating the potential utility of this technique for tracer studies with stable isotopes to be carried out.

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PROVENANCE STUDIES ON EARLY GOLD OF BRONZE AGES USING TRACE ELEMENTS AND ISOTOPE RATIOS

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Using laserablation, trace element fingerprints (ns-LA-ICP-QMS) and lead as well as osmium isotope ratios (fs-LA-ICP-MCMS) were determined. In contrast the use of one of these parameters only, the combination of these data allows a more precise provenance study. In the presented work different gold artifacts of the bronze ages, including the newly discovered famous “gold hoard of Gessel”, were analyzed. The results require a completely new discussion of the origin of the gold and the global trade routes in the bronze ages. The analytical challenge was the accurate measurement of Os isotope ratios in PGE inclusions in gold. For the wide range of the isotope variation different Os-isotope standards were used.

INITIAL EXPERIMENTS ON MONITORING TWO ISOTOPES IN SINGLE PARTICLE ICP-QMS

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Since *Degueldre et al.* have described the theoretical basis of single particle ICP-MS [1], many publications showed the general applicability of this technique to the analysis of natural and engineered nanoparticles. One of the main reasons of its popularity is that every laboratory equipped with an ICP-MS instrument can run this type of analysis without any further equipment. In general, single particle ICP-MS can provide manifold information using short dwell times (e.g. 5 or 10 ms). The frequency of “spike” signals can be related to the number of nanoparticles present in the sample, the ICP-MS intensity of these spikes to the mass of the analysed element in a certain nanoparticle, and the background signal is usually related to the dissolved metal species not bound to nanoparticles. So far, this technique was principally applied to the monitoring of only one isotope.

This work aims to overcome the restriction of monitoring only one isotope in single particle ICP-MS under special consideration of using a quadrupole-MS as mass analyser. Based on the fundamental comparison of “conventional” single particle ICP-MS first results will be presented on the analysis of silver-containing particles and dissolved silver species monitoring both isotopes of silver. A strategy will be described, which allows the determination of the number of particles, the concentration of the dissolved silver species and the direct access to the mass of individual nanoparticles without the need of any calibration.

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FUNDAMENTAL ION BEAM STUDY WITH RESPECT TO INSTRUMENTAL MASS DISCRIMINATION IN MULTI-COLLECTOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Mass discrimination in inductively coupled plasma - mass spectrometry (ICP-MS) refers to the non-stoichiometric composition of the detected ion beam with respect to the stoichiometry of the original sample material. Instrumental mass discrimination especially hampers accurate determination of absolute isotope ratios, which is of crucial importance in various scientific fields, such as geo- and cosmochemistry, archeology and nuclear applications, like half-live determinations or the analysis of used nuclear fuel. In case of relative isotope ratio determinations, mass discrimination is not an inherent issue, since a comparison of isotope ratios is relied on. Yet, also in this case, a small extent of mass discrimination is favorable over a larger one because fluctuations over time then affect the results less severe, while also the effect of a difference in matrix composition between sample and standard is mitigated.

In the present study, instrumental mass discrimination in multi-collector inductively coupled plasma - mass spectrometry (MC-ICP-MS) was investigated with respect to influences after ion extraction from the plasma and during ion beam formation. The radial distribution of isotopes was analyzed after implantation into solid targets by means of laser ablation MC-ICP-MS. Additionally, the bulk isotopic composition was investigated via conventional solution nebulization MC-ICP-MS. A strong variation with the radial position was found for the elements Cd, Pb and U. Due to low signal-to-noise restrictions, no such effect was observed for the lighter elements Li and Ni. The combination of bulk and spatially resolved data suggests a combination of coulombic repulsion and scattering effects as main contributors to instrumental mass discrimination.

Besides an immobilization of the ions by implantation with subsequent analysis, a selective clipping of the ion beam could be used to study the fractionation during the ion beam formation. Experimental setup and preliminary results of such an approach will be presented

USING ENRICHED STABLE ISOTOPES FOR TRACEABILITY PURPOSES: MANUFACTURED GOODS AND LIVING ORGANISMS

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The traceability of manufactured products and living organisms, described here, will be carried out using a method based on the addition to the manufactured product or living organism of two enriched isotopes of the same element, which may be already present within it, at a given molar ratio.

This dual-isotope approach will give a unique fingerprint to the tagged manufactured product/living organism. Further, the authentication of the tagged manufactured product/living organism will be obtained by comparison of the ratio of molar fractions experimentally measured by inductively coupled plasma mass spectrometry (ICP-MS) with the molar fraction ratio of the tagging mixture.

The novelty of this tagging method relies on working with isotope abundances and molar fraction ratios instead of the classical isotope ratios, and this fact constitutes the strong point of the described approach since the molar ratio is not affected by physical, chemical, or biochemical processes, and it is also not disturbed by environmental contamination with the natural abundance element. Furthermore, the use of molar fraction ratios overcomes the no homogeneous distribution of the tagging element within the manufactured product/living organism.

As the tagging element can be present at trace or ultratrace levels, a very small amount of enriched isotopes needs to be added, denoting a low cost solution. Also, the use of enriched stable isotopes of non-toxic elements will have negligible health effects or affect the environment.

Three fields of application are presented:

a) the study fish population and their migratory routes
b) the study of distribution of seeds of plants in order to evaluate their accommodation to changing climates
c) the tagging of inks/paper/paints for forensic purposes.

DETERMINATION OF GEOGRAPHICAL ORIGIN OF RICE BASED ON MULTI-ELEMENT FINGERPRINTING BY HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (HR-ICP-MS)

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Rice is one of the most important cereal crops, providing a staple diet for almost half of world’s population. The determination of rice authenticity is essential to prevent mislabeling and adulteration problems. The multi-element fingerprinting has a significant potential for the differentiation of rice grains. The capability of the high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) methodology for multi-element fingerprints of rice was studied. A total of 31 Thai (jasmine rice) and 5 foreign (from France, India, Italy, Japan and Pakistan) rice samples were analyzed by high resolution ICP-MS after acid digestion. Accuracy of the whole procedure was verified by the analysis of rice flour standard reference material (NIST SRM 1568a). The concentrations of individual elements were evaluated and used as chemical indicators to discriminate the origin of rice samples. The classification of rice samples, based on elemental composition, was carried out by a radar plot and multivariate data analysis, including principal component analysis (PCA) and discriminant analysis (DA). Thai jasmine rice could be differentiated from foreign rice samples by radar plots and multivariate data analysis. Moreover, the DA could classify Thai jasmine rice samples from different regions of Thailand (northern, northeastern and central one). Therefore, multi-element fingerprinting combined with the use of multivariate statistical techniques can be considered as a powerful tool for rice authentication.

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SEPARATION METHOD FOR MEASUREMENT OF CADMIUM, LEAD AND ZINC IN VEGETAL TISSUE SAMPLES BY USING ISOTOPIC DILUTION WITH ICP-SFMS

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The cadmium (Cd), lead (Pb) and zinc (Zn) measurement in biological samples like vegetables requires sensitive and accurate analytical methods. Even they are present in low content levels, it enters the food chain affecting first the living organisms and finally, it is accumulated in the human being. The food safety program of Mexico supported by SAGARPA-CONACYT Project focuses in toxic and essential elements, because the plants have complex and dynamic matrices, characterized by the local soil, flora and fauna that influence the water cycle, thus affecting the main food resources for man and animals. An ion-exchange chromatographic (IC) separation method of Cd, Pb and Zn in vegetables for its analysis using isotope dilution with inductively coupled plasma-sector field mass spectrometry (ID-ICP-SFMS) is presented. According to the Consultative Committee for Amount of Substance–Metrology in Chemistry (CCQM), ID-ICP-SFMS is considered to be a potentially primary method of measurement [1], which reaches high sensitivity and accuracy at low content levels; nevertheless, to achieve its full effectiveness in complex matrices, it is necessary to use methods that allow initial Cd [2], Pb and Zn separation from interfering high dissolved solids, elements and molecule ions such as those which formed with Mo, Zr, Nb, Cr and Mg, also the isobaric interference as the Sn, Hg, and Ni. Several separation methods exist, among which ion-exchange chromatography is characterized for using a minimum of reagents, with the advantage of avoiding sample contamination for low levels of Cd, Pb and Zn. The methodology of IC was developed allows measuring the mentioned elements by ID-ICP-SFMS. A strong base type I anion resin (Dowex 1-X8) was employed; the mechanism of separation is based on the formation of the anionic complex of the cadmium, lead and zinc chlorides, which are exchanged with the counter-ion of the ion-exchanger to carry out their separation. Measurement was performed by exact matching double isotope dilution mass spectrometry [3], with ^{111}Cd, ^{206}Pb and ^{66}Zn being the enriched isotopes used and without ratio correction using ICP-SFMS. The cadmium, lead and zinc measurement methods described above were evaluated by certified reference materials from the National Metrology Institute of Standards and Technology (NIST) from EUA. The developed methods were applied in the sample of *herb eclipta*, which was used in the international comparison among the National Metrology Institutes (NMI), which was coordinated by the CCQM. Results from this comparison were used to evaluate the performance of the method, which reaches an outstanding level of accuracy using all four cadmium isotopic ratios and three zinc isotopic ratios. For two lead isotopic ratios it was found a contamination problem, however the results were acceptable.

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B-b08

ANTIMONY ISOTOPIC ANALYSIS USING MULTI-COLLECTOR ICP-MS FOR PROVENANCING ROMAN GLASS

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Glass was first created about 3000 BC and it has been widely present all along the history of humankind. Particularly during the Roman period, glass was produced in volume in a extensive variety of artifacts (e.g., vessels, bottles, cups) and so, this material has been employed to study, among other, manufacturing technologies and/or trade routes that existed in the past. But still, several questions concerning the nature of the raw materials used and the geographical location of their transformation into finished artifacts remain unanswered [1].

It is assumed that raw glass was produced in primary workshops near the raw material sources, to be transported in the form of chunks or ingots to secondary glass houses, where the glass was colored and shaped into specific objects [2]. This suggests that the composition of formed glasses would closely resemble that characteristic for primary centers and no distinctive composition could then be attributed to the secondary working centers. However, there is an open debate regarding this glass production model [3]. An alternative model states that glass was made on a local level, each glass house using its own sand. Then, glass artifacts manufactured by each workshop could have a specific composition.

Antimony was deliberated added in the form of Sb-bearing minerals during the glass production process to obtain either colorless glass (< 1% Sb) or opaque glass (> 1% Sb) and so, Sb isotopic analysis could not only help in identifying the origin of the Sb used in the manufacturing of Roman glass, but also to reconstruct how such material was traded and transported, and how this can be integrated in the network of primary and secondary glass producers.

In this work, Sb isotopic analysis using multi-collector ICP-MS has been applied to Roman glass after isolation of the target element. Antimony isotope ratio data found were compared to results obtained from antimony ores situated in different Mediterranean areas in an attempt to unravel the possible location(s) of the glass production sites and their manufacturing technologies.

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B-b09

HIGHLY ACCURATE ISOTOPE COMPOSITION MEASUREMENTS BY A MINIATURE LASER ABLATION MASS SPECTROMETER DESIGNED FOR SPACE RESERACH

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In-situ measurements of isotope variations in extraterrestrial material are of considerable importance for future planetary space missions. The knowledge of the isotope composition and its variation can allow drawing the conclusion on the origin and evolution of our solar system. Studies of extraterrestrial materials (soils and regolith's) provide an insight to geochemical processes, radio-isotope chronology of planetary material (cristallisation ages), and can be robust tracers of pre-solar events. Accurate and precise measurements of isotope ratios of solar body materials can impose critical constraints on events and their chronology in the early stages of the solar system formation and can yield insight to the processes occurring on the surface of planetary bodies. Measurements on isotopic fractionation effects of non-radiogenic elements are also of interest because they yield information on the conditions in the early solar system. Precise measurements of isotopic pattern of bio-related elements, e.g., carbon, sulphur, etc., are of high importance for the question of the past and present life in our solar system.

Our group has designed a self-optimizing and highly miniature laser-ablation time-of-flight mass spectrometer (120 mm x Ø60 mm) for sensitive and accurate in-situ measurements of the elemental and isotopic composition of extraterrestrial materials [1-4]. Initial studies were conducted using IR laser radiation for ablation and ionisation of sample material, showing high instrumental performance in terms of sensitivity and mass resolution [3]. Current measurement campaigns were performed using UV radiation by focusing the laser beam to about Ø20 µm onto the sample surface. The instrument supports a high dynamic range of at least 8 orders of magnitude and a mass resolution $m/\Delta m$ of up to 800-900, measured at iron mass peak. Apart of highly sensitive measurements down to hundredths and tens of ppb for non-metallic and metallic elements [2], respectively, we will describe a dedicated measurement procedure, which allows for the first time to measure with a LIMS system the isotopic pattern of elements with a measurement accuracy and precision at per mill and sub per mill level, which is comparable to that achieved by well-known and accepted techniques such as TIMS, SIMS, and LA-ICP-MS [1]. At present we exchanged the UV laser system with a new femtosecond laser system (755 nm wave length, 1 kHz repetition rate and 150 fs pulse width). Initial measurements and results showed increased instrumental performance in terms of mass resolution, detection efficiency and laser beam stability, and a similar measurement accuracy on the isotopic composition in the per mill level was observed. A miniaturized laser-ablation time-of-flight mass spectrometer represents a dedicated instrument not only for in-situ investigations on the chemical composition of extraterrestrial materials but also for many different applications in laboratory environments.

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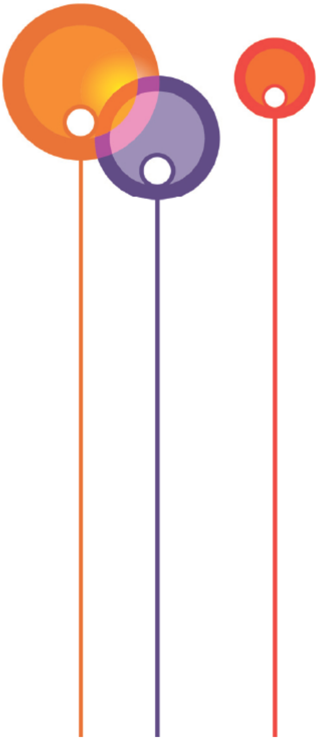
C section

Glow discharge



THE STORY OF THE JOURNAL OF ANALYTICAL ATOMIC SPECTROMETRY, JAAS, THE CHRONICLE OF PLASMA SPECTROMETRY

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Following the seminal International Conference on Atomic Spectroscopy, held in Sheffield in 1969, a distinguished group of atomic spectroscopists and analytical chemists decided that the rapidly expanding field of atomic spectroscopy needed a comprehensive reporting system to document the many advances being made with extraordinary rapidity. Out of this desire was born the ‘Annual Reports on Analytical Atomic Spectroscopy’ (ARAAS). These familiar red and white books were compiled by an Editorial Board drawn internationally and published initially by the Society for Analytical Chemistry (the SAC) based in London, England. When the SAC merged with the Royal Society of Chemistry, they took over publication. The review format proved invaluable to this new research field, especially since it was actively and critically reviewed at an annual editorial Board, held, like the original conference, in Sheffield.

This format was successful for many years but the economics of the publishing industry were against this type of review. When the late Professor John Ottaway joined the ARAAS Board, he injected a new enthusiasm and insights gained as Chair of the RSC’s Analytical Editorial Board. On a famous railway journey from London to Sheffield, John convinced Barry Sharp that ARAAS should transform into a journal with both original articles and review content. As the Editor in Chief of ARAAS I remember how, when they arrived in Sheffield, they took the Editorial Board by storm and JAAS, the Journal of Analytical Atomic Spectrometry, was born.

The RSC had not previously published a specialist journal and there was some opposition at the Publications’ Board, as well as difficult moments with those who were part of the atomic spectroscopy community but had understandable loyalties to other journals. These were overcome and JAAS was duly launched in 1986,in London at Pittcon, held appropriately in New Orleans that year. John Ottaway was the first Chair of the JAAS Editorial Board and Judith Brew, now Judith Egan-Shuttler, the first Editor.

Sadly John died suddenly and in his prime just a few months into the life of JAAS. It was already though obvious that JAAS would be a success, particularly as its launch coincided with the emergence of ICP-MS as a commercially available technique. I was asked to take over as Chair and JAAS grew in size and stature, particularly through its close association with the European Winter Plasma Conference.

This lecture will review the history of JAAS and its contribution to the development of plasma spectrometry. I will talk about some of the characters involved and the milestones upon the way.

PULSED RADIOFREQUENCY GLOW DISCHARGE TIME-OF-FLIGHT-MASS SPECTROMETRY FOR GAS AND SOLIDS DIRECT SPECIATION

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Analytical atomic spectroscopists are more and more attracted back to molecular spectroscopy (e.g. to carry out proper chemical speciation) and to quantifications of elements and of molecules alike. The design and construction of a MS set-up for small molecules, enabling three different types of chemical information: elemental (isotopes), fingerprints of the compound (fragments) and molecular mass (molecular ion) will be described. Complete analytical speciation in a single MS instrument of organic volatile compounds can be achieved by resorting to a pulsed radiofrequency GD which provides three different plasma regimes per pulse in time: the prepeak (isotopes and elements), the plateau (fragments) and the afterpeak (molecular mass). The source is coupled to a fast data processing system TOF mass analyser [1], allowing also a sensitive quantification of the species in the prepeak.

Traditionally GDs are widely used for direct solid bulk and depth-profiling analysis. In pulsed-rf-GD-(TOF)-MS the temporal control of the generated plasma can be accomplished by simply selecting the key pulse parameters: the instantaneous power (responsible for sputtering and ionization) can be chosen almost independent of the average power (responsible for thermal stress in the analysed solid sample) by just adjusting the duty cycle of the pulses. Coupling of such pulsed GD to an MS (TOF) analyser offers the ideal marriage because allows high rate of mass spectra acquisition for quasi-simultaneous multielemental detection in such fast transient signals [2].

A new rf-GD source, which can be operated in steady-state and pulsed rf modes, has been developed in our group and coupled to a fast orthogonal novel mass spectrometer (Tofwerk, Switzerland) equipped with a microchannel plate detector. Experiments showed that very good elemental depth profiles for layered materials could be attained at the nm scale using such prototype. Different designs of ms-pulsed-rf-GD ion sources for elemental and molecular analysis, both in direct solids and gas analysis, will be presented.

In the search for improved properties derived from nanoscale atomic or molecular organization many new nanostructured materials are being developed nowadays. Their characterization demands new analytical tools providing elemental and molecular information to control material synthesis and its quality after the manufacturing processes. The pulsed rf-GD-MS (TOF) for the elemental and molecular depth profile analysis of self-assembled metallic micro and nanostructures has been very successful [3]. Also, its use for detecting possible leaks and failure in nanostructure fabrication process as well as for fast control of diffusion processes occurring in nanoimplants in strategic microelectronic material synthesis [4] will be finally discussed.

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NO JOKE! HOOKAH SMOKE MIGHT MAKE YOU CHOKE

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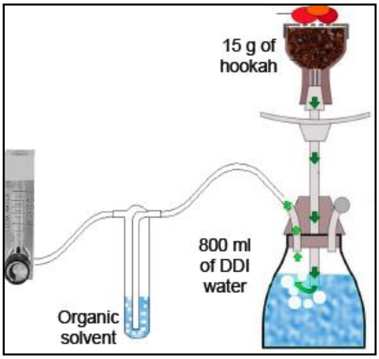
Many trace metal studies, as well as organics, have been performed on cigarette, cigar, and pipe tobacco, while virtually no studies have been performed on hookah tobaccos. It is well documented that other tobaccos are known to contain toxic metals such as As, Cd, Cr, and Pb [1]. However, little is known about the noxious and toxic contents in hookah tobacco and particularly in hookah smoke. Hookah has been popular in the Middle East and surrounding regions for ages. Early documentation of the hookah was written in a poem by Shirazi in 1535 A.D. [2]. The rapidly spreading use of the hookah world-wide makes it imperative to determine trace metal profiles, metal species, organics, polycyclic aromatic hydrocarbons (PAHs) and the subsequent lung cell damage and cytotoxicity. Its use has even been immortalized by modern character depictions (Disney) for those in Lewis Carroll's classic tale, *Alice's Adventures in Wonderland,* originally published in 1865.

Microwave assisted digestion in combination with ICPMS was utilized to elucidate the toxic metal content in an array of different brands/flavors of hookah tobacco from Middle Eastern and American formulations. Mo'assel was the particular formulation used, which is ~ 50% tobacco and ~ 50% matrix, which may include glycerin, honey, molasses, flavorings and even high fructose corn syrup. Other formulations vary the matrices and the proportions. The process used to burn the tobacco simulated the typical manner in which hookah tobacco is consumed as shown in the figure left. In this presentation we discuss trace elements in the hookah tobacco, hookah smoke and the presence of various toxic organic species, including PAHs, in the smoke. Damage to primary lung cells and their molecular level responses will be reported if available by conference time. At this point we see numerous PAHs with those from one smoking session equal to ca. from one smoked cigarette.



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CK-2

NEW DEVELOPMENTS CONCERNING ANALYTICAL GLOW DISCHARGES

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Glow Discharge Optical Emission Spectrometry (GD-OES) is one of the most frequently applied techniques for the direct analysis of solid materials, including the main components and the impurities. The dynamic range (≈100% ⇨ $\mu g \cdot g^{-1}$), high sample throughput (≈ 5 min/sample), good depth resolution ($dz/z \approx 5\%$) over the range from nm to > 100 µm depth and the multi-element capability (including the light elements) make this method unique among the other techniques for elemental analysis and has led to the introduction of this method for quality control in many industrial laboratories. In recent years we have seen many investigations about radio-frequency (rf) discharges for the analysis of non-conductors and pulsed discharges mainly for the reduction of thermal stress of the samples. The improvement of the lateral resolution at imaging spectroscopy when pulsed discharges are used is a hot research topic and may lead to 2 and 3 dimensional analyses in future. Some of these developments, such as the pulsed rf discharge, have already found their way into commercial instrumentation and some of them have this potential in the near future. As examples, I would like to mention the measurement of the electrical parameters of the rf discharge and the use of sputter craters with diameters below 1 mm.

Glow Discharge Mass Spectrometry (GD-MS) has become the industry standard for the analysis of trace and ultra-trace elements in metals and semiconductors. Since the introduction of the new GD-MS instrument Element GD by Thermo Finnigan in 2005, new features exist and the corresponding new possibilities will be discussed. The GD-ToF-MS instrument from Horiba Jobin Yvon also uses the same fast flow source concept. Nu Instruments and Mass Spectrometer Instruments Ltd. (MSI) have recently introduced new high resolution GD-MS instruments based on the source concept of the well tried VG9000 including cryo-cooling. Pulsed direct current (dc) discharges can also be used in the commercial Element GD and first results of rf discharges exist with the MSI instrument. This all shows that analytical glow discharges are alive, healthy and still experience much progress. Many developments are driven by European projects such as the Research Training Network “Gladnet”, which ended in 2011, but essential research and development is continuing in Europe and also going on in companies and academia in the United States and Asia.

Furthermore the low energy of the sputtering ions and atoms together with the high erosion rate make glow discharges useful for the preparation of samples, which are afterwards analyzed by other techniques, such as scanning electron microscopy, electron backscatter diffraction, etc. Examples for such applications will also be discussed.

ATOMIC EMISSION SPECTROMETRY WITH AN ATMOSPHERIC PRESSURE HELIUM DC GLOW DISCHARGE USING VARIOUS WAYS OF SAMPLE INTRODUCTION

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Many different types of glow discharges at atmospheric pressure since some years have been extensively investigated and they have been used as radiation and ion sources for atomic spectrometry. Among those a helium DC glow discharge at atmospheric pressure (He-APGD) has been investigated by Gielniak and Broekaert [1]. An optimization of the geometry and the working conditions at the power level below 100 W as well as the diagnostics of this source were described in detail. Within the frame of this work different ways of sample introduction for the He-APGD mentioned above were tested and analytical figures of merit have been determined.

For the He-APGD the sampling of analytes in the gaseous state for the source is very suitable. In the case of Hg the cold-vapor technique with $SnCl_2$ as reducing agent in a flow-cell is ideally suited and allows it to obtain a detection limit down to 0.2 $ng \cdot mL^{-1}$. In the case of $NaBH_4$ as reducing agent, however, the excess of H_2 produced considerably deteriorated both the stability of the source and the detection limits for Hg. This also applied in the case of chemical hydride generation using $NaBH_4$ as reducing agent for the determination of As and related elements. In electrochemical hydride generation the amount of H_2 produced in excess can be better regulated by adjusting the electrolysis current but also here the signal to background ratios obtained for the volatile hydride forming elements were poor. When isolating the hydrides by freezing and sweeping them into the plasma, however, the detection limit for As in the case of a collection time of 1 min is 12 $ng \cdot mL^{-1}$ and room for improvement is given by using a system with automatically switched valves [2].

The He-APGD proved to be excellent for element-specific detection in gas chromatography. As He is used as working gas the effluent of the gas chromatograph can be lead directly into the plasma without using high volume flows of a make-up gas. Further the halogens can be determined as due to the use of He as working gas both for Cl and Br highly sensitive atom lines can be efficiently excited. After an optimization of the power and the gas flows detection limits for halogenated hydrocarbons both with halogen lines as well as with the C 247 nm line are down to the 10 ng level, which is by an order of magnitude lower than in the case of miniaturized microwave plasmas [3, 4].

Initial experiments showed that also with other techniques, among which pneumatic nebulization of liquids, the He-APGD described can be well operated, provided a pneumatic nebulizer that can be operated with a low flow of He is used. Further, direct solids sampling methods making use of spark or laser ablation can be used very well and also electrothermal vaporization for the analysis of dry solution residues as well as for direct solids sampling of powders eventually after preparing slurries are promising.

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DEPTH-PROFILE ANALYSIS OF THERMOELECTRIC LAYERS ON Si WAFERS BY PULSED R.F. GLOW DISCHARGE TIME-OF-FLIGHT MASS SPECTROMETRY

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In this work the depth-profile analysis of thermoelectric layers deposited on Au and Cr covered Si wafers with the aid of pulsed radiofrequency glow discharge time-of-flight mass spectrometry (pulsed RF-GD-TOFMS also called plasma profiling TOFMS (PP-TOFMSTM)) is described. For thermoelectric materials the depth resolutions obtained with both PP-TOFMS and secondary ion mass spectrometry (SIMS) are shown to be well comparable and in the order of the roughness of the corresponding layers (between 20 and 3700 nm). With both methods a direct solid analysis without any preparation steps is possible. In addition, the analysis of the samples with PP-TOFMS proved to be faster by a factor of 26 compared to SIMS, as sputtering rates were found to be 80 $nm \cdot s^{-1}$, and 3 $nm \cdot s^{-1}$, respectively.

For the analyzed samples the results of PP-TOFMS and SIMS show that a homogeneous deposition was obtained. Quantitative results for all samples could also be obtained directly by PP-TOFMS when the stoichiometry of one sample was determined beforehand for instance by inductively coupled plasma optical emission spectrometry (ICP-OES) and scanning electron microscopy with energy dispersive X-ray fluorescence spectrometry (SEM-EDX). For Bi_2Te_3 the standard deviation for the main component concentrations within one sample then is found to be between 1.1% and 1.9% and it is 3.6% from sample to sample. For Sb_2Te_3 the values within one sample are from 1.7% to 4.2% and from sample to sample 5.3%, respectively.

CHARACTERIZATION OF A He ATMOSPHERIC PRESSURE GLOW DISCHARGE FOR AMBIENT DESORPTION/IONIZATION MASS SPECTROMETRY

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Ambient Desorption/Ionization Mass Spectrometry (ADI-MS) techniques have experienced considerable development in the last few years [1]. For instance, many new applications have appeared, including forensics [2], explosive detection [3] and food control [4]. Among the ion sources used in ADI-MS, atmospheric pressure glow discharges (APGDs) using He as the plasma gas have impressive performance since they can ionize molecules with a wide range of polarities through proton- and charge-transfer reactions. Furthermore, the negative ion mode is possible through the formation of nitrate and other adducts. Additionally, the heat production, inherent to the discharge, helps to improve the desorption without excessive heating.

The ion source used in our studies is a Flowing Atmospheric Pressure Afterglow [5]. The FAPA is formed between a tungsten pin electrode and a copper plate electrode with a hole in its center. This hole allows the exit of excited He species that react with atmospheric constituents to produce reactive ions that desorb and ionize the molecules present in the sample. The chamber is partially made of quartz and polyamide and provides a uniform flow in the area where the plasma is generated. A screw permits the precise control of the distance between electrodes.

In this communication, several studies related to the characterization of the He FAPA will be presented. In particular, Schlieren imaging has been employed to obtain information about the stream exiting the discharge cell and its interaction with a sample surface. Furthermore, mass spectrometric characterization of the background ion signal is presented and compared with gas temperature measurements of the exiting stream, showing that the proportion of different water clusters is closely related to the temperature of the transport stream. Finally, this work describes the analysis of several organic compounds, discussing the peaks generated in the mass spectra due to the formation of analyte adducts.

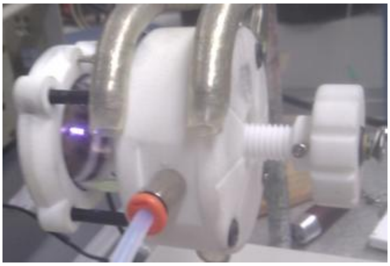

Fig.1. The APGD discharge design used in Oviedo.

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DEVELOPMENT OF A NEW DISCHARGE SOURCE WITH A 4-CM CATHODE SIZE FOR PLASMA IMAGING

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The project “Novel Instrumentation for Modern Elemental Speciation Analysis” has been finished recently, aiming to develop a plasma imaging system for metallomics and speciation analysis. A rf discharge is used because the samples to be analyzed are nonconductive. The discharge is powered in a pulsed mode to reduce the time for diffusion of sputtered atoms and thereby to improve the spatial resolution of the image [1][4].

A new discharge chamber with a cathode diameter of 4 cm was constructed (see Fig.1) to allow the analysis of large samples. The chamber is designed for samples of different forms and thicknesses. Depending on the material of the samples, dc and rf, continuous and pulsed discharges can be applied. A modular construction of the source enables flexible modification of the discharge geometry, and offers more possibilities to analyze different samples. Pressure waves, which can generate disturbing vibrations of electrical current and elemental emission [5], are suppressed by a tilted quartz window.

The plasma imaging properties of this chamber were tested with pulsed rf and dc discharges in combination with an acousto-optical spectrometer [4]. The electrical properties as well as the spatial resolution of the generated images were investigated (see Fig.2).

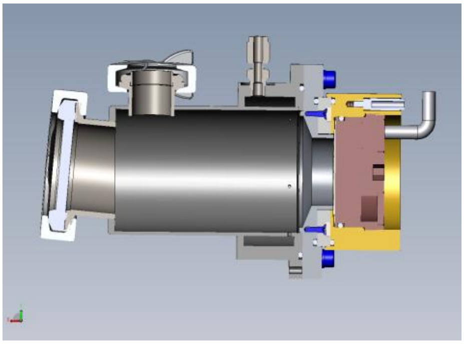

Fig.1 Scheme of the 4-cm discharge source.

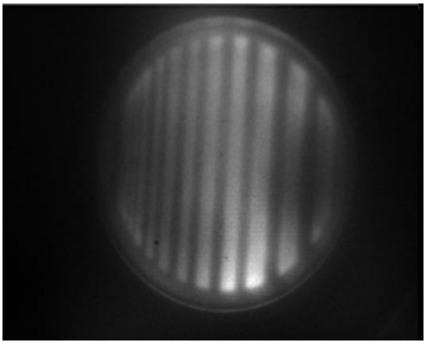

Fig.2 Plasma image of a special sample for spatial resolution measurement.

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NEW INSIGTHS IN PULSED-RF-GD-OES: STUDY OF THE SPACIAL AND TEMPORAL DISTRIBUTIONS OF EXCITED SPECIES AND EFFECT OF AN EXTERNAL MAGNETIC FIELD

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Glow discharge plasmas coupled either to optical emission spectroscopy (GD-OES) or mass spectrometry (GD-MS) have shown to be fast and sensitive analytical techniques for the direct chemical characterization of both bulk and coated materials. Moreover, it has also been demonstrated their great potential for the analysis of technological materials such as ultra-thin layers, nanowires or solar cells [1]. Moreover, the development of pulsed-GD sources has opened new possibilities in GD techniques due to the interesting properties that they present such as less thermal effects and different time-domains along the GD pulse which are related to different excitation/ionization mechanisms of the species present in the plasma. Furthermore, there is still a great interest in the development of new approaches to improve the sensitivity of this technique. In this sense, the application of external magnetic fields has been shown to produce enhancements in the excitation and ionization efficiencies of the GD plasma [2]. Previous studies carried out in our laboratory using magnetically boosted rf-GD-OES showed noticeable enhancements (up to twenty times) in copper atomic lines while the Cu detection limits in Al matrices improved one order of magnitude when a magnetic field of 70 mT was applied [3].

In this work, an in-house experimental set-up provided with a modified Grimm source [4] has been employed to carry out space and time resolved emission spectroscopy studies. Side-on as well as end-on observation of the plasma plume has been performed in pulsed-radiofrequency-GD (pulsed-rf-GD) to investigate temporal and spatial distribution of different species present in the plasma. In particular, argon and analyte (copper) emission has been evaluated during prepeak and afterglow time domains at different pulse frequencies. These results can help to understand the GD plasma dynamic and, thus, to improve the performance of the GD-MS instruments in which the mass transport plays an essential role.

This work also investigates the effect of applying a magnetic field to a pulsed-rf-GD, studying the changes in the optical emission along the pulse profile. The magnetic field is applied by using an electromagnet that allows regulating the field intensity inside the GD source up to a value of 70 mT. The results show that, due to the dynamic nature of the plasma, the magnetic field produces different effects depending on the time domain of the pulse and the species considered. In particular, it was found a high enhancement in copper (analyte) atomic lines in the plateau region and a light enhancement of the prepeak emission, while a decrease in the afterpeak emission intensity was observed.

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C-b03

DEVELOPMENT AND STUDY OF A PLAIN CATHODE DC DISCHARGE SOURCE OPERATED IN PULSE REGIME CURRENT CONTROLLED MODE

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Nowadays the so-called the analytical application of NLTE plasmas has a great importance. The aim of the development is partially to increase the analytical power and to improve the performance characteristics of the source. Beside that traditional DC and RF type sources the so-called pulse-controlled technique may provide further improvements either in the analytical power or in the use and construction of the instruments. Earlier we reported the development of a DC source operated in a pulse regime using a current generator. The use of a current generator instead of the traditional voltage-feed mode makes unnecessary the use of the so-called ballast resistor and by measuring the pressure of the filling gas and the voltage-drop on the source, all the important parameters of the discharge are known at any moment.

The pulse-regime control offers the advantage that the high power is applied to the source only for a predetermined short time (length of μs or ms), therefore the source does not warm up heavily and higher current can be applied, without the use of water cooling. Beside that the dynamic behavior of the source can also be studied and utilized if it turns out to be advantageous.

Beside the source, main parts of our system are the current generator, which contains the pulse generator, a spectrometer to detect the line intensities, a fast analogue-digital converter and an IBM-compatible computer running the controlling software program.

Based upon the pulse width modulation, both the pulse frequency and the duty cycle are software controlled and can be chosen in a wide range. The lowest frequency value is 122 Hz, the highest is 3600 Hz. As for as the duty cycle, it ranges from 1:254 to 254:1. The value of the pulse current spreads from 20 mA up to 200 mA, and can also be selected by the controlling software.

So far we have studied the signal intensity of an analyte element and that of an Ar line as the function of the pulse frequency, Ar-pressure and the discharge current.

Acknowledgement

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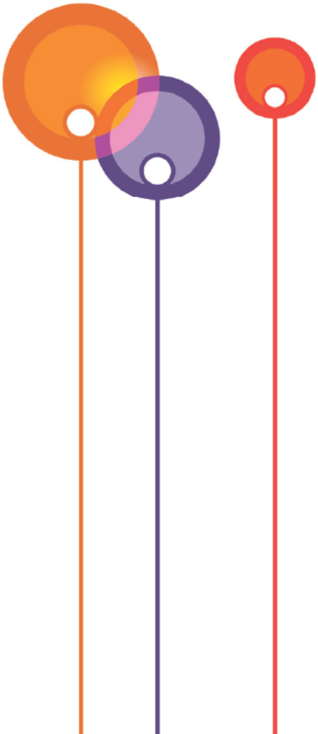
D section

Elemental speciation



FIFTY YEARS OF PLASMA ANALYSIS AND IMAGING, PERSONAL RECOLLECTIONS

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Spectroscopic and imaging analytical methodologies will be reviewed from a personal perspective, with special emphasis on plasma techniques. Selected examples from the laboratory experience of the author over his career will illustrate the constantly increasing sophistication (sensitivity, analyte selectivity, spatial discrimination) of analytical techniques over the last 4-5 decades, with an unfaltering evolution with ongoing scientific and technological progress, and, at particular occasions, unexpected and abrupt swerves in this development process.

ARE WE STUDYING THE IMPORTANT ELEMENT SPECIES OR ONLY THOSE WE CAN MEASURE?

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Looking at the flow of papers in which speciation analysis is featured we identify immediately that most of the papers employ elemental or molecular mass spectrometry or even employ both in parallel and even simultaneously. This has revolutionized our knowledge of certain elements in the past 20 years mainly in biological or environmental systems. The focus has been on the three elements: arsenic, mercury and selenium. Arsenic which exhibits a rich organic chemistry has been subject of many environmental studies but generates still a few surprises. When we look at mercury, speciation studies have focused for half a century only on the discrimination between inorganic mercury and methylmercury, although there is much more to be discovered and biologically relevant. Selenium has developed enormously especially in the field of metallomics since selenium is essential and forms stable bonds within the peptide chains of proteins and can therefore easily be traced in biomolecules.

Here during this lecture some general aspects of speciation studies will be highlighted which will illustrate that the majority of speciation studies have been conducted because we have had tools to determine the key species and not necessarily because there are interesting from biological, environmental or material science view.

Some recent case studies performed in Aberdeen over the past year will be presented and it is up to the audience to decide whether those studies demonstrate that the field of speciation has become a mature discipline so that results can actually be used in bio and environmental sciences or in legislation.

DK-1

FIELD-FLOW FRACTIONATION WITH ATOMIC SPECTROMETRIC DETECTION FOR CHARACTERIZATION OF ENGINEERED NANOPARTICLES

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Engineered nanoparticles (ENPs) have been used in various consumer products and their particle size is very important to their properties. This presentation will highlight the use of an efficient analytical method based on field-flow fractionation (FFF) with atomic spectrometric detection to perform size characterization of nanoparticles (NPs), including titanium dioxide NPs, selenium NPs (SeNPs), and silver NPs (AgNPs). The use of this hyphenated technique of FFF and atomic spectrometric detection is illustrated in more details for AgNPs. Field-flow fractionation was employed for particle size characterization of AgNPs in various practical examples including AgNPs prepared from various synthesis conditions, AgNPs leached from textile samples upon washing, AgNPs aggregation upon incubation in various environmental waters, AgNPs changes upon incubation in gastrointestinal conditions. The findings can be summarized as follows: 1) AgNPs from various preparation conditions showed different particle sizes.; 2) By washing textile containing AgNPs, detergent could approximately leach silver up to 66%, whereas only 0.5% and 1.4% silver were released by doubly deionized water and tap water, respectively.; 3) Upon incubation of AgNPs with natural waters, i.e., tap water; seawater; and ground water, rapid changes in particle size of AgNPs were observed.; and 4) The particle size of AgNPs changed from their original sizes upon incubation in gastric condition. Therefore, FFF is considered as an efficient tool for providing particle size information in various media, leading to more understanding of the fate of NPs.

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SIZE FRACTIONATED CHEMICAL ANALYSIS OF ENGINEERED NANOPARTICLES USING PLASMA MASS SPECTROMETRY

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Nanotechnology offers high innovation potential in both material and application development due to superior properties of nanoobjects, i.e. nanoparticles, -fibres or -plates. Reinforced ultra-light materials, resistant surface coatings or self-cleaning textiles are just some examples. However, for synthesis and embedding of nanoobjects into materials a proper monitoring of parameters, such as size, shape or chemical composition is important. On the other side, health and environmental concerns recently increased. Several studies predicted a certain toxic effects. Thus, knowledge about release of nanoobjects from products is mandatory for an appropriate benefit and risk assessment.

Both fields material science as well as environmental and health risk assessment require advanced analytical methods which allow size-fractionated and chemical quantification of nanoobjects. The most commonly used analytical methods in this field are light scattering to achieve size information and electron microscopy combined with energy dispersive x-ray spectrometry (EDX) to study morphology, size and chemistry.

Nevertheless, the high versatility of plasma mass spectrometry (ICPMS), especially the multi-element capabilities combined with high sensitivity leads to an increasing interest in this technique for analysis of nanoobjects. Beside classical sample preparation strategies like sequential filtration or centrifugation, especially single particle ICPMS or the coupling of techniques with size fractionation capabilities are of interest, e.g. asymmetric flow field flow fractionation system (AF4). Benefit and limitations of these techniques will be compared and aspects of sample handling will be critically discussed.

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DE

ASSOCIATION OF ICP MS AND HIGH RESOLUTION ESI MS FOR SPECIATION ANALYSIS: A POWERFUL TOOL FOR DEVELOPING NOVEL ANALYTICAL METHODS

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The parallel coupling of chromatography to ICP MS and ESI MS instruments is a practical tool frequently employed to get complementary information on elemental composition/concentration and on molecular form of metallated species of interest. The development of novel chromatographic techniques (such as HILIC chromatography for the separation of small polar metal-containing compounds), the improvement of the sensitivity and robustness of ICP MS instruments and the recent apparition of FT MS instruments adapted to hyphenated techniques (such as the ESI LTQ Orbitrap MS) that are sensitive and highly accurate mass spectrometer, offer, through their association, a promising tool for improving speciation analysis. For now on, Orbitrap based instruments offer the possibility for some applications to be as sensitive and specific as ICP MS instruments for speciation analyses of raw samples, which enables parallel chromatographic coupling with both instruments without preconcentration step. Indeed, high resolution molecular MS instruments are more specific for the detection of low molecular weight metal–containing compounds (especially for multi-isotopic elements) by giving a full insight of the information buried in the isotopic pattern of the detected molecules. However, the use of ICP MS remains essential to get easily accessible and reliable quantitative data and to follow species behavior during chromatography analyses.

The potential of this association is increasing with instrument improvement, especially for high resolution molecular MS instrument for which ranges of achievable mass resolution keep on improving regularly. Straight forward detection and quantification of metal-containing molecules are then possible and it can be used to determine the speciation of an element among the metabolites of a raw sample extract as well as to follow specifically metal-tagged and isotopically enriched compounds in complex mixtures.

Various applications and already obtained results for speciation analysis will be discussed.

D-a01

TITANIUM MONITORING IN BIOLOGICAL FLUIDS OF PATIENTS WITH METALLIC IMPLANTS: FROM IONS TO NANOPARTICLES.

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Titanium (Ti) is a light and corrosion resistant metal that either pure or alloyed has been successfully employed in orthopaedic and dental implants. Among others, fractures of the upper part of the femur (termed hip or proximal femoral fractures) may be surgically fixed using titanium implants. Additionally, Ti is one of the main components of metal prosthesis involved in total joint arthroplasty, in instrumental arthrodesis of spinal segments and also for implants in dentistry. Although Ti was consider as a “biologically inert” element, recent studies have revealed that Ti-based implants undergo corrosion and wear and the dissolved metal (either as Ti(IV) ions or as TiO_2) circulates in the body fluids. Thus, higher Ti concentrations in serum and urine of patients after total hip and knee arthroplasty have been reported [1]. However, up to now very little is known about Ti toxicity regarding the identity of the species released (TiO_2 nanoparticles or Ti(IV) ions) and their concentration. Therefore, the strict control of the Ti levels in the biological fluids of the exposed population is of general interest, in order to evaluate possible pathological conditions associated to concentration increments [2].

For this purpose, in this work we will present the studies conducted in our group to address first Ti release from prosthesis and implants of different nature. For such aim, we have developed a very sensitive and accurate method based on isotope dilutions analysis with DF-ICP-MS and using isotopically enriched ^{47}Ti. Secondly, we will illustrate the results on the quantitative Ti speciation to address the concentration of Ti associated to the different human serum biomolecules, based on an anion-exchange chromatographic system coupled to the DF-ICP-MS. Sample preconcentration strategies and the use of post-column addition of the ^{47}Ti spike (working at medium resolving power) is used for quantification of the eluting Ti species. Methodological accuracy and precision in total Ti analysis as well as in its speciation in serum are evaluated by using a serum reference material, certified in the total Ti content. Finally, we will discuss initial results on comparative toxicity experiments conducted with Ti(IV) and TiO_2 nanoparticles in osteoblasts (bone-cells).

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AM I WORKING WITH A NANOMATERIAL? HOW TO GET THE ANSWER BY SINGLE PARTICLE ICP-MS

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The term nanomaterial has been recently defined by the European Commission as: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm" [1]. The definition has been adopted by the EC to be used for regulatory purposes and it is based on an approach considering the size of the constituent particles of a material, rather than their hazard or risk.

In spite of the availability of a number of techniques for size and particle number measurements (TEM, SEM, AFM, light scattering, nanoparticle track analysis...), the implementation of the EC definition is a challenge from the point of view of the analytical chemistry, because it involves the development of feasible and reliable methods.

Single particle detection using ICP-MS is a methodology able of determining both the number concentration and the size distribution of a nanoparticle suspension. In single particle detection, when one nanoparticle is introduced into the ICP, the atoms of the analyte produce a pack of gaseous ions in the plasma, which are measured as a single pulse by the detector. The number of counts of this single pulse is related to the quantity of analyte atoms in the nanoparticle and hence to its size, if the composition, shape and density of the nanoparticle is known. On the other hand, the frequency of the pulses is proportional to the number concentration of nanoparticles. Working with sequential instruments, adequate dwell times and nanoparticle number concentrations must be selected to ensure that each pulse corresponds to just one nanoparticle.

Fundamental aspects of single particle ICP-MS will be discussed as well as sizing and quantification strategies using reference nanomaterials and standards [2,3]. A methodological approach for routine determination of size distributions and number concentrations of silver nanoparticles will be presented. Finally, the suitability of this methodology for implementing the nanomaterial EC definition will be addressed.

Acknowledgement

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ZINC SPECIATION IN THE CEREAL GRAIN

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Zinc is an essential trace element to plants. The human bioavailability of Zn in plant based foods is generally low, which leads to massive health problems with a wide range of different Zn deficiency related diseases, especially in regions where the main calorie intake comes from e.g. cereals [1,4]. There is strong evidence that Zn is primarily bound to small peptides and proteins in the endosperm of cereal grains [2,3]. Therefore, the Zn speciation in the storage proteins of the endosperm, which to date is virtually unknown, is emerging as a key-factor with respect to increasing the bioavailable Zn pools in edible plant organs, such as the cereal grain. However, methods for analysing the native Zn binding species *in planta* are currently absynt or immature. The reason for this is that most current methods are not considering the intact Zn-coordination complexes *per se* [3]. At University of Copenhagen, we combine state-of-theart plant molecular biology approaches with multi-elemental speciation analysis, using LCICP-MS, ESI-TOF-MS and MALDI-TOF-TOF-MS/MS to unravel Zn speciation in plants.

Currently, we are investigating the Zn speciation with ligands such as inositiol phosphates, metallothioneins, nicotianamine, phytochelatins and endosperm protein bodies. Also, we recently introduced laser ablation-ICP-MS for elemental fine mapping of grain tissue and isolated protein bodies. With these newly developed analytical methods, the elucidation of Zn speciation and compartmentation in cereal endosperms is progressing, and some major analytical achievements will be presented at the conference.

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ICP-MS DETERMINATION OF METALS/METALLOIDS AND ANALYTICAL SPECIATION OF ARSENIC IN A STREAM THAT RECEIVES DRAINAGES OF ABANDONED SILVER MINES IN GUANAJUATO, CENTRAL MEXICO

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For more than 400 years, the silver and gold mining activities in Guanajuato district had imposed a risk of environmental pollution with metals/metalloids and related threat to human health [1-3]. This work focuses on a 2.3 km long section of a small stream that receives two inputs from the abandoned mine drainages. Three sampling rounds were accomplished from April to June 2011, collecting water at five selected sites and sediments at three sites. Physicochemical parameters as a water flow rate, temperature, pH, electrical conductivity, oxidation-redox potential were assessed in the field, several metals/metalloids were ICP-MS determined in water and sediment samples and analytical speciation of arsenic in water samples was carried out by liquid chromatography with ICP-MS detection. The results obtained enabled for identification of a single point source of arsenic with as high as 300 $\mu g \cdot L^{-1}$ As in water, which declined naturally to 13.5 $\mu g \cdot L^{-1}$ As about 2 km downstream. Arsenate (As(V)) was the primary element species found at all sampling sites, yet traces of As(III), MMAs(V) and DMAs(V) were also detected. Principal component analysis revealed several associations among the parameters measured and confirmed that elevated oxidation potential and alkaline pH favor arsenic release to aqueous phase, while its elimination would be due to As association with solid phase containing Fe and, to less extend, Mn, Ca compounds. Since the flow system under study contributes to the water supply for the neighbor communities, the observed self-purification is relevant. On the other hand, this work provides additional experimental evidences on the putative effect of physicochemical parameter on the mobility of arsenic in the environment [4-6].

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D-a05

DETERMINATION OF Ti FROM TiO_2 MANUFACTURED NANOPARTICLES IN BIOLOGICAL MATERIALS BY Q-ICP-MS: OPTIMIZATION AND VALIDATION

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Manufactured nanoparticles (MNs) are commonly regarded as materials with at least one dimension below 100 nm, although there is no official definition. Their physico-chemical characteristics as size, optical properties, material strength and catalytic activity represents important properties allowing the use of MNs in the development of new applications in agriculture, engineering, processing, packaging, cosmetic and food sectors. For example, TiO_2 and SiO_2 MNs are used as additives, supplements and/or contact food materials. The expansion of nanotechnology applications has prompted discussions over the safety of these materials to human health. Some studies found that MNs are able to cross biological membranes and access cells, tissues and organs that larger particles normally cannot. MNs can also enter the blood stream via inhalation or ingestion and transported around the body and taken up by organs and tissues. Even in cases where nanoparticles do not show any acute toxicity, questions of long-term effects results from exposition to low MNs concentrations remain unanswered. To accomplish this, access to robust analytical methodologies is essential for detecting MNs in a range of matrix types. NANOGENOTOX project is a European Joint Action that the general objective brings added value by complementing Member States’ policies and contributing to improve citizens’ health and security. The aim of the Work Package 7 is to identify relevant organs for genotoxicity testing based on the determination of organ exposure to TiO_2, SiO_2 and Carbon Nano Tube MNs.

The objective of this work is to optimize and validate an analytical method for determination of titanium (Ti) from TiO_2 MNs in biological samples using Q-ICP-MS detection and microwave digestion. Optimization: We first assess the possible interfering elements on different Ti isotopes (m/z ratios) The volume and nature of digestion reagents, digestion program (pressure/temperature) were also optimized and tested on three spiked matrix (liver, kidney and muscle) and on six different pure TiO_2 MNs. Validation: Five IRM (brain, kidney, liver, muscle and heart) were in-house prepared and used for the validation process, each one differs from others in the spiking concentration and TiO_2 properties (eg., particles size). The optimized method has been validated according to the French standard NF VO3 110:2010 to elaborate the accuracy profile and to assess the limits of detection and quantification and the fidelity (repeatability and reproducibility). Linearity, sensitivity and specificity of the method were also assessed.

METALLOMIC AND METABOLOMIC STUDY OF ANTAGONISTIC METAL INTERACTIONS IN MICE *MUS MUSCULUS* UNDER CONTROLLED EXPOSURE

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The study of biological response of organisms under controlled exposure to toxic metals is the focus of numerous investigations, because many environmental issues are connected with the presence of As, Hg, Cd and others in natural areas, as a consequence of anthropogenic activities. On the other hand, the protective effect of some essential elements on toxic metals has been clearly established, becoming an expanding topic [1]. In this sense, selenium and zinc are extensively considered by their antagonist and synergistic actions with toxic elements such as cadmium and arsenic. The study of metal traffic, metabolism, homeostasis and perturbations in biological cycles and metal translocation between organs and tissues is mandatory to understand metals toxicity and interactions, and the use of techniques of massive information, the “omics”, such as metallomics and metabolomics are very valuable suitable tools for this purpose.

The aim of the present work are evaluated the consequences of exposure to toxic and non-toxic metals, such As, Cd, Se, and others, on the metallome of laboratory mouse *Mus musculus*. For this purpose a metallomic approach based on size exclusion chromatography (SEC) in combination with other complementary orthogonal separation techniques and heteroelements monitoring by ICP-MS was performed, followed by identification of metallobiomolecules by organic mass spectrometry. On the other hand, the simultaneous changes on metabolic expression of mice caused metals exposure (metabolome) was considered, exploring the application of direct infusion mass spectrometry (DI-ESI-QqQ-TOF-MS) to extracts from liver, kidney and urine of exposed animals. Subsequently altered metabolites were identified using MS/MS experiments. Conclusions on effects of these metals and their interactions on metal toxicity and their action on mice metabolism are assessed. These results can be used in further environmental studies involving free-living mice, *Mus spretus*, genetically related with the laboratory Mouse [2,3].

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D-a07

DETERMINATION OF SILVER NANOPARTICLES IN FOODSTUFF USING AF4-UV-Vis/ICP-MS AND TEM

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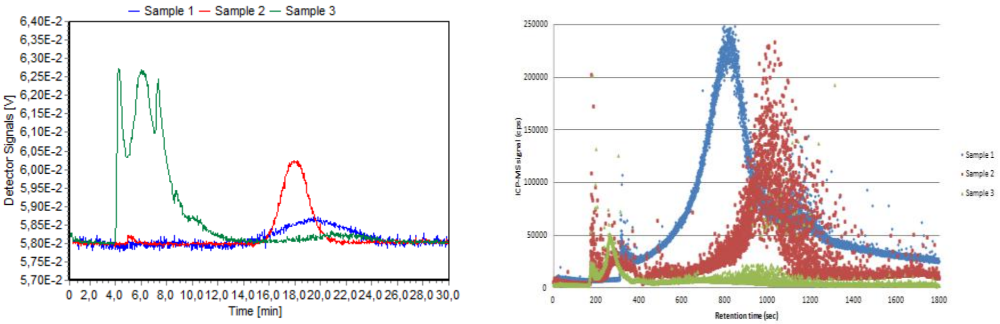
Silver nanoparticles (AgNP) are added to a number of consumer and medical products [1] due to its antimicrobial activity. Despite its evident benefices, its use also arises some concerns due to potential adverse effects on biological systems [2]. For this reason, there is a need to develop methods for the accurate analysis of these materials in foodstuff nowadays available on the markets.

In this work, an asymmetric flow field flow fractionation (AF4) multidetector system (UV-Vis, inductively coupled plasma mass spectrometry – ICP-MS) has been used for the detection and characterization of AgNP products. The separation of AgNP standards was optimized by applying chemometric methods. The mobile phase composition as well as the injection, focusing and elution conditions were considered because of their influence in the separation, resolution and recovery of the target compounds. Results demonstrated that the retention times of AgNP separated by AF4 correlated with their particle size. Optimal separation conditions were used for the analysis of AgNP in several foodstuff samples purchased from supermarkets in Madrid (Spain). The results showed a satisfactory agreement with those obtained by transmission electron microscopy (TEM). Results were also compared with those obtained by ultrafiltration through cut-off filters of 10 kDa.



a) b)

Fig.1 AF4 fractograms with (a) UV-Vis detection at 405 nm and (b) ICP-MS of the AgNP in selected foodstuffs.

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PLASMA-BASED INSTRUMENTATION FOR AMBIENT MASS SPECTROMETRY AND NANOPARTICLE CHARACTERIZATION

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Plasma-based instrumentation plays a major role in today's world of analytical chemistry. Thermal plasmas such as the inductively coupled plasma (ICP) are routinely used for elemental analysis while non-thermal plasmas such as the low-temperature plasma (LTP) probe [1] were used successfully as ionization sources in molecular analysis.

In the first part of this presentation, fundamentals and applications of LTP ionization for direct mass spectrometric analysis in the ambient environment will discussed. A home-built LTP probe was coupled to an Orbitrap high-resolution mass spectrometer (Exactive, Thermo Fisher Scientific) with a custom-built ion source interface. Fundamentals of LTP ionization [2] as well as important parameters for its optimization [3] will be highlighted. Exemplarily, the application of LTP-Orbitrap-MS to bioanalysis and lithium-ion battery research will be presented. Direct analysis of a variety of different samples was performed with analytical figures of merit very competitive compared to conventional mass spectrometric analysis. With this direct analysis technique, the identification of thermal aging products in lithium-ion battery electrolytes was carried out successfully. Typical analysis time per sample was less than 60 s and required no sample preparation.

In the second part of this presentation, the capabilities of ICP-MS in nanoparticle research will be discussed. When the ICP-MS is operated in time-resolved analysis mode, termed single-particle (SP) mode, it can be used to detect single nanoparticles (NP) [4]. This is accomplished by transient analysis of very dilute nanoparticle (NP) solutions. Atomization and ionization of single particles in the ICP produce discrete ion clouds, which in turn create detector signals that correspond to the particle size. Size characterization and quantification of commercially available nanoparticles was performed and the influence of sample introduction and ICP operating parameters on the performance was evaluated. Furthermore, the influence of the type of data acquisition system will be critically reviewed. Current challenges in single particle detection will be discussed as well as potential solutions to these challenges.

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D-a09

COMPARISON OF DIFFERENT METHODS FOR INVESTIGATION OF METALLIC ENGINEERED NANOPARTICLES

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Utilization of metallic engineered nanoparticles (ENP) in research, medicine, and consumer products is progressing rapidly, due to their unique chemical and physical properties. In consequence, characterization of metallic ENP is of increasing importance to better understand and tailor their performance for more specific, cost effective, and safer application. For such understanding a detailed characterization of its physico-chemical properties is inevitable. Therefore, only a combination of a series of techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) [1], field flow fractionation (FFF) coupled to various detectors [2], or single particle inductively coupled plasma mass spectrometry (sp-ICP-MS) [3] is providing information about the entire properties of ENP. Unfortunately, this detailed characterization is very elaborate and time-consuming. But in most cases such an in deep analysis is not necessary to improve or evaluate their benign attributes and possible risks. In fact this calls for reliable and fast analytical techniques able to determine only the most important parameters such as elemental composition, size/mass and the particle number concentration.

Therefore, a sample introduction system based on monodisperse microdroplet generation [4] which allows the transportation of single droplets into ICP-MS was proposed. This approach is promising due to high sensitivity, low consumption of sample material, 100% sample transport efficiency, temporally separated signals of single events corresponding to one droplet and possibility of calibrating the nanoparticle mass by using analyte solution.

In this work the advantages and limitations of the microdroplet introduction system, when compared to commonly applied, state-of-the art nanoparticle characterization techniques (SEM, TEM, FFF and sp-ICP-MS), will be discussed. For the study various ENP suspensions as well as complex mixtures of particles containing also dissolved analyte have been investigated.

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DEVELOPMENT OF LC-ICP-MS BASED IMMUNOASSAYS FOR TARGETED ANALYSIS OF BIOLOGICAL SAMPLES

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The employment of elemental labeled antibodies combined with ICP-MS based detection in biomedical diagnostics offers the possibility for elegant straightforward quantification of the labeled antibodies binding to various targets (e.g. cancer markers or cellular metabolites). Future applications are imaging via LA-ICP-MS [1] or ICP-MS based absolute quantification of targets in cellular samples via immunoassays.

Our work investigates the concept of elemental labeling combined with LC-ICP-MS based separation and detection. The assessed samples are characterized by a complex sample matrix and ultra-trace concentrations of the target compounds (e.g. a biomarkers), which need to be quantified in low sample volumes. As this task demands for highly sensitive, selective, accurate and robust quantification strategies, we are currently assessing the single steps of the workflow, i.e. the coordination of the selected element by the complexing moiety [2], the attachment of the complex to the antibody and the formation of the antibody-antigen conjugate.

A special focus concerns the impact of the applied labeling procedure on antibody properties (e.g. fragmentation, generation of intermediate products or diastereomers). Here, a detailed characterization of the elemental labeled antibodies is performed regarding the exact labeling degree, labeling sites, stoichiometry and antibody functionality, aiming at protocols to be implemented in quantitative bio-analysis. Within our presentation, benefits and limitations of the presented concept are discussed and promising future perspectives are highlighted.

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D-a11

DETERMINATION OF SELENOMETHIONINE IN AMBIENT WATERS

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Selenomethione (SeMet) is thought to be the key selenium (Se) species responsible for Se bioaccumulation and for the associated ecotoxicological risk for aquatic wildlife. It is well established that SeMet is present in the tissues of organisms exposed to elevated Se concentrations, both in its free form and incorporated into so-called selenium-containing proteins. SeMet has consequently often been used in toxicological bioaccumulation experiments, and is much more bioavailable than the inorganic Se oxyanions, selenite and selenate, commonly encountered in Se-impacted waters. However, there is to date no conclusive evidence that SeMet actually exists in ambient waters, which creates a significant gap in the understanding of the chemical mechanism of Se uptake into lower trophic organisms in aquatic food chains, particularly with respect to the linkage between Se bioaccumulation in nature and in laboratory Se exposure experiments.

In this project, we are investigating if SeMet is present in ambient Se-contaminated waters. The goal is to answer this question with detection limits in the low $ng \cdot L^{-1}$ range, so that it can be determined whether or not SeMet is present at a fraction of ≥ 1% of the total dissolved Se concentration in an impacted water body. SeMet is separated from other, similar organic Se species by anion-exchange chromatography with on-line detection by inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-ICP-MS). SeMet is tentatively identified by elution time and quantified by external standardization in model mixtures of Se species, in the culture medium of algae exposed to inorganic Se species, and in samples collected from water bodies impacted by industrial Se discharges. Any tentative SeMet identifications are then confirmed by AEC with electrospray-tandem mass spectrometry (ES-MS/MS) detection, with detection limits comparable to the AEC-ICP-DRC-MS method.

First results indicate that SeMet occurs in the culture medium of the algal growth experiments, just barely above the instrumental detection limits of both the AEC-ICP-DRC-MS and AEC-ES-MS/MS methods (around 10 ng Se/L). SeMet was also tentatively identified via co-elution by AEC-ICP-DRC-MS in field samples, but the AEC-ES-MS/MS confirmation of these results is still outstanding. SeMet is baseline-separated from all other Se species available to us as standards, but several other unknown Se species occur in the vicinity of the SeMet elution time, some of them in substantially higher concentrations. We also confirmed the presence of selenomethionine oxide in some samples using the same analytical methods, but it remains to be tested if this compound was present in the original samples, or whether it was formed between sampling and analysis. Due to the very low SeMet concentrations encountered, current experiments focus on the preconcentration of SeMet by solid phase extraction (SPE), in order to increase the confidence in the tentative identification and quantification of SeMet in ambient waters.

D-b01

SIZE-BASED ELEMENT SPECIATION OF NANOMATERIALS IN FOOD: THE POTENTIAL OF COMBINING ASYMMETRIC FLOW FFF WITH ICP-MS, LIGHT SCATTERING AND ELECTRON MICROSCOPY

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The novel properties of nanomaterials and their increasing use have led to enormous research and development activity and significant markets of consumer products containing nanomaterials [1]. A few studies have demonstrated that nanomaterials are not inherently benign, although there remains considerable uncertainty. In vitro nanotoxicology studies, in a short term, and the quantification of human exposure, in a longer term, will require of metrologically validated methods for the detection and characterisation of manufactured nanomaterials in complex matrices. Such methods are scarce and, therefore, urgently needed.

Given the complexity of nanomaterials and of the matrix in most consumer products, the use of a single measurement technique has often resulted in their ambiguous detection and characterisation. The use of multi-method approaches has, therefore, been proven essential to provide improved information and reduced bias, especially for nano-objects in complex matrices [1]. Such approaches, although time consuming and expensive, have the advantage of including a range of techniques that provide information on properties of nanomaterials (e.g. size, size distribution, elemental composition and isotopic ratio, surface charge, shape, agglomeration and aggregation, etc), which may be useful to their unambiguous detection and characterisation in their complex environment.

This work investigates the potential of combining asymmetric flow field flow fractionation (FFF) with a range of detection techniques including ICP-MS, multi-angle light scattering (MALS), UV-Visible spectroscopy and transmission electron microscopy (TEM) for the characterisation of metal oxide nanoparticles (e.g. TiO_2 and/or SiO_2) added to food. Element-specific detection by ICP-MS and post-FFF calibration with elemental standards is used to determine the elemental composition of size fractions on-line separated by FFF. FFF-MALS is used to obtain information on size and size distribution in food extracts. In particular, this hyphenated technique is useful in providing data on larger nano-objects or their aggregates. The feasibility of TEM is investigated for providing detailed information (e.g. size, shape, etc) on small particles (≤ 20 nm) in FFF-collected fractions. Quantitative data on mass balance will be given for the size-based speciation of the investigated inorganic nanomaterials in a food matrix.

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METHOD DEVELOPMENT FOR TOXICOKINETICS AND TISSUE DISTRIBUTION OF NANO-TiO_2 BY HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (HR-ICPMS)

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Human exposure to manufactured nanomaterials (MNs) used in consumer products may occur during several phases of their life cycle, from synthesis, production and inclusion in products to the release of these MNs into the environment. The lack of scientific knowledge and the absence of evidence demonstrating the safety of certain nanotechnology products make regulation very difficult (source: Opinion of Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR); 2009). Because of this, health and safety evaluation is attracting the attention of the public and of governments worldwide.

The toxicity and thus risk of a chemical and MNs is determined by its toxicokinetic behavior in the body, as this determines local (toxic) tissue concentrations. For toxicokinetics, *in vivo* studies are dedicated for the fate and tissue distribution of MNs in the body. Within this study, the kinetic parameters in blood and the tissue distribution are determined for various types of TiO_2 nanoparticles. Next to the chemical composition and size of the nanoparticles, attention is also paid to the surface properties of the nanoparticles.

Two issues need to be considered for the tissue distribution of any compound including MNs:

a) The material administered should not be overly toxic to the animals as toxicity may have an effect on metabolism and excretion thus effecting tissue distribution.
b) On the other hand, the doses should be sufficiently high to be able to detect MNs. This leads to the question: what amount of MNs should be administered to the animals for the *in vivo* studies? A tolerable dose of TiO_2 was identified. A dose of 2.3 mg per animal was found to be non toxic until 14 days after intravenous administration. The 2.3 $mg \cdot mL^{-1}$ was the highest possible concentration for obtaining a well dispersed TiO_2 nanoparticle suspension.

The non toxic tolerable dose was used to set up the detection methodology for TiO_2 in various organs [2]. The methodology for detection of the MNs was developed and validated; for this study, high resolution inductively coupled plasma-mass spectrometry (HR-ICPMS) is used.

By evaluating the tissue distribution, organs at risk for toxicity including genotoxicity may be identified by the presence of MNs in those organs. TiO_2 is still detected in various organs at day 90, with a gradual decrease in time and a variation in decrease (single and repeated intra-venous administrations).

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CHARACTERIZATION AND STABILITY STUDIES OF SILVER ION AND SILVER NANOPARTICLES. BIOCONCENTRATION BY ZEBRAFISH LARVAE

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The chemical characterization of natural and engineered nanoparticles is a recent challenge in analytical sciences**.** Silver nanoparticles (AgNPs) have become a subject of major concern in the last decades due to its wide range of applications and consequently, high level of production that will inevitably lead to their appearance in air, water, soils, and organisms. Therefore, many researches are focused in the evaluation of AgNPs toxicity, finding a clear relationship between the chemical stability of these nanoparticles and their in vitro toxicity. The widely accepted view is that there are many unanswered questions, although a large number of reports have been published discussing the potential environmental and health risks associated with their manufacture, use, distribution and disposal.

Determination of AgNPs between a certain range of size requires their stabilization in order to avoid both agglomeration or ionization. In this work, the addition of capping agents has been studied resulting 0.1% citrate plus 0.1% soluble starch the best choice for stabilization of silver nanoparticles. Discussion on how several physico-chemical parameters such as temperature, time, type of container walls, etc. affected the nanoparticles stability is included. Determination of AgNPs and/or Ag^+ has been performed by graphite furnace atomic absorption spectrometry (ZGF-AAS) and by flow injection inductively coupled plasma mass spectrometry (FI-ICP-MS).

Once stabilization of silver nanoparticles has been proved, a bioconcentration experiment has been designed following the protocol OECD 305 in order to evaluate both nano-silver and Ag^+. BCFs using zebrafish larvae as model have been calculated. This vertebrate model has been chosen due to unique advantageous features over other systems based on its highly genetic homology with humans and fast embryonic development. Results on the bioaccumulation capabilities of both analytes are presented and discussed.

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CHEMISTRY OF SILVER NANOPARTICLES IN BURNS HEALING: FROM *IN VITRO* TO *IN VIVO* BY ICP-MS

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For centuries silver (Ag) has been extensively used because of its antimicrobial properties, silver nano-sized particles (Ag-NPs) possess chemical and physical properties that make them more effective against pathogens compared to silver ions alone. Despite the enormous interest in this field a systematic study of the chemical composition and release kinetics of medical products containing Ag has only now been published [1]. The aim of this work is to investigate the behavior and safety of Ag-NPs for burns patients.

Preliminary in vitro experiments have shown that the dressing releases weak agglomerates of Ag-NPs. Further experiments on a three dimensional cell culture system of human skin fibroblasts were conducted: the dressing was applied on the cells, and every three days it was changed to simulate dressing changes by a clinician. The Ag concentration in the culture medium and in the used dressings has been measured by ICP-MS, the Ag amount absorbed by the cells has been evaluated by difference. In order to investigate the effects and toxicity of released Ag-NPs on skin fibroblasts, biochemical and histological techniques have been employed to determine both the viability and the spatial distribution of the cells during application of the dressing. The study has been scaled up by considering the effects in vivo on patients. Samples were collected from patients with extensive burn wounds treated with the Ag-NPs based dressing at the Burns Center of Padua. The amount of Ag released from the dressing and the fraction absorbed by patients have been evaluated by using different approaches. The Ag dose absorbed by the patients has been estimated as the difference between the original amount of silver in the dressing, and the Ag remaining in the dressings after use, together with the Ag released into the organic material attached to the dressings. The total Ag concentration has been measured directly on previously frozen whole blood and serum from the patients and, in order to identify the protein moiety to which Ag binds to in vivo, size exclusion chromatography (SEC) has been coupled on line with ICP-MS. Analysis of the serum and blood samples shows that Ag is bound to the proteins present in the high molecular mass protein fraction that has the same retention time as albumin.

The holistic and multilevel approach applied in this study is of paramount importance: it has been demonstrated that results obtained in vitro seldom represent effectively what happens in vivo and that a multidisciplinary strategy is necessary to obtain complete information on the safety of new NPs based products.

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FUTURE PROSPECTIVE OF SPECTROCHEMICAL ANALYSIS IN BIOINORGANIC TRACE AND SPECIATION ANALYSIS: FROM MACRO TO MICROANALYTICS

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In this presentation, development of innovative macro- and micro-digestion techniques and micro-extraction (ionic liquids, nanoparticles, cloud point extraction, graphene), including miniaturization of the instrumentation for sample preparation with the electromagnetic induction heating and subcritical water extraction method and pre-concentration of volatile species, (using carbon nanotubes) and spectroanalytical methodologies: atomic spectrometric techniques, such as flame atomic absorption spectrometry, chemical vapor generation atomic absorption and emission spectrometry, graphite furnace atomic absorption spectrometry, electrothermal vaporization, laser ablation, ultrasonic and multimode sample introduction techniques, capillary electrophoresis technique, microwave induced plasma optical emission spectrometry, with emphasis on macro- to micro interfaces will be described.

One of the goal of analytical atomic spectrometry is to attain the lowest limits of detection and the exploitation of total element determination and in the area of metallomic analysis in the context of speciation analysis of the elements in biological and environmental systems. The design and development of portable micro-structured analytical instruments and "*Lab-on-a-Chip*" devices will improve the (ultra)trace analyses (from mg/L(kg) to ng/L(kg) levels), as an advantage of micro-structured analytical instruments is the handling of ultra-small volumes.

In conclusion, the overall aim is to highlight not only the development in instrumentation for (ultra)trace element determination and speciation analysis in variety of biological and environmental matrices but the application of the developed techniques.

SeMeSeCys METABOLISM IN RATS FED WITH ^{77}Se-ENRICHED SAUERKRAUT

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Selenium (Se), an essential trace element for human health, has a well-known role in prevention of chronic diseases associated with oxidative stress and inflammation. As several millions of people worldwide do not reach the RDA of selenium, intake of Se supplements has been the most widespread approach to prevent Se deficiency. Several authors have reported preparation of Se-enriched foods by fermentation processes [1,2]. Fermented white cabbage, “sauerkraut”, a traditional North-East European food product with nutritional and health-promoting properties, has been prepared in presence of selenium salt (Na_2SeO_3) providing important amounts of SeMeSeCys. This Se species is recognized to have anticarcinogenic properties and, hence, consumption sauerkraut will contribute to the population well-being [3]. Nevertheless, there is a lack of knowledge about Se metabolism, distribution and safety in living organisms. Therefore, the aim of this work was to establish the metabolism of SeMeSeCys in rats fed with Se-enriched sauerkraut and to assess its distribution in different body organs.

Wistar rats weighing about 150 g were fed *ad libitum* with a standard AIN-93M diet containing ^{77}Se-enriched sauerkraut (20%) for an experimental period of 7 days. During the experiment, weight gain and the intake of food and water were monitored. On day seven, the rats were sacrificed and the organs were removed for further selenium distribution analysis. For this purpose, an analytical methodology based on previous works for trace element determination in rat tissues was applied [4-6].

In the present communication, bioaccumulation and distribution of exogenous (^{77}Se) and endogenous selenium in different organs as liver, heart, brain, testicles, etc. as total selenium using HG-AFS and IDA-ICP-MS will be reported. Se-species identification in the different organs will be performed by applying several sample treatments and chromatographic columns of different mechanisms. Quantification of the Se-species will be carried out by IDA in combination with LC-ICP-MS. The results obtained will achieve deeper insights about the metabolisms of SeMetSeCys in living organisms.

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CHALLENGES IN NANOTOXICOLOGICAL STUDIES OF SILICON AND TITANIUM DIOXIDE USING AN ANALYTICAL PLATFORM BASED ON REACTION CELL ICP-MS AS ELEMENTAL DETECTOR

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Engineered inorganic nanomaterials (iENMs) are being manufactured in ever increasing quantities and used in a wide range of applications. However, owing to their relative novelty, the risks to human health and the environment are not yet well characterized raising concerns about long-term consequences of widespread use. Assessing the potential risk of iENMs requires imaging and analysis methods that can be successfully employed in experimental studies addressing their interaction with biological systems. Characteristics of iENMs that affect their behaviour and toxicity include size, shape, surface properties, aggregation state, solubility, mass concentration and elemental composition.

Among the analytical tools used to determine relevant properties in nanotoxicological studies, ICP-MS plays a major role. It can be used as a detector of unparalleled sensitivity for the measurement of the mass concentration of iENMs in biodistribution studies, whereas single particle ICP-MS and hyphenated ICP-MS-based techniques (AF4-ICP-MS) have a tremendous potential as characterisation tools. So far, ICP-MS has been used primarily for the detection and characterisation of iENMs based on noble metals. Application to oxide nanomaterials, especially SiO_2 and TiO_2, has been largely hampered by analytical challenges, i.e., high background and substantial spectral interferences. Detection of unlabelled oxide iENMs in testing media and biological samples is problematic and complicates their safety assessment. Nano-SiO_2 and TiO_2 are produced in high tonnage volumes and are among the most common material used in food and consumer 'nanoproducts'. Furthermore, there is evidence that the corresponding bulk substances authorised as food additives (E171, E551) contain a nanosized fraction and may add to the overall dietary exposure of the general population. Therefore, there is a urgent need to assess their potential toxicological significance.

The challenges of *in vivo* nanotoxicological studies of SiO_2 and TiO_2 using an ICP-MS-based analytical platform are reviewed along with the approaches developed in our laboratory to overcome them. Means to reduce the elemental background in biological tissues and identify suitable doses for investigating toxicokinetics and tissue distribution of nano-SiO_2 in the context of genotoxicity studies [1] are presented. Issues related to contamination during sample handling and elemental release from analytical equipment are addressed. Chemical resolution of polyatomic interferences on Si and Ti masses by gas phase reactions is then considered. Finally, investigation of the stability of suspensions, aggregation behaviour of nanoparticles [2] and their detection in tissues following intravenous and oral administration are discussed emphasizing the potential of ICP-MS in time resolved mode.

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HYPHENATED TECHNIQUES USING PLASMA MASS SPECTROMETRY TO STUDY THE TRANSPORT, DISTRIBUTION AND METABOLISM OF METALLODRUGS

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The study of the biochemical activity of pharmaceuticals benefits from the analysis of the active compounds and their metabolites within the physiological environment. In the case of metallodrugs, where the active center is related to a metal, this metal can also be used as a kind of tag to recognize the compounds formed by the interaction of the drug with biological molecules. In this way highly sensitive and selective hyphenated techniques for speciation analysis, such as LC-ICP-MS or laser ablation coupled with ICP-MS for the imaging of biological systems can be used to study the transport, distribution and metabolism of metallodrugs. The combined use of such techniques allows for the highly sensitive detection of the metal-containing species (LC-ICP-MS), their quantification (LC-ICP-MS) and their distribution analysis in target biological systems (LA-ICP-MS). Using examples such as platinum-based chemotherapeutics, Gd-based contrast agents and other metallodrugs, the type of information that can be gained from the use of such hyphenated techniques will be discussed.

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QUANTITATIVE DETERMINATION OF ARSENIC METABOLITE-PROTEIN INTERACTION BY ELEMENTAL SPECIATION ANALYSIS

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Arsenic trioxide (ATO), belonging to the oldest remedies known, was recently approved by the FDA for the use in the treatment of relapsed/refractory acute promyelotic leukemia (APL). Since the introduction of ATO in chemotherapy, we keep learning about the cytostatic activity of the drug. Still the knowledge on the intracellular chemistry of ATO with regard to the activity profile of the drug is however fragmentary. The debate continues if ATO can be applied for other blood and solid cancers. [1,2] The controversy about scientific results in this case and the established concepts of mode of action for ATO was motivation for this work.

The intracellular metabolism of ATO concerning the binding dynamics between cytosolic compounds with special emphasis on the interaction with glutathione and the formation of its oxidized form was extensively studied. Sensitive versus resistance cancer cell models as well as cell lines derived from different types of cancer were subject due to this investigation. First, spiking experiments using cell extracts and sub-µM concentration of ATO (resembling relevant (pre)clinical concentrations) were performed in order to investigate kinetics of ATO adduct formation with biomolecules. Moreover, cells were exposed to 10 µM drug, lysed at different time points and fractionated by the use of centrifugal filtration (10 kDa cut-off) into protein and small molecule fraction, to obtain a clearer perspective on uptake and distribution in the selected cell models. ICP-MS addressed the quantification of drug uptake, intracellular distribution and quantification of protein bound drug versus low molar mass fraction. Chromatographic separation of ATO and its metabolites species was based on a weak-anion-exchange stationary phases. [3] Glutathione in reduced and oxidized form were studied by HILIC-MS-MS using isotopically enriched standards.

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THE USE OF CCT MODE WITH THE iCAP Q ICP-MS: SENSITIVITY IMPROVEMENT BY COLLISIONAL FOCUSING AND EFFECTIVE REACTION CHEMISTRY IN CHALLENGING IC-ICP-MS BASED SPECIATION APPLICATIONS

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The use of collision/reaction cell in quadrupole based ICP-MS is a well established technique to remove or circumvent the extent of spectral interferences affecting the detection of certain isotopes.

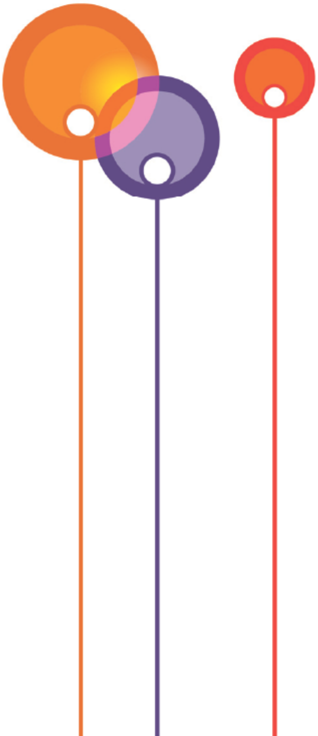
Often, a certain amount of ions is lost when using a collision cell, so that the attainable sensitivity is decreased. Additionally, for some elements like sulphur, which are heavily interfered in aqueous matrixes, the use of a non reactive gas such as He and kinetic energy discrimination is not successful, so that reaction chemistry is necessary through e.g. the use of O_2 as a cell gas. This gas may impede the simultaneous detection of other elements, as these either tend to form oxides or are not able to exit the cell as they suffer from collision with the O_2 molecule.

This paper presents an alternative mode of cell operation using the new iCAP Q ICP-MS with proprietary cell technology. When operating with pure He, an increase of sensitivity is observed for mid- and high mass elements (up to a factor of three), mainly due to collisional focusing in the QCell^{TM}. When reactive gases such as oxygen are introduced, sensitive detection of elements such as sulphur is possible (sub ng·g^{-1} limits of detection), while still offering reasonable detection sensitivity for other elements such as metals, with the exception that they must not tend to form oxides. This opens the door to new applications for the CCT mode in different types of analysis.

In this work, the performance of both operation modes of the CCT mode is demonstrated, on the one hand for improvement of detection sensitivity for heavy elements, on the other hand as a powerful tool for e.g. elemental speciation analysis of sulphur as a part of proteins or peptides. Also the determination of inorganic ions such as sulfate, sulfite or thiosulfate at trace levels using IC-ICP-MS becomes possible.

E section

Laser ablation and elemental imaging



A 45-YEAR JOURNEY IN ICP-AES: FROM ACADEMIC RESEARCH TO INDUSTRIAL PROBLEM SOLVING

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Entering the field of academic research needs some chance when starting a new technique as it should be at the right time, i.e., neither too early because an advanced technology is still missing for at least one major component, nor too late because an alternative technique is already well-established. It will imply that you have to develop instrumentation, which means that you need to test and understand the role of each component so as to optimize their selection or development, and to provide specifications to a potential manufacturer. This step is certainly tedious and time-consuming, but provides deep knowledge in the operation and the practical characteristics of the instrument. In the case of ICP-AES, generator and torch design, sample introduction, photon collection, specifications for the dispersive system, and photon detection were all of concern. Once the research instrument is working properly, evidence must be provided that it may bring significant improvements over previous techniques in solving analytical problems, e.g. more elements that can be determined, lower limits of detection/quantitation, less matrix effects, higher sample throughput, or in reducing investment and running costs. These improvements should be illustrated with real-life, complex samples. Following the acceptance of the technique, there is a need to simplify and summarize complex knowledge obtained in a research laboratory. Dissemination of the simplified information through publications, training, consulting, facilitates the routine use of the instrument through method development, optimization and diagnostics. Collaboration with instrument companies implies that a compromise must be found between an ideal system and a one that can be made commercially available at a reasonable cost. Even when the technique becomes mature, there is still room for development, particularly in assisting users, for instance in calibration strategy, multiline-based analysis, proper use of internal standardization, estimation of accuracy validity domain, selection of appropriate limit of quantitation, self-diagnostics, and fair comparison with alternative and emerging techniques. In conclusion, a scientific career in analytical sciences can be summarized by the following sequence: developping, understanding, applying, simplifying, disseminating and supporting.

FUNDAMENTALS AND APPLICATIONS IN LASER ABLATION-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Laser ablation-inductively coupled plasma mass spectrometry is successfully applied to a wide variety of solid samples for major, minor, trace element analysis or isotope ratio determinations. Besides remaining limitations and little understanding of ICP processes it has been shown that the precision and accuracy in direct solid analyses improved continuously within the last years. Some of these improvements were achieved by progress in laser technology and increased knowledge about sampling, aerosol transport and excitation processes. The expectation on improving the quantification capabilities in LA-ICP-MS by using fs laser ablation, which is more and more applied, is very high. Therefore, some typical fields of application and some figures of merit will be discussed.

The most recent trend in LA-ICP-MS is focused on quantitative, high spatial resolution elemental mapping, which is required to reconstruct the trace element distributions in tissues, in stalagmites or in alloys and steel samples, meteorites and many others. Therefore, sample-geometry independent ablation cells and low washout cells are required to achieve high resolution. An atmospheric sampling system, currently in the third generation ($0.8\ \mathrm{L \cdot min^{-1}}$ exchange capacity), allowing analysis of samples without an airtight ablation cell will be explained and first isotope ratio determinations will be discussed. Furthermore, the working principle of a very fast washout cell, enabling high-resolution images will be explained and some applications (material science and biology) will be shown.

Non-matrix matched calibration is currently the method of choice to quantify solid samples. However the results differ in precision and accuracy. Therefore, laser-generated aerosols and single particles were vaporized within the ICP under wet and dry plasma conditions. The onset of vaporization was detected by using optical emission spectroscopy and laser light scattering. The results and implications for quantification of laser-generated aerosols will be discussed.

Furthermore, flame synthesis was used to produce homogeneous calibration materials (particle size of approx. 20-30 nm) for micro-beam techniques. Carbonates and silicates were synthetically produced and doped with various trace elements. The ablation behavior of these materials is very similar to glass samples and some fields of application of such materials will be discussed.

LASER PLASMA SPECTROCHEMISTRY: LIBS AND LAMIS

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Laser plasma spectrochemistry has received a great deal of attention with the Mars landing of Curiosity; the rover contains a LIBS (Laser Induced Breakdown Spectroscopy) sensor to analyze elements on the Martial surface. The capabilities of laser plasmas led NASA to choose LIBS for this mission. These capabilities include little or no sample preparation, no consumables or waste, real-time measurements, spatial and depth resolution [1]. The first paper on laser plasma spectrochemical analysis was presented in 1962 [2]. Fifty years of fundamental research has led to established performance metrics for sensitivity and accuracy in many applications. LIBS recently has been advanced to include isotope abundance measurements [3] with a new technology called LAMIS (Laser Ablation Molecular Isotopic Spectroscopy), and the ability to achieve sub-micron spatial resolution with attogram absolute mass detection [4]. The ability to perform plasma spectrochemical isotopic analysis at remote distances is another possibility for LIBS/LAMIS [5]. This lecture will discuss the advances and capabilities of laser plasma spectrochemistry, to include laser ablation, LIBS, LAMIS, and femtosecond filamentation.

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CALIBRATION STRATEGIES FOR LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY - POSSIBILITIES AND LIMITATIONS

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Laser ablation inductively coupled plasma mass spectrometry (LA ICP MS) is considered as a very attractive technique mainly because it allows to perform direct, multi elements analysis of any solids. LA ICP MS is widely used not only to determine the content of major, minor and trace elements but also to evaluate their distribution over the surface as well as in sub-surface domains, with high spatial resolution.

The main advantageous of LA ICP MS lies in its micro-destructive feature, it allows direct micro-sampling of solids by laser ablation accompanied by very good sensitivity of ICP MS. It has been successfully used for various applications, although the lack of suitable matrix-matched solid standards is still recognized as its severe limitation for the accurate quantitative analysis. The wide assortment of liquid standards allows their adequate selection if solution is analyzed. Contrary, the limited collection of solid reference materials impedes the assurance of the quality control of the results ofmeasurements of solids.

The efficient and robust procedures for the preparation of in-house solid standards enabling the calibration versus powdered solid standards was developed for the direct determination of the elemental composition in solids. Various calibration strategies tailored towards specific applications were developed as to assure the accuracy of the results obtained by LA ICP MS. This will be exemplified with the description of developed strategies used for the investigation of cultural heritage (e.g. glasses, metals, bones) or powdered samples of environmental origin. The example of the in-vivo inspection of elements distribution in cells of plant tissues, the identification of metals bounded with proteins after its separation by gel electrophoresis, as well as the investigation of in-deep profiles of element distribution in solid membranes used in solid electrodes will be also given.

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ANALYSIS AND THICKNESS DETERMINATION OF ULTRA-THIN LAYERS BY TWO COMPLEMENTARY TECHNIQUES: LA-ICP-MS AND RF-GD-TOFMS

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Nanometer-scale depth resolution, accurate thickness determination, high sensitivity and elemental/molecular information are increasingly required for the chemical characterization of thin and ultra-thin layers, which are extensively used in industry and in many research fields in order to develop innovative materials. In this sense, Laser Ablation Inductively Coupled Plasma (LA-ICP) and Pulsed Radiofrequency Glow Discharge (pulsed-rf-GD), both coupled to mass spectrometry (MS), are established and powerful complementary techniques for fast and sensitive direct analysis of solid (conducting and insulating) materials with high spatial resolution [1,2].

LA-ICP-MS has been applied to determine the thickness of 0.5, 1, 3, and 6 nanometer metallic layers (metallic Nd was deposited onto Si wafers and covered by a 10 nm Al coating). Integrated ion signals corresponded to the layer thickness, indicating that external calibration provides accurate data. Additionally, utilizing sensitivity ratios obtained from ablation of a glass standard reference material (SRM) and the Al layer as reference, the deviations between prepared and measured layer thickness were less than 10% [3]. Furthermore, it is well known that the interaction of the laser beam with the material can lead to a matrix dependent degree of melting of the near-surface regions. This effect creates an artificial mixing zone, which disturbs an otherwise sharp transition of layers and thus reduces the attainable resolution in depth profiling. These mixing and thermal effects are investigated for the determination of impurities in ultrathin layers of photovoltaic samples.

As a complementary technique, Pulsed-rf-GD plasma sources provide a dynamic plasma due to the temporal evolution of applied power (with time domains along the GD pulse profile, denominated pre-peak, plateau, and afterglow) [4]. This pulsed mode allows high instantaneous power, increasing the atomization, excitation, and ionization processes while minimizing thermal conversion of the sample. Direct solid analysis of ultra-thin layers, including photovoltaic materials, is investigated using Pulsed-rf-GD coupled to Time-of-Flight mass spectrometry (TOFMS), combining positive and negative ion detection modes. Distributions of major, minor and trace elements are evaluated as well as the potential to obtain molecular information.

Acknowledgement

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DEVELOPMENT AND APPLICATIONS OF LASER-ASSISTED PLASMA SPECTROMETRY TECHNIQUES

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Techniques of laser-assisted plasma spectrometry are convenient for direct analysis of solids where either spatially resolved information is required or solution analysis is troublesome due to complex and/or incomplete sample dissolution. Elemental imaging and local analysis may provide significant information on technological materials, biological tissues, geological materials such as individual mineral grains in rocks, archaeological findings and objects of cultural heritage including authentication and provenance determination.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) represents efficient analytical tool for such analyses and is frequently combined with physical methods of surface analysis and complementary methods for molecular imaging. Laser-induced breakdown spectroscopy (LIBS) represents less expensive alternative for elemental mapping. Double pulse (DP) LIBS brings improved detection limits for some elements in comparison to the single pulse LIBS.

Laser ablation sampling enables coupling of methods currently employed in solid sample analysis. In our laboratory, a special ablation chamber has been developed for simultaneous combination of DP-LIBS and LA-ICP-OES techniques. This equipment was designed to study the influence of DP conditions on the LIBS properties, e.g. generating of aerosol, basic parameters of laser-induced microplasma at the analysis of various matrices. In this context, biominerals, geological and archaeological samples are investigated from the viewpoint of provenance analysis, elemental mapping and quantitation.

The same topics are studied by LA-ICP-MS, moreover, our attention is paid to biological tissues as well. LA-ICP-MS application in biomedical sciences could bring essential information important for a better understanding of processes in living organisms, which might be helpful in medical treatment. The first field of our research activities is devoted to imaging of tumor tissues via distribution of Cu and Zn bound to proteins.

Biomedical sciences comprise also study of various biominerals from the viewpoint of their formation, growth and influence of ambient environment. Uroliths represent such biomineral objects that are interesting not only with respect to biomedicine but also as an example of complex analytical material.

Moreover, presented topics constitute both applications, investigation of fundamental processes responsible for influence on quality of analytical results, preparation of matrix matched calibration standards, and development of appropriate calibration procedures.

Acknowledgement

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HIGH-RESOLUTION ELEMENTAL BIO-IMAGING OF Ca, Mn, Fe, Co, Cu, AND Zn EMPLOYING LA-ICP-MS AND HYDROGEN REACTION GAS

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Imaging of trace metal distribution in tissue sections by laser ablation- inductively coupled plasma-mass spectrometry (LA-ICP-MS) is typically performed using spatial resolutions of 30 μm^2 and above. The resolution is limited by detection sensitivity which is not sufficient to determine the elemental profiles of single cells. This presentation explores the use of hydrogen reaction gas to improve the signal-to-noise ratios of a number of biologically relevant isotopes that are subject to prominent spectral interferences. At low (<1 $mL \cdot min^{-1}$) H_2 flow rates, greater spectral interference due to H^+ adducts was observed for ^{55}Mn, ^{57}Fe, and ^{59}Co. At higher flow rates of up to 3 mL H_2 per minute, the spectral interferences were reduced leading to improved limits of analysis. This enhanced sensitivity with the reaction cell allowed construction of high resolution (6 μm^2) images of ^{56}Fe in a mouse brain that approached the dimensions of single cells.

E-a03

LASER ABLATION ICPMS FOR DIRECT ELEMENTAL AND ISOTOPIC ANALYSIS OF DRIED URINE SPOTS

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Collection of biological fluids on clinical filter papers shows important advantages from a logistic point of view, although analysis of these specimens is far from straightforward. Concerning urine analysis, and particularly when direct trace elemental analysis by laser ablation-ICP-mass spectrometry is aimed at, several problems arise, such as lack of sensitivity or different distribution of the analytes on the filter paper, rendering obtaining reliable quantitative results quite difficult. In this paper, a novel approach for urine collection is proposed, which circumvents many of these problems. This methodology consists on the use of pre-cut filter paper discs where large amounts of sample can be retained upon a single deposition. This provides higher amounts of the target analytes, and thus, sufficient sensitivity, and allows addition of an adequate internal standard at the clinical lab prior to analysis, therefore making it suitable for a strategy based on unsupervised sample collection and ulterior analysis at referral centers. Based on this sampling methodology, an analytical method was developed for the direct determination of several elements in urine (Be, Bi, Cd, Co, Cu, Ni, Sb, Sn, Tl, Pb and V) at the low $\mu g \cdot L^{-1}$ level by means of LA-ICP-MS. The method developed provides good results in terms of accuracy and LODs ($\leq 1\ \mu g \cdot L^{-1}$ for most of the analytes tested), with a precision in the range of 15%, fit-for-purpose for clinical control analysis [1].

The methodology developed could also prove useful for implementing screening protocols based on isotopic analysis. For instance, Cu isotopic analysis could open new possibilities to detect Wilson's disease (WD), a well-known disorder related with Cu metabolism that is difficult to diagnose at young age, precisely when its medical treatment would be more efficient. The potential of a method based on the use of a 257 nm femtosecond (fs) laser ablation (LA) device operating at a high repetition rate (10 000 Hz) coupled to multicollector (MC)-ICPS will be demonstrated in this particular context.

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MULTIPLEXED QUANTIFICATION OF SELECTED PLANT PROTEINS USING LANTHANIDE LABELLED ANTIBODIES AND LA-ICP-MS

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Highly selective and multiplexed quantification of five plant proteins in a complex matrix was achieved with excellent sensitivity. Laser ablation (LA) inductively coupled plasma mass spectrometry (ICP-MS) was utilised to evaluate the protein abundances of pre-selected proteins in isolated thylakoid membranes from plant leaves. Protein antibodies were labelled with lanthanide elements and the relative protein levels were quantified in a multiplexed manner by means of external calibration using matrix-matched calibrants.

Photosynthesis is the primary driver controlling plant growth, converting CO_2 and H_2O into carbohydrates and O_2, using sunlight. The efficiency of photosynthesis can be affected by several environmental factors here among availability of the transition metal co-factors Mn, Fe and Cu that play essential roles in the electron transport processes. Reduced plant availability of Mn, Fe and Cu has been shown to affect the composition of the protein complexes present in the thylakoid membranes, thereby reducing the overall efficiency of photosynthesis resulting in decreased yields and poor plant quality of agricultural crops. Thus, multi-protein analysis of thylakoid membrane proteins is of major relevance when studying nutrient use efficiency in plants and developing improved plant cultivars.

In the present study, thylakoid membranes were isolated from chloroplasts of the model plant *Arabidopsis thaliana* and separated using SDS-PAGE. The separated proteins were blotted onto thin nitrocellulose membranes and immuno-reacted with a mixture of antibodies raised against 5 pre-selected proteins, each labelled with a specific lanthanide via 1,4,7,10-tetraazacyclododecane-1,4,7-trisacetic acid-10- maleimidoethylacetamide (mma-DOTA) conjugation. Lanthanide labelled lysozyme was added to each sample in order to test its function as internal standard by comparing it with the abundance of a house-keeping protein. Individual samples were analysed using LA-ICP-MS and the lanthanide signals were quantified by means of matrix matched calibrants, indirectly indicating the presence of the antigens and the internal standard.

NEW LASER DESORPTION SAMPLE INTRODUCTION TECHNIQUES FOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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New techniques for determination of trace elements in submicroliter sample volumes, substrate-assisted laser desorption (SALD) [1,2] and diode laser thermal vaporization (DLTV) [3] inductively-coupled plasma mass spectrometry (ICP-MS) will be presented.

Samples for SALD ICP-MS are deposited onto a plate made of absorbing substrate, such as poly(ethylene terephthalate) glycol. After drying, samples are desorbed with 213 nm laser at a relatively low laser power density ~10 MW·cm^{-2} in a commercial laser ablation chamber and analyzed with an ICP quadrupole mass spectrometer. Ten laser pulses desorb nearly 99% of sample with spot-to-spot reproducibility below 10%. The limits of detection of Cr, Cu, Co, Fe, Ni, Sn and Zn are in the range of ~10–100 fg. SALD ICP-MS exhibited a constant signal over a wide range of laser power density, the independence of signal on acquisition modes and linear dynamic range over six orders of magnitude. Examples of applications include determination of copper in disulfiram-treated myeloid leukemia U937 cells and in deposits of defensive secretion in dorsal pouches of termite Neocapritermes taracua [4]. The low limits of detection allow using SALD for off-line coupling of microcolumn separations to ICP-MS for speciation analysis; the performance of off-line capillary electrophoresis coupling to SALD ICP-MS is demonstrated on speciation of 1 pg of Cr(III) and Cr(VI).

In the case of DLTV, sample is desorbed from a substrate, such as paper containing a suitable absorber, using a continuous-wave 808 nm diode laser. The laser induces pyrolysis and/or burning of the substrate and the generated aerosol is carried out into the plasma torch. The technique does not require an expensive high-energy pulse laser, which makes it a promising alternative to nebulizers. The limits of detection and reproducibility for selected metals are in the range ~1–10 pg. In addition to a commercial ablation chamber, we also designed a simple tubular chamber. Rapid (1-minute) line scans across a calibration set and unknown samples can be performed with the prototype chamber placed on a common syringe pump serving as the moving stage. The technique was applied to determine lead in whole blood, cobalt in a drug and tin in canned food.

In summary, the both SALD and DLTV ICP-MS are suitable for quantitative elemental analysis of low-volume samples (typically 100–500 nL) and represent an alternative to nebulizers. Advantages are also easy archiving, transportation, prearrangement of calibration sets and high throughput due to minimization of memory effects. In addition, biological samples, such as metalloproteins or metal complexes can be analyzed in other detection modes (MALDI-MS or fluorescence) from the same sample, which can provide supplementary information, e.g. protein mass or identity.

Acknowledgement

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INVESTIGATION OF SULPHUR ISOTOPE FRACTIONATION AND SIGNAL SMOOTHING DURING THE ANALYSIS OF SULPHIDES BY LA-ICP-MS

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A method has been developed to analyse sulphur isotopes by LA-ICP-MS, using a New Wave UP193ss laser ablation system coupled to an Agilent 7700s ICP-MS. The factors influencing the fractionation of sulphur isotopes during analysis were investigated, including laser-induced fractionation, ICP-MS mass bias, and the configuration of the interface tubing between the laser and ICP-MS instruments.

The ICP-MS tuning parameters for the collision cell were optimized using a Xe-He mixture (10% Xe) as a reaction gas to effectively remove the diatomic oxygen interferences on both ^{32}S and ^{34}S isotopes via charge transfer [1], while minimising the instrument mass-bias. With no gas in the collision cell the background on mass 32 contained ~15% O_2, which was effectively removed using a flow of 0.05 $mL\cdot min^{-1}$ of the reaction gas. The mass bias of ~2.5% per amu was corrected using a standard bracketing approach.

The laser parameters of fluence, spots size, and geometry (spots verses line rasters), were investigated in terms of their effects on sulphur isotopic fractionation as well as analytical precision. Laser induced matrix effects between pyrite, pyrrhotite and bornite were also investigated.

The pulsed laser source produces an inherently noisy signal and smoothing this signal is crucial for precise isotopic, and trace element, analyses by LA-ICP-MS. Smoothing primarily occurs by interaction of the sample aerosol with the interface tubing which connects the laser ablation sample cell to the ICP-MS. In this study several different configurations of this tubing and smoothing devices were tested to effectively smooth the signal while maintaining a fast response time and rapid washout between analyses. The technique developed achieves 0.15% precision of the sulphur isotopic ratio in sulphide minerals, with the response time at the start of ablation of < 2 seconds.

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E-a07

EFFECTS OF SMALL AMOUNT OF N_2 ON THE DRIFT IN RELATIVE SENSITIVITIES IN LASER ABLATION ICP-MS FOR GEOLOGICAL AND BIOLOGICAL APPLICATIONS

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Nitrogen, and other diatomic gases, are well-known to increase the efficiency of ionisation of the dry plasma for laser ablation ICP-MS analysis. Addition of small amounts of N_2 to the dry sample carrier gas in Ar-based ICPMS instruments (0.5-5 $mL \cdot min^{-1}$ to the total flow of Ar and He carrier gas of 1.4-1.7 $L \cdot min^{-1}$) increases sensitivity by changing a number of plasma parameters such as electron density, higher temperature, plasma size and shape.

This study discusses the effect of N_2 addition on the time-dependent drift in relative sensitivities of a wide range of elements across the mass spectrum. The instrumentation involved, is a Resonetics RESOlution laser ablation system equipped with a Coherent 193 nm ArF excimer laser (~20 ns pulse width), connected to an Agilent 7500cs ICP-MS. The RESOlusion instrument was equipped with a newly designed large-volume, constant geometry ablation cell S155 by Laurin Technic P/L. The ablation cell is a two volume design, with a small funnel fixed in the centre of the cell in which ablation takes place. The sample holder, 130 mm by 166 mm, is located within the large cell and can hold up to 15 one-inch round samples. The ablation location is centred under the funnel which has a 4.2 mm orifice at the bottom to allow for laser beam access to the sample and aerosol removal to the ICP-MS. The sample holder is moved beneath the funnel into position by a computer-controlled stage. Stage movement reproducibility is better than 4 um, which allows for automated sequences to be programmed. Sample exchanges are followed by cell evacuation to ensure efficient removal of air.

Ablation takes place in an atmosphere of ultra-high purity He which flows over the sample at 350 $mL \cdot min^{-1}$ and exits upwards into the funnel where it is mixed with Ar carrier gas flowing at ~1 $L \cdot min^{-1}$. The flow of He into the cell forms a "curtain" at the funnel’s edge around the ablation spot, resulting in a very short residence time of He in the cell. The Ar/He carrier gas delivers ablated material to the ICP-MS through a signal smoothing device, “the squid”, to smooth signal fluctuations from individual laser pulses. All tubing used is clean nylon 6 or stainless steel. N_2 gas is added to the carrier gas after it exits the ablation cell. The design is characterised by an even response across the cell (rsd < 1.5%) and low-noise signal (rsd < 0.7% at count rates above 50,000 counts).

A significant source of instrumental drift in LA-ICP-MS is the change of sensitivities caused by the small variations in the amount of trace air in the instrumentation, which can be assessed by monitoring the amount of mass 56 (ArO^+). Higher amounts of diatomic gases, common at the start of an analytical session, lead to enhanced sensitivity of light masses relative to heavy masses. The diatomic gases are from outgassing of surfaces of the cell, permeation from the samples, and permeation of ambient air through plastic tubing. During an analytical session, the amount of air usually decreases as the surfaces degas. As for most LA-ICP-MS applications the internal standard elements used for quantification are usually light masses (e.g., Ca, Al, Mg, Si, Fe), and the elements of interest are usually heavy masses, the decreasing amount of air in the system results in the drift of relative sensitivities.

We found that an addition of small amounts of N_2 to the carrier gas stabilises the sensitivity of the light masses, regardless of the amount of trace air in the system, thus eliminating the drift. The amount of N_2 required to buffer the drift depends on the amount of residual air. When the tubing and the ablation cell surfaces were exposed to air for prolonged periods of time, up to 5 $ml \cdot min^{-1}$ of N_2 is required to eliminate the drift at the beginning of the session, whereas in well-flushed systems 1-2 $mL \cdot min^{-1}$ of N_2 is sufficient. Our results also confirm earlier observations that addition of N_2 generally enhances sensitivity of the LA-ICP-MS instrumentation by ~ 30-40% across the mass range, when ablation occurs in pure He, which is mixed with Ar en route to ICP-MS.

USE OF Zr XEROGEL FOR ELEMENTAL ANALYSIS OF CRUDE OIL BY LIBS

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There are a great importance to know the metal composition in crude oil samples and their products, that can help to better understand the mode of interaction among the fraction in the crude oil, its mobility around the mother rock and like quality parameters at refineries. For this reason, this work propose trap crude oil in zirconium xerogel and use it as solid material for quantify heavy metal on pelletized solid samples by laser induced breakdown spectroscopy (LIBS). The highly homogeneous dispersion of the analyte in the solid material obtained with the xerogel formation process leads to a significant improvement in signal repeatability and to an increase in the precision of measurements. The main analytical figures of merit were obtained and some Venezuelan crude oil samples were analyzed to test the applicability of the method.

BETTER IMAGING ANALYSIS BY LA-ICP-MS – AN ANALYST'S TOOLKIT

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LA-ICP-MS has been utilised to create 2-dimensional maps of tissue sections since 2003, [1] although due to the complexities of data reduction this did not become a common technique until around 2005, when the multi-element capabilities of LA-ICP-MS were also fully utilised to measure element distributions in both tissues and SDS-PAGE gels [2]. Imaging has also extended into geological/geochronological analysis [3] and materials analysis [4], amongst others.

Among the key goals of the imaging process are achieving high sample throughput without compromising spatial resolution, and it is often (falsely) believed that to achieve one the other must be sacrificed. This presentation will discuss this and lay to rest some common myths and misunderstandings about what spatial resolution means, its application to imaging by LA-ICP-MS and how to achieve the desired spatial resolution in the minimum time possible.

Another feature of importance in recent publications on bioimaging is the ubiquity of quantitative analysis of tissues, with more recent methods having been established for the determination of elements in tissue [5-7]. Whilst absolute concentrations of elements in tissues prove to be of little practical use in clinical circumstances they are important as a tool for comparison of distinct analyses. In this presentation different approaches to calibration will be compared and contrasted.

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USE OF THE JET INTERFACE FOR IMPROVED PERFORMANCE OF LASER ABLATION WITH SECTOR-FIELD ICP-MS

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The use of a different sample and skimmer cone geometry (Jet Interface) together with a high capacity dry interface pump has been shown to dramatically improve the sensitivity of Sector Field ICP-MS for the analysis of liquid samples [1].

In this presentation we describe the use of the Jet Interface with Sector Field ICP-MS to improve performance for laser ablation applications. With increasing interest in the use of micro sampling by laser ablation in applications such as biological imaging, the small spot sizes required naturally lead to reduced absolute amounts of material ablated. In order to increase the elemental range available to analysts in such applications, improvements in both laser sampling and ICP-MS instrumental sensitivity are required.

In this presentation the use of small spot laser sampling from a robust, high performing 193 nm excimer laser system together with the improved sensitivity from the jet interface on sector field ICP-MS will be shown to significantly improve detection limits in LA-ICP-MS applications.

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RESULTS FROM THE ELEMENTAL ANALYSIS WORKING GROUP(EAWG): IMPROVING FORENSIC GLASS COMPARISON ANALYSIS USING LA-ICP-MS

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Glass is a type of trace evidence often encountered in forensic investigations. When glass gets broken in the course of a crime (e.g. break-and-enter, theft from a car, injury or murder), glass fragments can be transferred to the clothes of the offender. These fragments can be recovered from the clothing and be compared to broken glass found e.g. at the scene of crime. Matching physical and/or chemical properties of recovered glass fragments and the control glass from the crime scene can in this case provide a possible link between a suspect and the scene of crime.

The significance of any associations made as a result of these comparisons is improved when more discriminating analytical methods are used. The comparison of elemental composition between glass samples has proven to enhance the value of an association when one is found, and to reduce false associations between different sources that may result when less discriminating methods, such as refractive index measurement, are used.

With the increasing use of methods of elemental analysis by forensic laboratories, the need for consistent analytical protocols and interpretive criteria has been recognized. The Elemental Analysis Working Group (EAWG), made up of forensic glass examiners and research scientists from North America and Europe under the direction of researchers at Florida International University with funding from the US National Institute of Justice, was formed to develop robust analytical protocols and to assess the accuracy of various criteria used for source comparison.

A total of 24 analysts at 18 laboratories participated in four interlaboratory tests and provided elemental data of glass analyzed by μ-XRF, digestion-ICP-MS, LA-ICP-OES and LA-ICP-MS. All tests were blind to the participants. The first two tests were used to optimize the participants' methods. The second, third and fourth tests contained pairs of samples that were selected to study the capabilities of the techniques to discriminate glass produced in the same manufacturing plant at different time intervals (i.e., manufactured years, months, and weeks apart) and to associate samples that originated from a single source.

This paper will focus on the results from LA-ICP-MS analysis.

E-a12

EFFECT OF LASER WAVELENGTH AND PULSE WIDTH ON LASER PRODUCED AEROSOLS: IMPLICATIONS TO FS-LA-ICP-MS

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Laser parameters, typically wavelength, pulse width, irradiance, repetition rate, pulse energy are the critical parameters which influence the laser ablation process and thereby influence the LA ICP-MS signal. In recent times, femtosecond laser ablation has gained popularity owing to reduction in fractionation related issues and improved analytical performance which can provide matrix-independent sampling.

In this study, we have systematically studied the influence of wavelength, laser pulse width (40 fs – 6 ns) and energy on LA-ICP-MS signal intensity, particle size distribution, particle counts and repeatability using brass and NIST samples. Experiments were performed using single spot ablation mode as well as rastering ablation mode and the elemental ratios (Cu/Zn, U/Th, U/Pb) were monitored to investigate fractionation effect. The results show that lower detection limits are attainable using lower wavelengths in fs-LA-ICP-MS. Initial results also show slight pulse width effects in fs regime, while the effect becomes more pronounced when moving from femtosecond to picosecond and nanosecond regime. Optimum Cu/Zn ratio and RSDs (< 2%) were obtained in 200-400 fs regime for the given experimental conditions (spot size – 100 µm, laser wavelength – 800 nm, energy >100 µJ, Ar flow rate – 1 Lpm). ICP-MS signal from size resolved monodisperse aerosol showed fractionation effect for brass aerosols. Atomic emission spectroscopy (AES) is performed at laser ablation site to understand fs-LA processes and correlate the AES signal with particle size distribution and LA-ICP-MS signal. The results of this study provide a comprehensive picture and additional insight into complex laser ablation mechanisms influenced by critical laser parameters pursuant to quantitative matrix-independent LA-ICP-MS analysis of solids.

DEVELOPMENT AND APPLICATION OF NEW METAL-BASED DIAGNOSIS METHODS

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For cancer detection in clinical diagnosis, many disease-related proteins (biomarker signatures) have to be identified and if possible quantified. But the quantification of biomarkers by immunohistochemical probes is presently not possible and most often only one marker after the other can be analyzed the immune-assay.

Therefore, the analytical tool of choice should be able to detect many biomarkers simultaneously (multiplexing) with high sensitivity and accuracy [1]. ICP-MS is such a powerful tool and first examples are described in literature where hetero elements like phosphorus, sulphur or metals had been used as natural tags for specific protein detection by ICP-MS.

Our strategy is not based on hetero element detection, but on indirect protein detection via tagged antibodies. For this purpose, we have developed multi element tagging strategies of antibodies for simultaneous detection of many different proteins in one single immunoassay by laser ablation (LA-) ICP-MS [2].

Different application of the lanthanide tagged antibodies will be shown, in particular for protein expression profiling using a new multiplex microarray and for immunoimaging using a multiplex immunohistochemical approach for cancer tissue sections.

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NEW STRATEGY FOR THE QUANTITATIVE ANALYSIS OF SOLID MATERIALS BY ON-LINE ISOTOPE DILUTION LASER ABLATION ICP-MS

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been widely investigated as a powerful analytical technique for the direct analysis of different types of solid samples. It offers the spatial resolution, detection limits, and element range required by a wide range of biogeochemical applications [1]. However, LA-ICP-MS suffers from various non-stoichiometric effects through ablation, aerosol transport, ionization, and transmission processes which can induce changes in signal intensity of the analytes, defined as elemental fractionation. Moreover, one of the main limitations in LA-ICP-MS is the quantification of analytical results, which is mainly due to a lack of suitable certified reference materials with a matrix composition similar to that of the sample. Different quantification approaches are currently employed, including external calibration using solid standards (matrix-matched and non matrix-matched strategies) or solution standards. Nevertheless, LA-ICP-MS is still far from being completely accepted as a universal method in analytical techniques.

Isotope dilution mass spectrometry (IDMS) is internationally regarded as an absolute measurement method directly traceable to the International System of Units [2] and it can be employed as a reference calibration technique for trace element determinations using LA-ICP-MS. The application of isotope dilution in LA-ICP-MS can correct for some common fractionation and matrix effects arising during the laser ablation process that cannot be addressed using other calibration procedures. If a homogeneous distribution of both isotope-enriched spike and analyte is achieved, all fractionation effects can be eliminated by the measurement of isotope ratios. Until now two different types of strategies have been applied for the quantification by using LA-ICP-IDMS: solid-spiking and on-line IDMS [3,4]. Promising results were found using such strategies although the requirement of preparing isotopically-enriched pellets and the inability to correct for errors derived from the ablation processes, respectively, limit the applicability of these quantification methodologies.

In this communication, we present a new strategy for the quantification of trace elements in solid materials by on-line isotope dilution LA-ICP-MS. In the proposed methodology, the above-mentioned limitations are overcome and the validity of the approach is demonstrated with the analysis of certified reference materials. The influence of laser operating conditions, isotope equilibration and possible fractionation effects were carefully studied. The application of the methodology to the analysis of glasses, soils and sediments as model samples will be also presented.

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E-b03

RED STONEWARE ANALYSIS TOWARDS AUTHENTICATION OF THE REAL HISTORIC OBJECTS BY SEM-EDS AND LA-ICP MS

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The secret of stoneware production was discovered at c.a. 1707 by an alchemist, Johann Friedrich Böttger and was a significant stage in the development of porcelain in Europe. The first red stoneware followed the forms of Chinese porcelain or European metalwork from this époque. Unfortunately the authenticity of some objects is questioned nowadays, what was the reason for undertaking a detailed chemical analysis of some stoneware collections. The advantages of two methods: Scanning Electron Microscopy equipped with X-ray Spectroscopy (SEM-EDS) followed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP MS) were exploited in analysis of unique stoneware objects from the collection of the Wilanów Palace Museum in Warsaw.

Laser Ablation ICP MS is a micro-destructive method allowing direct sampling from solids and multi-elemental determination with low limits of detection and a high sensitivity. Laser ablation was executed either during direct sampling from the surface of the analyzed objects or during investigation of micro-samples taken from the objects prior to the measurements. A direct laser ablation from objects offered the possibility to obtain not only quantitative information about trace, minor or major elements but also the reconstruction of their depth profiles. Laser ablation (LA) of historic stoneware objects was executed in a standard closed (c.a. 60 cm^3 of intrinsic volume) or a home made open ablation cell (4.5 cm^3) by performing direct ablation from the object or after mechanical sampling.

The advantage of using micro-samples was connected with possibility to analyze sampled material by the two selected instrumental methods and facilitated the final interpretation of the results. The same micro-samples of the red stoneware objects ($n = 60$) were analyzed by SEM-EDS and LA-ICP MS. The reference material 679 Brick Clay in the form of pressed pellet was used to test the accuracy of quantitative elemental results obtained for ceramic objects and was found satisfactory for the both methods used within this work.

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E-b04

CASSITERITE FINGERPRINTING BY LA-ICP-MS

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Cassiterite (SnO_2), the most important ore mineral for tin, is one out of four ore minerals which have been specified as 'conflict minerals' by an U.S. Government Act [1]. This requires all companies that use 'conflict minerals' in their products to conduct due diligence to verify that these minerals did not originate from conflict regions in the Democratic Republic of the Congo where an ongoing violent conflict is fueled by illegal mining, taxation and trade with those minerals. Possible strategies to meet these requirements are 'closed pipe' principles or tagging systems based on written documents which certify the origin of the minerals [2,3]. Direct chemical analyses of minerals, with the aim to confirm the regional sources of the materials, are measures to support those strategies in case of doubt of the available documents. BGR developed a geochemical fingerprint method for cassiterite based on LA-ICP-MS analyses.

The formation of cassiterite deposits is closely linked to the intrusion of granitic magmas and related melts and/or fluids. In cassiterite deposits the tin ore does not appear as a homogenous "rock" but as heterogeneously distributed cassiterite grains (< 1 mm up to several cm in diameter) within a solid matrix of low commercial value (so-called gangue material). The task of the miner or a mineral processing plant is to concentrate the valuable cassiterite grains from the less valuable matrix. Those concentrates which still do contain matrix minerals from several weight percent up to several tenths in weight percent are called 'cassiterite concentrates' and are traded commercially. These concentrates are the samples for which a geochemical fingerprint needs to be carried out. The cassiterite grains are analysed by LA-ICP-MS and exhibit variable trace element concentrations within single grains and to a greater extent between grains of the same origin.

As a consequence the following points have to be taken into account if a cassiterite fingerprint from LA-ICP-MS data shall be deduced. First of all, only cassiterite grains are analysed by LA-ICP-MS, because the ratio between cassiterite and barren gangue within one concentrate is not source specific but the result of the miner's or mineral processing plant's skills in separating cassiterite from barren gangue. Second, the heterogeneity of cassiterite grains within one concentrate must be met by analyzing a sufficient number of single cassiterite grains and third, the applied statistics for the comparison of samples should be based on the distribution of element concentrations.

A prerequisite for the above mentioned fingerprint application of LA-ICP-MS data is that it can be demonstrated that concentrates independently taken from the same cassiterite deposit are all representative for this location. This is done using the Kolmogorov-Smirnov statistic.

The duty of the cassiterite fingerprint is to remove or confirm doubt on the declared origin of a sample. This requires a pair-wise comparison of a sample in question with those of known origin stored in a data base. The Wilcoxon rank sum test is used to calculate a distance measure for this.

The cassiterite concentrate data base at BGR is continuously extended and comprised at the time of this study (October 2012) LA-ICP-MS data for 185 cassiterite concentrates with 8014 analysed single cassiterite grains. Within this data base 43 concentrates exist for which multiple samples from the same location are available.

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A HIGH SPEED INTERFACE FOR COUPLING LASER ABLATION TO ICP-MS

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Laser ablation is now an established technique for the analysis of solids; most of the fundamentals are understood and have been translated into practical analytical protocols for the analysis of a variety of sample types.

Two areas that are becoming increasingly important are imaging, e.g. of biological targets, and the analysis of micron sized particles, e.g. for nuclear forensics or environmental monitoring. The principal limitation for these applications is the response time of current generation laser ablation cells these being typically of the order of a few hundred ms, although reports are beginning to emerge of wash-out times down to 20 ms. To image a 10mm x 10mm target, at 10 μm resolution (which is of the same order as a single cell) requires 1000 x 1000 = 10^6 pixels or 10^5 seconds (28 hours) for signal pulses that are baseline resolved in 100 ms. This may be acceptable for high value research samples, but is much too long for routine or clinical use. A further limitation associated with slow response times is limited signal-to-noise ratio, spreading the total signal ion count over a longer period of time introduces more background count thus elevating the noise level.

Whilst improving the response time has many advantages, it is the case that most current generation mass spectrometers, other than TOFs, are not designed to cope with fast transient signals.

This paper describes recent work in our laboratory that seeks to address these issues in order to produce response times approaching those of in-plasma LA.

EVALUATION OF INTERNAL STANDARDS FOR QUANTITATIVE TISSUE IMAGING

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The strength of LA-ICP-MS lies in the spatially resolved, quantitative analyses of major, minor and trace elements on a µm scale. The technique is therefore widely used for imaging in biology, medicine, material sciences, and geology, yielding new insights into these sciences. However, the quantification in particular in biological and medical applications remains difficult, which is mainly due to two major limitations: (i) external reference materials and suitable internal standards for the quantification are not readily available [1,2], and (ii) processes during the ablation and in the ICP (vaporisation, atomisation and ionisation) are not yet investigated in detail [3-5]. Imaging of tissues does not only reveal element distribution within the samples, but in combination with immunoassays using isotope labelled antibodies, the technique enables the spatially resolved determination of protein expression levels [1-6]. However, a comprehensive analysis ideally includes quantification of the latter.

Therefore, this work investigates suitable internal standards for tissue imaging, which is a prerequisite for quantitative analysis by LA-ICP-MS. The use of carbon as internal standard was not considered due to the results obtained in our laboratory, which showed not only a matrix dependent partitioning of gaseous and particulate carbon species, but also a dependency on carrier gas impurities upon this partitioning [5]. For quantitative tissue analyses possible internal standards should be (i) homogenously distributed within the tissue sections, (ii) of known concentration, and (iii) consider the tissue thickness, since a constant thickness and density of cells cannot be assumed since a constant thickness and density of cells cannot be assumed. Therefore, possible internal standards for tissue imaging were tested, and the partitioning of the corresponding elements in the particulate and gas phase was investigated. Furthermore, possible external standards were evaluated.

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E-b07

MEASURING CALCIUM CONCENTRATIONS OF FLUID INCLUSIONS BY MICROTHERMOMETRY AND LA-ICP-MS

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Fluid inclusions, tiny amounts of liquids and/or vapors trapped in crystals millions of years ago, are an important representative of ancient fluids from e.g. deep hydrothermal systems. Microthermometric measurements of fluid inclusions can provide minimum estimates of p-T conditions during fluid trapping and apparent salinity. Laser ablation inductively coupled plasma mass spectrometry was found a useful method to determine elemental concentrations in these inclusions using the salinity (NaCl equivalent) provided by microthermometry as internal standard [1]. The determination of calcium concentrations in fluid inclusions by LA-ICP-MS suffers from some difficulties. The main calcium isotope ^{40}Ca is only accessible by a dynamic reaction cell (DRC) method [2] due to the interference of ^{40}Ar. The ^{44}Ca isotope suffers from a ^{28}Si^{16}O interference coming from the quartz host, one of the common host minerals for fluid inclusions. The addition of hydrogen to the carrier gas to enhance the sensitivity for other measured elements [3] causes an enhanced background on ^{42}Ca due to hydrogen interferences.

To keep the multi-element capability of the LA-ICP-MS analysis of fluid inclusions and enhanced sensitivities by hydrogen addition, we applied a new microthermometry approach for calcic-sodic brines. The determination of two melting temperatures, i.e. hydrohalite and either ice or halite, defines the position in the H_2O-NaCl-$CaCl_2$ ternary system. A recent mathematical description of this ternary system [4] was applied to obtain absolute sodium and calcium concentrations in fluid inclusions by microthermometry instead of just NaCl equivalent concentrations from last ice-melting temperatures. This approach allows more accurate trace element concentration measurements in calcic-sodic brine fluid inclusion due to a well constrained internal standard. Furthermore, the microthermometry method allows quantification of calcium in fluid inclusions trapped in a calcium containing host like fluorite (CaF_2).

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LA-ICPMS^2: LASER ABLATION SAMPLING WITH COMBINED ICP-Q-MS AND MC-ICP-MS DETECTION FOR SIMULTANEOUS TRACE ELEMENTAL AND ISOTOPE RATIO ANALYSES

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In situ analysis by laser ablation offers significant advantages to users in a range of applications including geochronology but interrogating the sample for all of the information required may not be possible in a single measurement. Laser ablation is a destructive sampling technique and while many samples are large enough to allow for multiple analyses on a range of instruments, geochronologically relevant samples are often so small as to preclude multiple analyses. These samples are often unique and once sampled by laser ablation, they are lost and no further information can be extracted.

In this presentation, a system for the simultaneous isotopic and elemental characterization of zircon ($ZrSiO_4$) is described. A high performance 193 nm excimer laser (Photon Machines Analyte G2) is used to sample ~50 µm diameter pits in the zircon, and the He carrier gas containing the entrained sample is split between ICP-Q-MS and MC-ICP-MS systems. A new high performance ICP-Q-MS system (Thermo Scientific iCAP Q) is used for the quantification of trace elements (both transition metals and rare earth elements) and MC-ICP-MS (Thermo Scientific Neptune Plus) is used for high precision Pb and Hf isotope ratio measurements.

The advantages afforded by such combined, simultaneous isotopic and elemental analyses of growth zones of minerals will be highlighted in the presentation

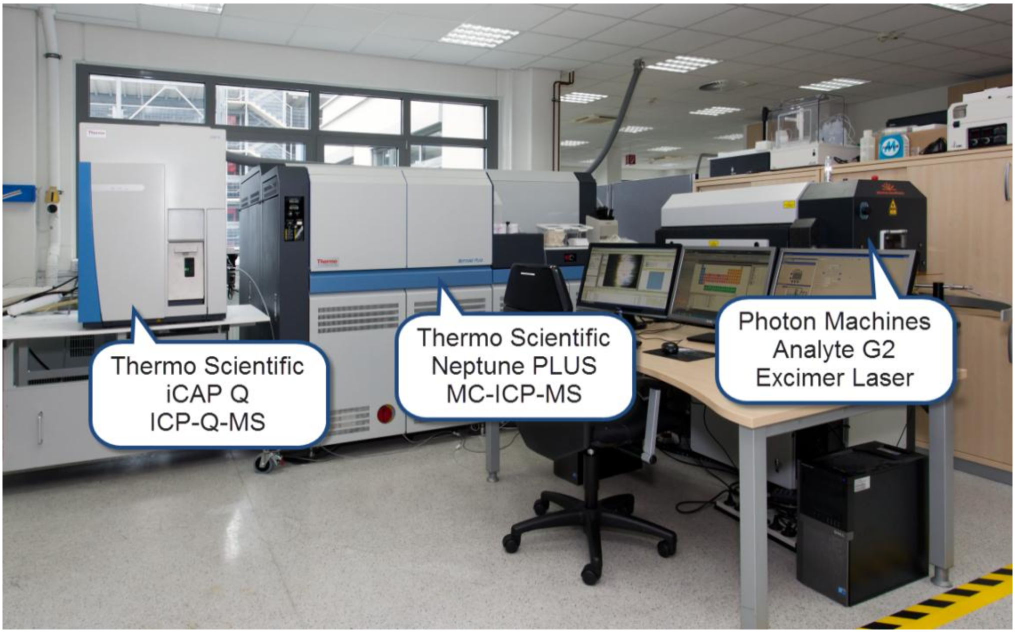

Fig.1. The LA-ICP-MS^2 system as used in this study.

E-b09

QUANTITAVE ANALYSIS OF PHOSPHORYLATES PROTEINS BY LA-ICP-MS

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Reversible protein phosphorylation is deemed to be one of the most important posttranslational modifications which is involved in regulatory protein processes and signal transduction and depends on cell activity and environmental factors. As signal transduction is often impaired in diseases such as cancer or diabetes the analysis and quantification of phosphorylated proteins is an important endeavour [1].

The combination of gel electrophoresis (GE) and laser ablation (LA) offers an easy way for protein separation and subsequent analysis by inductively coupled plasma mass spectrometry (ICP-MS) [2,3]. Transferring the proteins onto a membrane via Western blot prior to LA enables strategies like immunoassay [4]. Because direct detection of phosphorus with ICP-MS is impeded by its high ionisation energy and isobaric polyatomic interferences, the alternative use of metal-containing stains or metal-tagged antibodies for phosphorylated proteins look promising and have been investigated in our research work.

One-dimensional sodium dodecyl sulfate polyacrylamide-gel electrophoresis (SDS-PAGE) was used to separate different phosphorylated and unphosphorylated proteins. After staining either gels or membranes with metal-containing stains and drying, LA-ICP-MS was performed to analyze the protein with LA-ICP-MS. Thus, phosphorylated protein standards down to 1 µg per sample could indirectly be detected and results will be presented which show a good linear correlation between the amount of phosphorylated protein and the measured signal intensity.

To assess the phosphorylation status of defined proteins, antibodies specific for the protein and for its phosphorylated form were used in connection with analysis by LA-ICP-MS. The antibodies were tagged with different metals and applied concomitantly on a multiplex Western blot. In this way we found alterations in the phosphorylation status of the signal transduction proteins ERK1 and c-jun in Caco-2 human colon cells treated with different concentrations of the carcinogen benzo[a]pyrene. First results will be presented.

In summary, the use of metal containing stains in combination with LA-ICP-MS provides a simple and easy way for detection and analysis of phosphorylated proteins. Metal-tagged aniphosphoprotein antibodies can be applied for the analysis of specific phosporylated proteins. The duplex approach by simultaniously uing antibodies to the protein and its phosphorylated form allows to determine the phosphorylation degree. The ICP-MS offers the possibility to monitor different phosphorylation sites by means of additional tagged antibodies in a multiplex strategy.

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E-b10

LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR INVESTIGATIONAL PURPOSES IN THE PHARMACEUTICAL INDUSTRY

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In recent decades laser-induced breakdown spectroscopy (LIBS) has evolved from an obscure technique consigned to the study of fundamental plasma physics to a relatively common technique that has found application in a remarkable number of fields. Most recently, it has garnered intense public and media fascination due to its incorporation in the ChemCam system of the Mars Curiosity Rover. However, despite such increased attention and success as an analytical tool in disciplines ranging from environmental science to forensics, the pharmaceutical industry has been slow to adopt such a novel technique, perhaps owing to its reliance on more traditional and extensively validated techniques such as NIR and Raman. The majority of research utilizing LIBS has been relegated to its use a means of monitoring blend uniformity and coating thickness.

While LIBS has shown great promise in our lab for counterfeit determination and characterization, residual catalyst quantification and tablet surface hardness evaluation it has found its greatest utility as a rapid and simple tool for pharmaceutical foreign matter investigational work. Such an analytical investigation in the pharmaceutical industry is akin to a traditional forensic analysis; the primary objective being to fully characterize and source a foreign matter that could compromise the quality of a product. Such investigations are initiated for a variety of reasons, including contaminants discovered on tablet surfaces, foreign material discovered in bulk batches and unidentified substances on processing equipment. Due to its micro-destructive nature, little-to-no sample preparation, rapid analysis time and elemental specificity, LIBS has evolved into a valuable tool in the Atomic Spectroscopy group at Bristol-Myers Squibb for the preliminary characterization of such unknown foreign matter. Results that demonstrate the applicability of LIBS towards such a critical part of the drug development process will be presented, including its use to identify elemental components and positively source a variety of foreign matter (glass, stainless steel, rust) discovered in pharmaceutical batches or on processing equipment.

TruLine™ - A NOVEL, HIGH-PERFORMANCE SAMPLE CELL FOR LASER ABLATION

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The analytical needs of laser ablation users have spurred the development of large, high-performance ablation cells (> 100 mm x 100 mm working area) in which many samples can be housed at one time. In 2005, New Wave Research supplied the first commercially available large-volume ablation cells to Rio Tinto to improve analytical performance, decrease cost-per-sample and increase throughput and productivity, thereby introducing the world to off-the-shelf two-volume cell technology in the process. New Wave Research's original design has been refined to give both the 100 mm x 100 mm standard ablation cell and the 150 mm x 150 mm large format cell currently volume ablation cells as a standard fit item for all new laser ablation systems.

As a part of ESI's continuing development program for its laser ablation division the ESI scientific and engineering teams developed a brand new ablation cell that takes two-volume design to the next level – the TruLine cell. The TruLine cell exceeds the performance characteristics (wash in/out, signal stability, spatial reproducibility, etc.) of the previous generation of cells in every respect with the added benefit that there is a totally constant and totally linear sample transport geometry from the ablation site to the ICP, thereby eliminating fractionation caused by variation in tube bend radius.

We will present details of all key aspects of the TruLine cell's analytical performance.

E-b12

Sr ISOTOPE RATIOS IN CALCIUM-RICH MATRICES BY (LA)-MC-ICPMS: AN ONGOING CHALLENGE

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Sr isotope ratios have been used for decades as powerful means to address various research questions in the field of analytical ecogeochemistry, amongst others for the investigation of migration, mobility and movement due to its outstanding properties of regional difference and Sr abundance in nature. Beside the application of the traditional, radiogenic ^{87}Sr/^{86}Sr ratio, the variation of the only until recently believed to be stable 88Sr/86Sr ratio has increasingly been used to answer new scientific objectives.

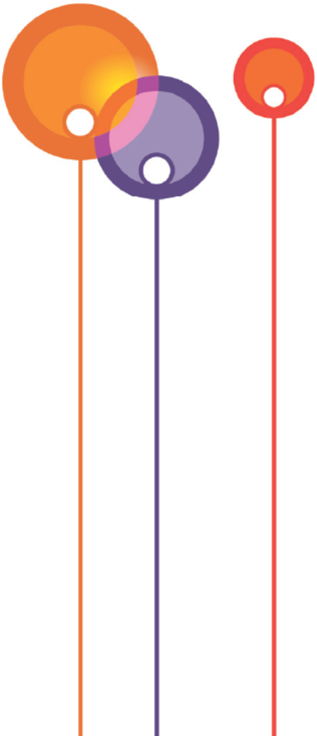
Laser ablation coupled to multiple collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) stands out due to its attributes as a semi-invasive means for the fast and direct investigation of Sr isotope ratios and marginal sample preparation required. However, direct stable Sr isotope ratio measurements in calcium phosphates and carbonates suffer from significant matrix-related interferences such as molecular ions, e.g. $(^{40}\text{Ca-}^{31}\text{P-}^{16}\text{O})^+$, $(^{40}\text{Ar-}^{31}\text{P-}^{16}\text{O})^+$, $(^{43}\text{Ca-}^{44}\text{Ca})^+$ as well as in many cases concomitant atomic ions, e.g. $^{87}\text{Rb}^+$, $^{174}\text{Hf}^{2+}$. Interferences on Sr isotopes analyzed by LA-MC-ICPMS have been subject to numerous debates and discussions among scientists during the last couple of years. Interpretations of generated data are highly diverse regarding the trustworthiness of LA-MC-ICPMS, as corrections are approached in different ways and diverse sources of interferences are presumed. The major part of observations report trends towards higher ^{87}Sr/^{86}Sr ratios for LA-MC-ICPMS compared to solution-nebulisation based MC-ICPMS when analyzing apatite matrices and lower ratios in case of calcium carbonate matrices.

This study is dedicated to the systematic investigation of the effect of interferences and instrumental mass discrimination on Sr isotopic investigations using (LA)-MC-ICPMS and the assessment and validation of possible correction strategies. This includes evaluating the fractionation behaviour of Rb, Sr and Zr, their differences and the potential of the implementation of externally added Zr for mass bias correction during Sr isotope ratio analysis.

The major focus was set on analyzing human tooth samples, fish hard parts and geological carbonates. Laser ablation data and corresponding data established using solution nebulisation based approaches were compared and potential sources of interferences identified by using high resolution ICPMS. The combined corrections of interferences and adequate mass bias correction procedures lead to a better agreement of LA data and data generated by solution-based analysis, though increased uncertainties have to be taken into account. The obtained results are discussed with respect to the total combined uncertainties entailed and along with coexisting approaches for data correction in laser ablation analysis.

section F

Fundamentals and instrumentation



APPLICATION OF MS/MS REACTION CELL IN THE NEWLY DEVELOPED TRIPLE QUADRUPOLE ICP-MS (ICP-QQQ) FOR THE DETERMINATION OF S, P, Si AND Cl IN THE ORGANIC SOLVENTS

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The collision/reaction cell technology in ICP-MS has been the most popular technique for removing polyatomic interferences, since the analytical performance has been greatly improved. There are two types of the cell operation mode; one is the collision mode and the other is the reaction mode. The collision mode has been dominantly used because of its ease of use and the versatility for various applications. In the meantime, it is known that the reaction mode gives the superior interference removal capability in some applications, though it has been limitedly used for only simple and consistent interference problems. It is because the analytical performance of the reaction mode is largely affected by coexisting elements in samples. Reaction mode with MS/MS configuration in the ICP-QQQ overcome such defects in the conventional reaction mode of operation, and result in expanding the use reaction mode to more complex interference problems.

The reaction mode in ICP-QQQ was applied to the measurement of non-metal elements such as S, P, Si and Cl in organic solvent. The theory of operation and analytical results will be discussed.

FP-2

COMMON ANALYTE INTERNAL STANDARDIZATION (CAIS) AS A TOOL FOR MASS DISCRIMINATION CORRECTION IN MULTI-COLLECTOR ICP-MS

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Multi-collector (MC) ICP-MS is a powerful tool to determine isotope ratios. However, the instrumental mass discrimination needs to be adequately corrected for to compensate for the non-uniform sensitivity along the mass range [1].

Common analyte internal standardization (CAIS) is a chemometric technique developed to correct for signal drift and for non-spectral (matrix) effects in ICP-MS [2,3]. It is based on the difference in behavior between the analyte on one hand and an internal reference on the other, and allows correction for the measurement error arising from the variation of instrumental and sample parameters. A linear relationship (K) is assumed between the signal intensities for analyte and internal standard, as can be seen in the equation below. Moreover, even when the relation between the variation of both elements is not linear, this approach still is feasible.

$$\left(\frac{{}^{i}X}{{}^{j}X}\right) = K \cdot \left(\frac{{}^{n}Y}{{}^{m}Y}\right)$$

in which ^{i}X and ^{j}X are the intensities measured for the analyte and ^{n}Y and ^{m}Y those measured for the the internal standard.

To the best of the authors’ knowledge, this approach has not yet been relied on for mass discrimination in MC-ICP-MS, but the approach should also work in this context. Therefore, in the present work, the capabilities and limitations of common analyte internal standardization (CAIS) as a method for correction for mass discrimination were assessed using both a low mass (Boron) and a medium mass (Antimony) element. The merits (in terms of precision and accuracy) will be also compared to those of several commonly used mass bias correction methods [4] (e.g., exponential law, standard bracketing, revised Russell law [5]).

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APPLICATION OF THE DAMAGE-FREE MULTI-GAS PLASMA JET TO SOLUTION ANALYSIS

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In the field of ambient mass spectrometry, plasma ionization sources such as the Flowing Atmospheric–Pressure Afterglow (FAPA) [1] and Low-Temperature Plasma (LTP) [2] probe were developed that physically and electrically isolate the discharge from the ionization region. These techniques help to reduce discharge instabilities, memory effects, and fragmentation that are often found in alternative configuration where samples are passed directly through the discharge. Because it operates with an electrode DC glow discharge, the FAPA source provides relatively high analytical sensitivity at a relatively high discharge gas temperature (>200°C). The LTP source can be applied to many materials including human skin due to the moderate gas temperature (30°C) but the analytical sensitivity is typically lower compared to FAPA because it operates with a dielectric barrier discharge. Therefore, if an electrode glow discharge source with a moderate gas temperature is realized, it will be an effective ionization source for ambient mass spectrometry.

We focused on the damage-free multi-gas plasma jet that was developed in the Okino laboratory (Fig.1). In this plasma source, a glow discharge is established between electrodes and the plasma is pushed into the open atmosphere by the gas flow. This remote-type plasma has almost room temperature and no risk of electrical shock. This makes it readily applicable for living tissue analysis including human skin. In a previous study, we have developed the Atmospheric Plasma Soft Ablation method (APSA) and tried to apply this plasma source for the sampling of materials on the surface without damaging the substrate [3].

In this study, we tried to apply this plasma source as ionization source for ambient mass spectrometry. To demonstrate the analytical capacity, the method was used for direct solution analysis of model compounds. For example, 50 μL acetonitrile was spiked with acetaminophen, placed on a heated glass plate (heated to approx. 100°C), and then directly probed with the He damage-free multi-gas plasma jet from above. Ionized species were introduced into an Orbitrap mass spectrometer (Exactive, Thermo Fisher Scientific, Bremen, Germany) and analyzed. As a result, a calibration curve was obtained with a correlation coefficient of R^2=0.9924. Exemplarily, the signal of the sample and the calibration curve are shown in Fig.2 and Fig.3, respectively. We also investigated the optimal conditions of plasma, solvent, and glass plate temperature and these results will be presented as well.

Fig.1

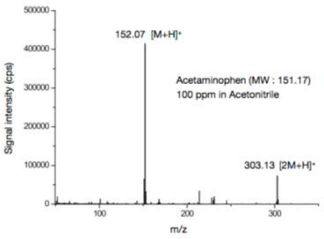

Fig.2

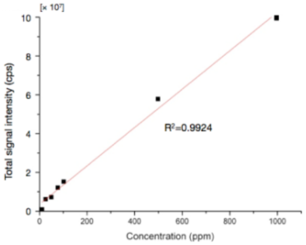

Fig.3

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FP-4

MINI COLISION CELL FOR ICP-MS

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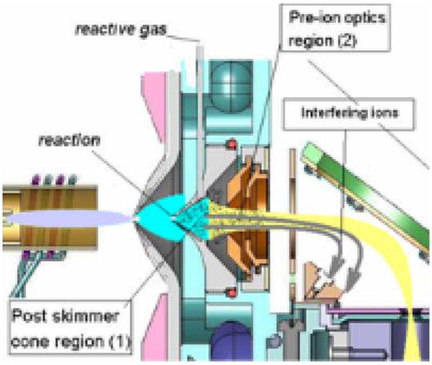
Typically traditional collision/reaction cells are 10-20cm long. The long ion travel distance provides long relative residence time to be spent there by ions. This should allow for low density of used reactive/collision gas, but also requires guiding mechanism for ions to travel towards the cell exit to overcome collision loses. These ion guides known as RF only driven multipole devices - quadrupoles, octopoles, etc are quite complex in tuning and need regular maintenance procedure. The efficiency of interference attenuation using these traditional Reaction Cells is proportional to the reaction rates and density of the reactants used.

Proposed Bruker mini Collision Reaction Cell Technology is effective and inexpensive interference removing device, which doesn't require any maintenance. It doesn't require RF ion guiding mechanism as it operates in free flowing plasma region. The same way as traditional Collision Cells the efficiency of interference attenuation by mini Collision Reaction Cells is proportional to the reaction rates and density of the reactants used. As the density of reactive gas used within Bruker mini Collision Reaction Cell is much higher compared to the traditional cells the efficiency of interference attenuation also is remarkably high. The use of Ion Mirror 3D ion optics behind Bruker mini Collision Reaction Cell, which is capable of Kinetic Energy Discrimination of molecular ions, enhances the interference removal efficiency.

Theoretical efficiency of interference removal by Bruker mini Collision Cell - mini-CCT will be discussed.

Further ion energy optimisation in the ion beam transport has enhanced the Bruker mini-CCT sensitivity in Helium mode dramatically.



NUMERICAL SIMULATION OF DROPLET-PLASMA INTERACTIONS IN AN INDUCTIVELY COUPLED PLASMA

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The sequence of processes in an inductively coupled plasma (ICP) that give rise to an analytical signal include droplet desolvation, vaporization of the remaining particles, production of gas-phase atoms and finally, ionization and excitation. A full understanding of such processes is important since each step will require locally available energy in the plasma to proceed. Droplet-plasma interactions can alter plasma properties surrounding a droplet (or particle), and local cooling [1] and energy transport within the ICP can determine sample loading limits prior to reaching non-robust conditions. Experimental work required for such studies are often complex and involve multiple probes based on optical emission, fluorescence, and light scattering [2]. Alternatively, numerical modeling can be utilized to provide useful information that is crucial in designing novel sample introduction systems and more robust plasma sources with better sample loading capabilities [3].

In our on-going research in this area, a two-dimensional, time-dependent ICP model along with a spray model is used to numerically simulate the thermo-fluid fields inside a NexION 300 ICP source, as shown in Fig. 1. The gas phase is solved using the Eulerian method. A discrete parcel method combined with a stochastic Monte Carlo method is used to solve the spray equation and to determine the outcome of droplet collisions, breakup, and evaporation. Both mono- and poly-disperse groups of droplets are used for this work.

A report on the work in-progress will be presented on the latest results obtained from the numerical simulations of droplet-plasma interactions.

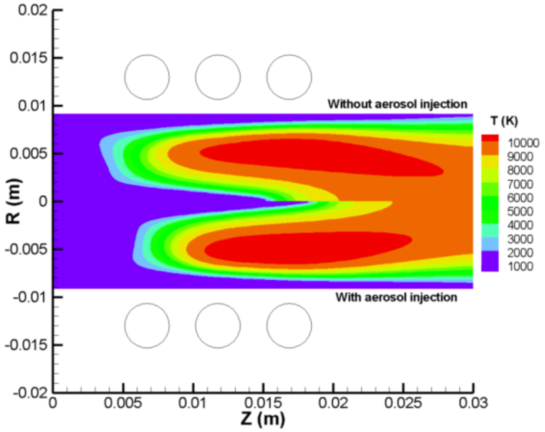

Fig. 1 Example of simulated temperature fields in a typical ICP source before (top half) and after (bottom half) aerosol injection.

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STRATEGY FOR OPTIMIZING LOW-TEMPERATURE PLASMA AMBIENT IONIZATION FOR HIGH-RESOLUTIION MASS SPECTROMETRY: DESIGN OF EXPERIMENTS

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Low-temperature plasma (LTP) probe is an attractive non-thermal plasma source for the direct mass spectrometric analysis of complex samples. Desorption and ionization of analytes is performed at the sample surface in the ambient environment. For example, LTP ionization was used successfully to detect explosives, drugs, and pesticides directly on the target.

In this study, we coupled a home-built LTP probe [1] to a high-resolution mass spectrometer with Orbitrap detector (Exactive HCD) and developed a software-aided method to optimize the overall performance. Specifically, optimization of the ionization source parameters was performed with a design of experiments (DOE) approach. DOE allows screening for and optimization of multiple parameters in an organized fashion. Furthermore, interplay of different parameters can be easily explored and optimized. A variety of parameters such as the geometry of the ion source, positioning of the probe, and operating parameters were optimized for best analyte signal intensities. With this approach, the dynamic range for, e.g., 4-acetamidothiophenol could be extended and the limit of detection was improved by approx. a factor of 10.

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LOW-TEMPERATURE PLASMA AMBIENT DESORPTION/IONIZATION HIGH RESOLUTION MASS SPECTROMETRY: FUNDAMENTAL STUDY OF THE IONIZATION CHARACTERISCTICS COMPARED TO ESI AND APCI

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Low-temperature plasma (LTP) probe high-resolution mass spectrometry (HR-MS) is an attractive method for the direct analysis of complex samples. Desorption and ionization of analytes is performed at the sample surface in the ambient environment. Benefits of the method include high sensitivity and mass accuracy and little to no sample pretreatment. In the present study, the ionization behavior of selected compound families was investigated in LTP-HR-MS and directly compared to electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI).

The home-built LTP probe is based on a design published earlier [2]. In principle, a dielectric barrier discharge is formed in helium by applying a high-voltage, alternating current waveform between two electrodes separated by a glass tube. The LTP was coupled to a high-resolution Orbitrap mass spectrometer. Several model analytes of different compound families were studies. Ionization efficiencies for amides, amines, aldehydes, imides, polycyclic aromatic hydrocarbons (PAHs), ionic species, a nucleoside, and a pharmaceutical were determined and directly compared to ESI and APCI.

In general, LTP can be considered to be a relatively soft ionization method because little fragmentation of model compounds was observed. Further, it was found that LTP shows comparable ionization characteristics to APCI for amides, amines, and aldehydes. A benefit of LTP over conventional methods is the possibility to successfully ionize PAHs and imides. Here, the studied model compounds could be detected by neither APCI nor ESI. LTP can be classified to be an attractive method for the ionization of low molecular weight compounds over a relatively wide polarity range.

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DETECTION OF NANO-SIZED ORGANIC AEROSOLS BY TIME-OF-FLIGHT MASS SPECTROMETRY WITH SOFT PLASMA IONIZATION SOURCE

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Nano-sized organic aerosols, nanoparticles ($d_p < 50$ nm), in the atmosphere have attracted a lot of attention in recent years because of concern about an effect on human health. A new system for gaseous analysis combining a soft plasma ionization (SPI) [1] with a time-of-flight mass spectrometer (TOFMS) has been successfully developed. This system allows for direct on-line measurements of component including nanoparticles in smoke generated during combustion.

Smoke from mosquito coils was used as a simulated sample of organic aerosol. The mass spectra of smoke samples were examined in conjunction with the effect of discharge gas species (air, Ar and He), the discharge gas pressure (1600–2600 Pa) and the discharge current (10–130 mA). We also studied spontaneous emission spectra to investigate the ionization mechanism in the SPI source.

The mass spectrum results indicated that a maximum mass of *m*/*z* 1576 was detectable when the following optima SPI conditions were satisfied: a He gas pressure of 1000 Pa with an air pressure of 1600 Pa and a discharge current of 110 mA. Specific patterns at a peak interval of 74 which corresponds to C_6H_2 were observed in the mass spectrum. In addition, long-chain aliphatic compounds and polycyclic aromatic hydrocarbons (PAH) were observed in the low mass region.

Emission band spectra of N_2 and N_2^+ were observed in the region of between 316 and 471 nm. The emission intensities of the Ar–air and He–air mixture plasmas were approximately two-fold higher compared to those of air. The drastic increases in emission intensity suggest that N_2 is more likely to be excited and ionized in the presence of noble gas.

Considering the results for emission and mass spectra, the ionization mechanism of SPI suggest that the excited N_2 which is efficiently generated by adding noble gas would be facilitated the ionization of component in the sample smoke.

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NOVEL APPROACH TO LIFE SCIENCE APPLICATIONS USING TRIPLE QUAD ICP-MSMS (ICP-QQQ)

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Life science applications are dominated by the use of organic mass spectrometry for a variety of analyses. In recent years however, the emergence of inorganic elemental analysis via ICP-MS within the life sciences has become more widely used especially when metals were involved.

Hyphenated single quad ICP-MS is primarily used in conjunction with chromatographic separation, HPLC (high pressure liquid chromatography), for analysis of proteinaceous molecules. Specifically, metallo-protein analysis and speciation via ICP-MS has proved integral to many research applications within the life science field [1]. As requirements for lower detection limits (DL) arise, both within the fields of organic and inorganic mass spectrometry, it has become increasingly difficult to achieve the required levels of sensitivity, especially for analyses of challenging analytes such as sulfur and phosphorous [2]. The difficulties in achieving these low DL requirements are mainly due to the inability of single quad ICP-MS to reduce the amount of polyatomic interferences to below the desired levels.

Recent introduction of ICP-QQQ enables such analyses that require very low detection limits, achieving accurate, unbiased, interference-free analysis. This capability is attained due to the ability of the ICP-QQQ to allow only the desired mass and its associated polyatomic interference to enter the collision/reaction cell (CRC). The single most important piece of information, “what entered the CRC,” is now available to the analyst. Now, we are able to accurately predict and perform chemical reactions thus removing any associated polyatomic interference to ultimately achieve unbiased analysis.

Here we will present data for the absolute quantitation and analysis of phospho-peptides and small sulfur-containing pharmacological molecules. We have also embarked on a difficult quest of protein quantitation within a single myosin cell. We will further provide preliminary data for the analysis of a single, 100 cell, and 1000 myosin cells.

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PROBLEMS IN THE DETERMINATION OF SELENIUM BY ICP-MS IN BIOLOGICAL MATERIAL

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Selenium is one of the elements playing a key role in the proper course of life in living organisms. In contrast to other bio-elements, it is characterized by a narrow range between its therapeutic and toxic doses and, for this reason, its concentration levels in tissues have to be carefully controlled. Although there are many methods and procedures developed for analytical examination of selenium, its accurate and precise determination in biological materials is still difficult problem, which has not to this day been entirely satisfactorily resolved.

In order to test the reliability of the ICP-MS method in selenium quantification the certified reference materials of blood, serum and hair were analyzed. The samples were digested in a microwave system and the signal were measured with the use of ELAN DRC (Perkin Elmer) apparatus under well-defined conditions. Atomic fluorescence spectrometry with hydride generation system (HG-AFS) was exploited as the reference analytical method.

It was stated that selenium was determined in all tissues examined with serious systematic errors achieving 80% (in case of the serum samples). Furthermore, the curious phenomena was that from among two selenium isotopes considered – 77Se and 82Se – the first one was determined mostly with considerably greater accuracy. It was also proved that the determination errors was caused mainly by ionization effect produced by alkali metals present in a sample assayed. Creation in plasma of some adducts of the same m/z ratios as those of selenium isotopes was also suspected as a source of additive interference effects occurred. For this reason the recovery values can not serve in this case for evaluation of accuracy of analytical results.

The performed examinations revealed a need of particular and careful proceeding with biological samples when ICP-MS is decided to be used for determination of selenium.

EVALUATION OF THE COLLISION REACTION INTERFACE (CRI) FOR ANALYSIS OF SOIL TREATED WITH VINASSE

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Spectral and non-spectral interferences in inductively coupled plasma quadrupole mass spectrometry (ICP-MS) may affect several trace element analyses. To overcome these difficulties, some alternatives based on sample preparation, instrumentation set up and calibration strategies have been used. The use of mathematical correction equations, cool plasma, and collision and/or reaction gases is frequent for correcting polyatomic interferences and the use of matrix matching and internal standards is common to correct for non-spectral interferences in ICP-MS [1].

In this work, the performance of a collision-reaction interface (CRI) for correction of spectral interferences in BCR sequential extracts of samples of soil treated with vinasse (residue from alcohol industry) on As, Cd, Cr, Cu, Pb, V and Zn determinations and strategies of calibration to reduce matrix effects were evaluated. Hydrogen or He gases were introduced through sampler or skimmer cones of the CRI for promoting collisions and reactions. Background equivalent concentrations (BEC) and signal-background ratios (SBR) were the parameters chosen for evaluating CRI performance.

In the evaluation of the CRI, it was found that the flow rates of 60 mL min^{-1} of H_2 and 80 mL min^{-1} of He introduced through the skimmer cone were the ones that showed better efficiency in the correction of interferences and it was necessary to perform matrix matching of analytical calibration solutions and blanks for major inorganic constituents. The use of Sc (to Cu, Zn and V), Rh (to Cd) and Bi (to Pb) as internal standard were necessary for the determinations of V and Pb in acetic acid medium, Cr and Cu in hydroxylamine hydrochloride medium, Cu, Zn and Cd in ammonium acetate medium. The trueness was checked by analysis of a certified reference material (BCR 701).

The sequential extraction of soil samples treated with vinasse showed that the addition this agro industrial residue contributes to the increase of the concentration of Cu in the exchangeable fraction.

Acknowledgement
CAPES, CNPq and FAPESP.

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LOW VOLUME INJECTION AUTOSAMPLER FOR ICP-MS

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The ability to sample and inject decreasingly small samples is ever increasing in science and for ICP-MS. Traditional sample introduction for ICP-MS may consume between 1 and 8 mL of sample depending on the method. This however is problematic when dealing with samples of sub-milliliter size. Dilution of samples is not always an option, especially when analyte concentrations begin at trace levels. Analysts conducting elemental analysis of low volume samples have little choice in autosampling when it comes to injection into an ICP-MS. In this study we present a low volume autosampler capable of injecting microliter sample sizes. Data interpretation and figures of merit are discussed and future applications explored.

A SPECIALIZED DESOLVATING NEBULIZER AND WASHOUT SYSTEM FOR U-SERIES DATING WITH MULTICOLLECTOR ICP-MS

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Multicollector ICP-MS instruments are specialized devices for high-precision isotope ratio measurements. Prepared liquid samples may be concentrated (100 to 1000 μg L^{-1}) in elements of interest; these higher concentrations can cause longer analyte washout times and signal spikes.

This paper with describe a low flow (50 to 200 μL min^{-1}) desolvating nebulizer system with a fast washout capability. This nebulizer system is also coupled with a dedicated autosampler that has a dual-flowing rinse capability to minimize any sample carryover. Wetted parts are composed of fluoropolymers such as PFA (perfluoroalkoxy) for lowest trace metal blanks and maximum chemical resistance.

Optimum operating conditions for the nebulizer system with a contemporary multicollector ICP-MS will be detailed, with data concerning signal enhancement and stability, interference reduction, and washout characteristics for U-series dating measurements.

INTELLIGENT, FULLY AUTOMATED AUTO-DILUTION FOR HIGH THROUGHPUT ICP-Q-MS ANALYSES

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In this presentation a new system for intelligent, fully automated auto-dilution, the PrepFAST from Elemental Scientific Inc., will be described. When used in combination with the new Thermo Scientific ICP-MS, the iCAP Q, sample racks can be simply loaded onto the autosampler and left for analysis. A combination of intelligent software and robust hardware then performs both prescriptive and pre-emptive autodilution of unknown samples – all with an inert, non-contaminating, robust sample flow path that employs syringe pumps and not peristaltic pumps to manipulate sample and diluent. Full integration with the quality control (QC) functions available inside the iCAP Q's Qtegra control software allows for unattended automatic dilution to address a variety of common analytical problems. For example, unknown samples presented for analysis that on analysis initially give recoveries outside defined QC control limits (for example in United States EPA Methods 200.8 and 6020A) are intelligently auto-diluted to allow them to pass the defined QC test.

Through the combination of the PrepFAST autodilution system with the new iCAP Q ICP-MS, significant improvements in efficiency, throughput, and accuracy for metals analysis by ICP-MS can be achieved.

SPECTRAL AND SPATIO-TEMPORAL CHARACTERIZATIONS OF AN ATMOSPHERIC DBD PLASMA JET

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In direct sample analysis domain, atmospheric pressure sources are widely investigated for ambient desorption/ionization mass spectrometry and atmospheric-pressure ionization mass spectrometry [1-4]. Dielectric barrier discharge (DBD) can be used as plasma source to generate low temperature plasmas at atmospheric pressure and create soft ionization [5]. Coupled to mass spectrometry detection, high selectivity and sensitivity can be obtained according to the source efficiency.

A dielectric barrier discharge source has been developed with a future aim of source coupling with a Time Of Flight Mass Spectrometer (TOF-MS) and analytical investigations. This source is composed of a large cylindrical dielectric chamber with a capillary termination. The different electrodes cover both cylindrical chamber and capillary tube, creating a plasma in the cylinder and generating a plasma jet out of the capillary tube. The source is operated in flowing rare gases and is powered by a square alternating voltage (tens of kHz). The study is based on electrical and optical diagnostics. Voltage and current measurements are made using respectively a Tektronix P5210 50MHz Active Differential Probe, a Pearson current monitor 6585 250MHz and a Tektronix TDS7104, 1GHz, 4 channels, 10 GS s^{-1} digital phosphor oscilloscope. Optical measurements are achieved using an Ocean Optics spectrometer (USB4000) operating in the spectral range (350 nm-950 nm) with an optical fiber (spectral range of 300 nm-1100 nm). The spatial and temporal characterizations are obtained by a gated ICCD instrument (Princeton PIMAX-1K-RB, 1024x1024 pixels) allowing the observation of the plasma distribution during variation of the power supply signal.

In this work, the operating gases for the plasma discharge are neon, helium and argon. The parameters of the study will be the maximum voltage and the frequency for the electrical excitation and the gas flow rate. The spatial and temporal distributions and the emission spectra will be presented and discussed according to the previous parameters. The future step will be to optimize the plasma conditions and to couple the dielectric barrier discharge source with the TOF-MS.

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PORTABLE AUTOMATED SEPARATION SYSTEM FOR ROUTINE PURIFICATION AND/OR PRE-CONCENTRATION OF RADIONUCLIDES BASED ON COLUMN CHROMATOGRAPHY

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Because of its high sensibility, short analysis time and relatively easy operation, mass spectrometric methods (i.e. TIMS, ICP-MS or MC-ICP-MS) are nowadays successfully applied for determination of isotopes of uranium, thorium, ^{90}Sr, ^{99}Tc, ^{129}I, ^{226}Ra, ^{241}Am, ^{244}Cm *etc.* in environmental, biosystems and waste samples [1,2]. However, due to formation of possible interferences on the m/z of analyte as well as for pre-concentration purposes, selective separation/purification steps of radionuclides of interest prior to the measurement is also required, that in resent years has grown increasing interest in analytical chemistry [3].

.In this study, a new compact and portable stand-alone equipment permitting automatisation of various separation tasks was developed. The new system allows perform quick and reliable automated separation of selected radionuclides. Since there is no need for permanent manual control of the separation procedures (automatic loading of the sample, washing and stripping solution on the column are controlled via a computer program) the system can be operated overnight. The new system posses the possibility of more variable control for the separation process and could be universally equipped with any prepared or on the market available chromatographic column.

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ION OPTICS FOR ICP-MS

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Before mass separation, a beam of positive ions has to be extracted from the plasma and focused into the mass-analyzer. It is important to separate the ions from UV photons, energetic neutrals and from any solid particles that may have been carried into the instrument from the ICP.

Traditionally, ICP-MS instruments have used transmitting ion lens arrangements for this purpose. Examples include the Einzel lens, the Barrel lens, Omega Lens [1], Shadow Stop [2], Quadrupole Deflecting lens [7], Deflecting Energy Analyzer lens [6,8]. Another approach is to use ion guides (quadrupoles, hexapoles, or octopoles) to guide the ions into mass analyzer along a path away from the trajectory of photons or neutral particles.

The discussion will cover properties of 90 degree reflecting parabolic "Ion Mirror" optics [3], which was designed not only to provide more efficient ion transport into the mass-analyzer but also a very small ‘focused’ ion beam diameter [9]. This results in dramatically higher sensitivity [4,5] when compared to other contemporary quadrupole instrument designs.

Principles and further development of ICP-MS Ion Mirror optics for ion beam formation, focusing properties and ion transport efficiency will be discussed with emphasis on the ion beam control for improved signal intensity required for high performance Laser Ablation and Nano-particles applications.

Required condition criteria for the best ion beam extraction from plasma will also be considered.

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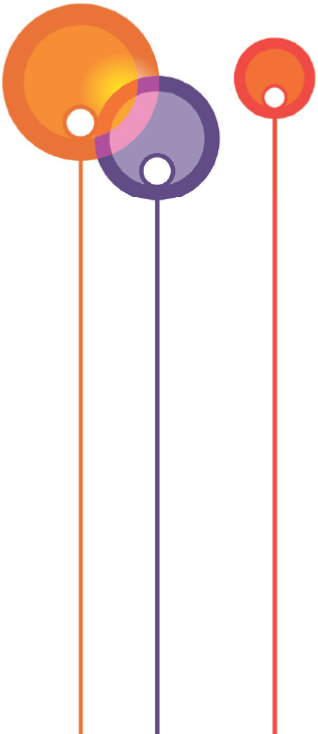
G section

Sample preparation and introduction



GP-1

INTRODUCTION OF A NOVEL SEPARATION METHOD FOR URANIUM AND THORIUM BY SURFACE FUNCTIONALIZED NANOPARTICLES FOR URANIUM AGE DETERMINATION

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Radioactive decay is an important analytical tool for age dating of materials. Age determination of samples containing uranium is carried out by measuring the isotope ratio of ^{234}U and its decay product ^{230}Th. Widely used in the field of geology and life sciences [1], uranium age determination is however more challenging in the field of nuclear safeguards and forensics. Here, samples are relatively young; thus the concentration of ingrown ^{230}Th is very low. Moreover, severe interferences of the high uranium matrix render accurate ^{230}Th determination by inductively coupled plasma mass spectrometry (ICP-MS) impossible [2]. In consequence, it is necessary to perform a separation of thorium from the uranium matrix previous to ICP-MS measurements.

To this moment, U-Th separations have been performed on extraction chromatographic resins [3]. However, this approach is cumbersome and time consuming as it requires (1) conditioning of the column, (2) elution with large amounts of concentrated acids, followed by their evaporation and (3) destruction of organic resin residues.

This work proposes a novel U-Th separation method by surface functionalized nanoparticles. Here, uranium solutions are mixed with silica MCM-41 nanoparticles with strong cationic exchange groups on the particle surface. Under optimized reaction parameters (such as pH, particle mass, time) thorium is extracted selectively, while uranium remains in the supernatant solution. Centrifugation of the suspension and removal of the supernatant liquid leads to the separation into thorium and uranium fraction. Subsequently, the nanoparticles are resuspended in HNO_3, dissolved by HF and both fractions are measured directly by ICP-MS for their U and Th contents.

Consequently, the dispersed particle extraction offers a significant reduction of time and reagent amounts. Moreover, the performance of all sample preparation steps in one vial improves the reproducibility and minimizes the risk of cross-contamination and sample loss. In short, in comparison to established standard procedures this method allows a fast, easy and efficient separation of interfering U and enrichment of Th.

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PASSIVE SAMPLING AS A TOOL FOR TIME-INTEGRATED ANALYSIS OF METAL AND METAL SPECIES IN MARINE WATERS USING ICP-MS-MS

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The monitoring as well as the assessment of the current marine environmental status within the context of the Marine Strategy Framework Directive (MSFD) requires new approaches for theaccurate and sensitive determination of contaminant levels as well as their potential effects.

Contaminants show a great distribution variability in the marine environment due to their diverse chemical characteristics, different input pathways or their continuous remobilization from sediments caused by anthropogenic activities. For that reason it is really difficult to achieve a good environmental status as defined by 11 Descriptors within the Marine Strategy Framework directive (MSFD). Furthermore 33 “historical” pollutants are listed in the Water Framework Directive and only 5 of them are inorganic substances, but there are a lot of new emerging contaminants, which could reach the marine environment for example nanoparticles, rare earth elements, pharmaceuticals and personal care products.

In addition current monitoring approaches are often based on low frequency spot sampling, which provides only snapshot information about the current contamination status, in particular when working in dynamic environments such as the German North Sea.

A solution could be the use of time-integrated sampler’s approaches namely passive and active sampling. In comparison to conventional spot sampling passive sampling allows the detecting of very low concentrations. Because of possibility to sample for a long period passive sampling is more reprehensive than point strategies because of determination of time integrated average contaminant concentrations. In addition passive sampling provides information about bioavailability of target pollutants. Currently the most commonly used passive sampling devices for the time integrated analysis of metals and metal species are DGT (diffusive gradients in thin films), polymeric sheets and Chemcatcher.

This poster contribution provides some first results about optimization of cleaning and extraction methods for selected passive samplers, which are mandatory for the successful future application of the selected devices for the measurement of some metal and metal species. This results will be used for calibrate the samplers and deploy them for monitoring the marine environment. To overcome possible interference problems, which often influences the determination of many environmentally relevant trace elements, ICP-MS-MS has been optimised for the accurate and sensitive determination of the targeted elements.

GP-3

DETERMINATION OF ^{90}Sr AT ULTRATRACE LEVELS USING AN AUTOMATED CHROMATOGRAPHIC SYSTEM COUPLED TO HIGH RESOLUTION ICPMS

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Radionuclide strontium (^{90}Sr) has been released to the environment by global fallout following atmospheric nuclear explosions, by nuclear waste discharges and fallout from nuclear accidents. In environmental monitoring, it is desirable to detect radionuclides at very low levels. This helps to establish a baseline value, which can be used to evaluate the impact of an accidental release of these radionuclides into environment. In addition, the ability to determine their activity at low environmental levels should help to a more accurate estimate of the dose received by the population.

Most analytical procedures and for a large number of samples in radioecological, environmental and oceanographic studies, the determination of ^{90}Sr requires cost-effective, time-consuming and expensive steps. In fact, to achieve low detection limits, large samples are generally required in conjunction with long counting times. The majority of radiochemical separations are designed around the concept of minimising the presence of spectral interferences and improving detection via sample pre-concentration.

A fast and sensitive method for determining ^{90}Sr at trace levels in ground waters and diluted nuclear spent fuel leachates by high resolution Inductively Coupled Plasma Mass Spectrometry (ICPMS) coupled to an automated chromatographic system has been developed. Potential interferences, sensitivity and selectivity issues of the newly developed method will be discussed. Analytical columns packed with a specific stationary phase that selectively enacted the retention of Sr, for its separation from the matrix elements, followed of a concentration step are optimised in order to enhance sensitivity and improve detection limits of the developed chromatographic method.

GP-4

BATCH AND MINIATURIZED COLUMN EXPERIMENTS AS TOOLS FOR THE SAFETY ASSESSMENT OF A CLAY BASED LONG TERM WASTE DISPOSAL SITE FOR HIGH-LEVEL NUCLEAR WASTE

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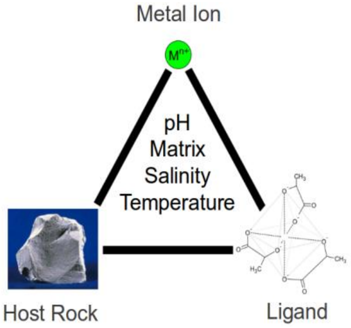
Nowadays, a broad and international consensus has been reached about the final disposal of high-level nuclear waste (HLW) in deep and stable geological formations. A multi-barrier concept consisting of a technical, geotechnical and geological barrier has to ensure an adequate protection of the environment from the stored toxic and radioactive materials over a long period of time. Among the possible host rock materials, such as salt, granite, and clay, the latter is a very promising candidate due to its favorable properties such as a very low hydraulic conductivity, a high sorption capability, an efficient filtration ability for colloids and larger molecules, small solubility of the clay components in water, and a high chemical buffer capacity. In order to guarantee the sufficient retardation of radionuclides along their path of migration in the case of an intrusion of water caused by an incident, the interactions with the host rock material leading to sorption and mobilization processes have to be examined. Batch experiments and miniaturized column experiments both can be valuable tools for this purpose.

Opalinus clay consisting of a mixture of different clay minerals has been chosen as reference material. Apart from uranium, europium and gadolinium as homologues of the actinides americium and curium represent the metal ions leaching from the stored waste. These metal ions can interact with naturally occurring ligands either being of organic (e.g. lactate, salicylate) or inorganic (e.g. borate) origin. In this ternary system, the metal speciation, formation behavior and stability of coordination complexes, sorption onto clay and formation of precipitates or colloids is examined.

For the batch experiments small amounts of homogenized clay are equilibrated under the conditions of interest as given in Fig. 1. Once equilibrium has been reached, the remaining amount of e.g. the metal ion of interest is analyzed using inductively coupled plasma mass spectrometry (ICP-MS). This set of experiments with an excess of water acting upon a small amount of clay represents a case of average in a possible storage chamber with subsequent formation of clay suspension. In contrast, the miniaturized column experiments simulate the processes that occur during a pressure driven migration of metal ions through intact host rock. They are performed using home-made HPLC columns with compacted clay as stationary phase and UV-Vis- as well as ICP-MS-detection. Besides these methods, complexes are also characterized by nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC).



Acknowledgement

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METAL MOBILITY IN CLAY - FROM BATCH EXPERIMENTS TO MINIATURISED COLUMN EXPERIMENTS WITH COMPACTED CLAY

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Nowadays, there is a broad scientific consensus on the technical merits of the disposal of high-level nuclear waste (HLW) in deep and stable geological clay formations. For the long-term disposal of radioactive waste, detailed information about geochemical behavior of radioactive and toxic metal ions under environmental conditions is necessary.

In our project europium, gadolinium (homologues of americium and curium) and uranium were used and their sorption and desorption behaviour onto Opalinus clay was studied [1]. Natural organic matter (NOM) can play an important role in the immobilisation or mobilisation of metal ions due to complexation and colloid formation. This complexation could interfere the sorption of metal ions onto clay. In addition to humic acid (HA) we used other natural appearing organics in Opalinus clay like lactate, formate or propionate [2]. Therefore, we investigated the complexation behaviour of the metal ions with NOM as well as the influence of present NOM on the metal sorption onto clay [3].

Capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry (CE-ICP-MS) has been used to study the complexation behaviour of Eu(III), Gd(III) and U(VI) with HA. The influences of metal concentration as well as the presence of competing cations from clay dissolution [4] as well as cations from clay porewater on the complexation behaviour was analysed [5]. For the sorption/desorption behaviour common batch experiments with mineral suspensions are performed, and in comparison a miniaturised column setup with compressed clay was used to study the influence of NOM on the metal mobility in compact Opalinus clay.

Acknowledgement

The authors thank the BMWi for financial support (grant no. 02E9683, 02E10196 and 02E10991).

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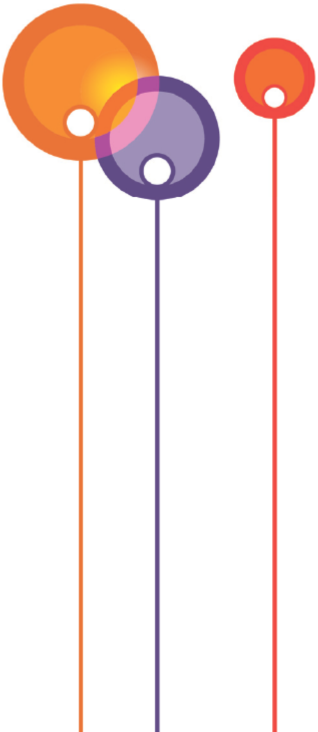
H section

Applications of plasma spectrometry



INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) LINKED IMMUNOASSAY USING GOLD NANOPARTICLES (AUNPS) AS ELEMENT TAG FOR CHLORAMPHENICOL DETECTION

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This work demonstrates the feasibility for trace analysis of chloramphenicol using a novel immunoassay by coupling competitive measurement of chloramphenicol (CAP) to ICP-MS by use of CAP labeled with AuNPs. Polyclonal rabbit anti-mouse immunoglobulins (anti-mouse IgG) were pre-coated on the 96 well polystyrene microplate solid support to allow the retention of mouse monoclonal to chloramphenicol antibody (MAb-anti-CAP) on the pates. Samples containing CAP as an antigen premixed with CAP-BSA protein labeled with AuNPs as an immunogenic tag were added to the MAb-anti-CAP bound solid support, physically separated from non-reacting molecules. The AuNPs were measured by ICP-MS to indirectly determine the CAP concentration in the samples. For 10 nm AuNPs, the optimal condition for CAP-BSA protein conjugation was pH 9.5 and 120 $mg \cdot L^{-1}$ of CAP-BSA protein. The detection limit, linearity range, and precision (intra-assay, inter-assay) were 4.52 $ng \cdot mL^{-1}$, 0-20 $ng \cdot mL^{-1}$, and less than 20%, respectively.

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As QUANTIFICATION IN HEAVY DISTILLATES BY ICP-MS

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A large number of papers is available for the quantification of arsenic in petroleum distillates [1-4], generally obtained by AAS.

We report the determination of As in petroleum heavy distillates (400-550°C) that was accomplished by Agilent ICP-MS 7500ce (reaction cell).

The preparation of the samples consisted of an acidic digestion in a microwave oven (closed vessels, temperature controlled), similar to the standard procedure UOP [4] but optimized.

It was possible to use a very low amount of acids so that both contamination and matrix interferences for instrumentation were at a minimum. After digestion, the acidic solutions were concentrated to get further better sensitivity. A simpler extraction was also tried in the meantime.

Two different As contents (0.28 and 0.07 $ng \cdot mg^{-1}$) in distillates were tested for repeatability and the relative standard deviations or coefficient of variation (CVs) were under 10%.

The instrumentation was set both in normal conditions and with the use of reaction gases (He and H_2): no interferences were found in our case.

The limit of quantification of the method is 15 $ng \cdot g^{-1}$ in the operating conditions while the instrumental limit of detection is 2-3 $ng \cdot L^{-1}$.

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ULTRA-TRACE ANALYSIS OF GOLD AND PLATINUM GROUP ELEMENTS IN GEOLOGICAL SAMPLES USING ICP-MS WITH MIXED GASES

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The use of mixed gases and addition of auxiliary gases to improve sensitivity for some elements in ICP-MS analysis, particularly in dry plasma conditions such as GC-ICP-MS and Laser Ablation ICP-MS has been known for some time [1]. Addition of carbon for example is known to improve sensitivity for As and Se [2]. More recently, the addition of nitrogen to the carrier gas flow has been shown to improve the sensitivity by an order of magnitude or more without compromising plasma robustness or matrix tolerance [3] for a wide range of elements.

In this work, the use of auxiliary gas addition to the carrier gas was studied and optimized in order to reduce the method detection limits for gold and the platinum group elements in geological samples. Continuing increases in the value of gold have lead to the need to detect lower and lower levels in geological survey and ore samples. When digested, these samples are high in total dissolved solids and contain very high concentrations of aqua regia, resulting in the need for significant dilution before analysis by ICP-MS. The result is the need for sub-ppt detection limits. Preliminary work in our laboratory has demonstrated detection limits for Au and Pt in dilute aqua regia at less than 1 ppt (Fig.1 a, b). Additional optimization is expected to further reduce the method detection limits.

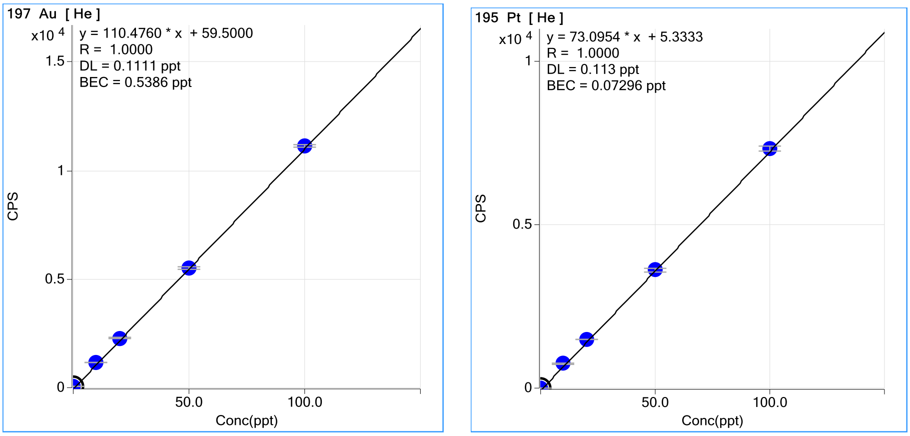

Fig.1 (a left, b right). Calibration curves for Au(a) and Pt(b) in dilute aqua regia using nitrogen addition to argon carrier gas and helium collision mode. Detection limits are calculated to be 0.11 ppt for both. BEC is sub ppt in both cases.

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HP-4

QUANTIFICATION OF CRITICAL ELEMENTS IN FERRO-CHROME SILICON/LEAD TETROXIDE BASED DELAY CHARGE ELEMENTS FROM MILLISECOND ELECTRIC DETONATORS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Ferrochrome silicon alloys (Fe_xSiCr_y) and lead tetroxide (Pb_3O_4) are commonly used in pyrotechnics for the production of delay charge elements in millisecond electric detonators (DEMs). The ferrochrome silicon alloy acts as a fuel and lead tetroxide is added as the oxidizing agent. Generally, a ferrochrome silicon alloy is made by the fusion of quartz with high-carbon ferrochrome alloy where the silicate takes the carbon source from the high-carbon ferrochrome alloy resulting in elemental silicon formation and evolving carbon dioxide. The minor elements presented in the DEM are common impurities from quartz (Mg, Al, Ti and Ca). The ignition delay of DEMs is depending on the purity of the raw materials and the molar ratio between the major elements. Therefore a very accurate and efficient analytical method is required.

Due to the lack of reference material, six different concentrations of lead tetroxide powder were mixed with a ferrochrome silicon alloy with known certified composition. The sieved powders (between 0.8 and 0.022 mm particle size) were homogenized by 3 mixing sessions according to the industrial production process. The concentrations of lead tetroxide in the DEM samples were ranging from 30 till 70 weight %.

Microwave acid digestion was chosen for decomposing the samples. To cover the differences in homogeneity of the sample, 0.2 g was weight in a polytetrafluoroethylene-per-fluoroalkyl vinyl ether copolymer (PFA/Teflon) beaker and the powders were digested each 3 times (n=3). In a first stage the variability in acid concentrations was tested on the efficiency of mineralization. Evaluation was done by gravimetrical measurement of residuals on a filter paper (Whatman, 8 µm). A mixture of 2.5 mL hydrofluoric acid (48%), 5.5 mL nitric acid (67%) and 2 mL hydrogen peroxide (30%), has been found to give the highest yield. After pre-digesting for 60 minutes at room temperature, the samples were microwave digested under common conditions (Berghof SW-4). All solutions were prepared in pre-cleaned polypropylene flasks [1].

The measurement by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was performed on a Varian instrument equipped with a single quadrupole mass spectrometer but without collision cell. The aerosol generation was done by use of a PFA concentric micro-nebulizer due to its resistance to hydrofluoric acid. Internal standardization in ICP-MS analysis is convenient because it is expected that the matrix will influence the efficiency of nebulization and change the plasma [2]. To compensate these changes, internal standards (^{9}Be and ^{193}Ir) were added into the solutions. These internal standards might correct the aerosol formations and transport into the plasma, moreover they are on the outer borders of the isotope masses of interest and are not presented in the samples. The selected isotopes for the measurement of major elements were ^{29}Si, ^{52}Cr, ^{56}Fe and ^{208}Pb. For the minor elements ^{24}Mg, ^{27}Al, ^{46}Ca and ^{49}Ti isotopes were selected.

The overall recoveries for the major elements were ranging from 87.1 till 117.0%. A plot of the measured concentration of the major elements versus the real concentration of the lead tetroxide weight concentration resulted in linear regression values (R^2) ranging from 0.9706 (^{208}Pb) till 0.9933 (^{52}Cr). For the minor elements similar data was obtained.

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DETERMINATION OF Hg IN ENVIRONMENTAL WATERS USING THE BRUKER AURORA M90 IN HIGH SENSITIVITY MODE

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On 23 October 2000, the “Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy” or, in short, the EU Water Framework Directive was finally adopted. Mercury and its compounds are part of this directive. Environmental quality standards (EQS) define the maximum allowable concentration (MAC) for primary substances and other pollutants.

The following procedure outlines a simple yet sensitive method for the direct analysis of Hg in environmental waters and demonstrates the capacity of the aurora M90 ICP-MS for direct Hg determination in water samples without any accessory.

USING ICP-MS FOR RESEARCH OF HEMODIALYSIS PROCEDURE ON STATE OF BLOOD IN PATIENTS WITH HEPATITIS C WHO ARE ON REPLACEMENT RENAL THERAPY

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Various kinds of viral hepatitis with a parenteral transmission mechanism are still a global problem for healthcare. Parenteral viral hepatitis study is especially important for the patients having final stage of renal disease who are undergoing replacement therapy procedure (hemodialysis) at the same time.

Assessment of the course of HCV infection in patients on hemodialysis using standard medical indicators is limited. Additional indicators are required and this research is an attempt of using micro elemental concentration information as a useful additional diagnosis indicator. ICP-MS mass-spectrometry technique, particularly available at the lab Bruker ICP-MS**,** has been suggested to evaluate effectiveness of this new approach as a low detection limits would be required. Analysis of microelements has been studied using Bruker ICP-MS which is renowned for its excellent sensitivity, robust plasma and interface.

The purpose of our study was to define the content of microelements and the main cytogenetic values in lymphocyte culture in periphery blood for stage 5 chronic renal disease patients. The study included both of patients groups - infected and not infected by hepatitis C. Lymphocyte cultivation and chromosome specimen preparation was carried out by a standard semi-micro method [Hungerford D.A., 1965].

We have examined samples from the patients having stage 5 chronic renal disease. Those patients were undergoing scheduled hemodialysis procedure – CRD 5D (44 samples). Also we examined samples from patients with stage 5 chronic renal disease. The later patients were undergoing scheduled hemodialysis procedure and at the same time they were having chronic hepatitis C (replicative phase) - CRD 5D + CHC (18 samples). All tests have been done before and after the hemodialysis procedure.

After dialysis, according to ICP-MS analysis, all patients had decreased concentration of barium, phosphorus, potassium, and boron, while initially these values were pretty high. In patients who had hepatitis C the concentration of aluminum, sodium, magnesium, and zinc have fallen to normal level after the dialysis. The only iron and cesium concentration were different between the groups.

It has been confirmed by this study that hemodialysis procedures bias the clinical course of chronic hepatitis C in stage 5 chronic renal disease patients. The patients who were on the replacement therapy the viral effect could be dependent on the genetics.

DIRECT ANALYSIS OF Cr, Ni, Pb AND V IN ETHANOL FUEL BY MICROWAVE-INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY

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The presence of metals in fuels may reduce the engine performance and/or deteriorate the quality of the fuel by catalyzing reactions of oxidative decomposition [1]. In the case of ethanol fuel—from sugar cane, some potentially toxic elements can be naturally present as a result of the soil composition where the plant was grown. Alternatively, these elements can be introduced into the fuel during its production, storage and/or transport. Thus, after fuel combustion, these elements can significantly increase air pollution. In this work, the direct analysis of ethanol fuel was evaluated for the determination of Cr, Ni, Pb and V using microwave-induced plasma optical emission spectrometry (MIP OES). All measurements were carried out with the Agilent 4100 MP-AES. This instrument is based on a nitrogen plasma which is generated by magnetically coupled microwave energy and is operated at 1.0 kW of applied power. Nebulizer pressure and viewing position were automatically optimized for each analyte, and a 5 s signal integration time was used in all cases. An external gas control module (EGCM) was used to inject air into the plasma and prevent carbon deposition on the torch or the optical components. This device also contributes to maintain the plasma stability and reduce background emission. Ethanol fuel samples (hydrated ethanol) were obtained in local gas stations of São Carlos, SP, Brazil. These samples were diluted 10-fold in 1% v/v HNO3. Standard reference solutions used in the external calibration method were prepared by diluting adequate volumes of inorganic standard solutions of Cr, Ni, Pb or V in 1% v/v HNO_3. Ethanol was also added to each standard reference solution to a final concentration of 10% v/v. The limits of detection (LOD) varied from 0.3 to 40 $\mu g \cdot L^{-1}$, and are compatible with legislation requirements based on environmental impact and engine performance. The MIP OES is especially advantageous for refractory elements such as Cr and V. In this case, the higher temperatures reached in the plasma allow for lower LODs, without any addition of special gases as would be the case for FAAS determinations with nitrous oxide-acetylene flame [2]. To check the method accuracy, spike studies were performed with at least two different concentrations of each analyte. Recoveries between 84 and 108% were obtained for all samples. These results indicate that MIP is probably less prone to matrix effects commonly caused by organic compounds and concomitant elements such as Na, K and Fe.

Acknowledgments

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DEVELOPMENT OF METHOD FOR TRACE ELEMENTS SCREENING IN NEWBORN BABIES BLOOD BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Trace elements determination in blood is of primary importance to evaluate individual exposition, particularly in children who are more sensitive than adults to trace elements health negative effects. Dried blood spots (DBS) are routinely collected from newborn babies' heel for performing screening of inborn errors of metabolism and other disorders. This minimally invasive method for collecting blood samples can be used to detect a large variety of other markers including trace elements exposition. ICP MS has become powerful tool for multi-element determination in biological fluids. However different approaches including the choice of the filter membrane supporting the DBS and the analytical procedure can be distinguished. The aim of the work presented here was therefor to develop a method for screening trace elements (Sb, As, Be, Bi, Cd, Co, Cu, Pb, Mo, Mn, Hg, Ni, Se, Sn, Tl, V and Zn) that could be conducted in routine surveillance for newborn babies.

The presentation describes the choice of the methodological approach aiming at (1) optimizing the recovery rates of the different elements investigated, (2) minimizing the contribution of the filter membrane to the background signal and (3) fitting with the low samples uptake. The best results were obtained for acid mineralization of the DBS supported on hydrophilic PVDF filter membranes. Validation data, including linearity, reproducibility, recovery levels, quantification limits and comparison of the results obtained by our method with those obtained after liquid blood sampling will be presented.

HP-9

INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS OF PHYSICOCHEMICAL NANOMETROLOGY

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Nanomaterials (NM) open huge prospects for innovation in different fields such as medicine, electronics, cosmetics and materials [1]. However, their uses raise questions about possible risks to the environment and humans [2]. The development of suitable protocols for the physicochemical characterization (size distribution, shape and chemical composition) of such materials is a fundamental issue for coming years [3]. To meet the needs of various industrial producing or using NM, UT2A has developed new analytical approaches dedicated to nanometrology.

According to the needs expressed by industry, two approaches were considered. The first one is focused on the determination of the size distribution of nano-scale particles using Dynamic Light Scattering detector (DLS) and a splitting system (by size and weight) such as Asymmetric Flow Field Flow Fractionation hyphenated with a Multi Angle Laser Light Scattering detector (A4F-MALLS). The second approach is based on a comprehensive physicochemical characterization made by the combination of A4F-MALLS with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

The first part of the work has consisted in the size control of Metallic NanoParticles (MNP) and Carbon NanoTubes (NTC) respectively used in paints and computer science. The main difficulty resided in the sample preparation protocol. To do so, the nature and concentration of the surfactant and the mechanical means were considered. Subsequently, the work was focused on the optimization of industrial processes. The development of a new method for monitoring aeronautical degreasing baths containing surfactant micelles (nanoscale entities) by DLS improved their managements and significantly reduced costs and the volume of effluents. An industrial process of cheese manufacturing has also been optimized by evaluating the influences of the temperature and the homogenization step on the final cheese texture by analyzing the size distribution of milk creams.

The second part of the work was focused on the development of A4F-MALLS-ICP/MS for the physicochemical characterization of NM in sunscreens. The protocol of extraction of NM (solvent, centrifugation, dispersion, etc.) and the optimization of the separation step were implemented (mobile phase composition, fractionation step, etc.). The same hyphenated system was also used to evaluate the physicochemical characteristics of environmental colloids and their interactions with various metallic pollutants. The analysis of leachates have demonstrated that most of metals (Cu, Zn, Ni, As, Cd) investigated were dissolved instead between 20 and 90% of Al, Fe and Pb were associated with particles from 50 to 350 nm.

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COGNAC ANALYSIS USING THE AGILENT 4100 MICROWAVE PLASMA-ATOMIC EMISSION SPECTROMETER

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Cognac, famous all over the world for hundreds of years, is a brandy produced in the French region near the town of Cognac. Quality control is important throughout the wine making a preserving process to assure the product is of the highest quality. For this purpose, elemental analysis in cognac has been performed using the innovative Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (MP-AES). This new technology runs on air, eliminating the need for flammable or expensive gases. The 4100 MP-AES is able to perform fast multi-element analyses with the lowest running costs and better analytical performances compared to flame atomic absorption spectroscopy (FAAS).

This paper presents the Cognac analysis results obtained using the Agilent 4100 MP-AES. Al, Ca, Cd, Cu, Fe, K, Na, Pb and Zn were measured in Cognac samples containing 40% ethanol without any preparation prior to analysis. Detection limits down to ppb levels and good long-term stability were achieved.

CHARACTERISATION OF NANOPARTICLES RELEASE FROM COMMERCIAL PRODUCTS BY A4F-ICP-MS

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In the last years, research on nanomaterials (NMs) is gaining an increasing relevance in several fields, and their applications are growing exponentially, ranging from materials with enhanced surface properties to health care and environmental pollution remediation. However, the need of information on risk implications on NMs is arising as recognized by many international authorities, such as the OECD and the European Commission, and regulatory initiatives are yet ongoing. Although a lot of efforts have been made to find proper analytical methods to detect and characterize NMs and NM-based products, data are still far from being exhaustive, especially when dealing with real samples, due to the lack of standardized and validated protocols. In this framework the hyphenated techniques coupling separation (i.e. asymmetric flow field flow fractionation – A4F) and detection methods (i.e. inductively coupled plasma mass spectrometry-ICPMS) are very promising, and many studies dealing with their improvement are currently ongoing [1].

This work aims to characterize the release of NM from commercial products by developing an on-line coupled A4F-ICP-MS method suitable for the detection of a multi-size/multi-element mixture of metal based-nanoparticles. The instrumental method was optimized by performing preliminary tests on gold, silver and palladium nanoparticles [2]. It was then applied to real samples (commercial products) undergone simulated environmental ageing conditions, such as daylight (UV lamp) and rain (bath of mild acid solution). The comparison of the results obtained with A4F-ICP-MS technique with those collected by other complementary techniques (e.g. dynamic light scattering analysis, transmission electron microscopy, stand-alone ICP-MS) will allow to further investigate the behaviour of released nanomaterials. Furthermore, it suggests indeed the potential application of AF4-ICP-MS into the regulatory setting, as they might allow to achieve information in line with the Recommendation for the Definition of Nanomaterials published by the European Commission [3].

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HP-12

URINARY CHROMIUM AND NICKEL IN THE UK SURFACE ENGINEERING INDUSTRY

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A three-year project from 2008-2011 was undertaken by HSE and HSL in collaboration with the Surface Engineering Association to investigate the use and control of carcinogens in the UK surface engineering industry. The elements of concern within the surface finishers work are hexavalent chromium, nickel and cadmium. Hexavalent chromium and nickel compounds are defined as asthmagens and cadmium; hexavalent chromium and nickel are proven human carcinogens as defined by the International Agency for Research on Cancer. Occupational hygiene visits were made to 51 companies across the UK where working practices and exposure controls were assessed and quantitative exposure was determined using biological monitoring and wipe/air samples.

More than 3000 urine samples were collected and analysed for elemental analysis. Following an initial visit, repeat biological monitoring work at 6 and 12 months were undertaken as well as revisits to the sites if there were any results of concern from the initial visit. All urine analysis was carried out using ICP-MS in normal mode for urinary cadmium and nickel and in collision cell mode for urinary chromium. The 90th percentiles urinary concentrations for cadmium, chromium and nickel were 8.1, 8.6 and 23.9 $\mu\text{mol}\cdot\text{mol}^{-1}$ creatinine. The air, hand washings and wipe sample results will also be described. Repeat biological monitoring work at 6 and 12 months showed a 25-35% reduction in exposure for nickel and chromium. Generally, correlations between urinary results and air samples or hand washings/wipe sample were moderate however a strong correlation (r=0.71) was observed for hand wash results and urinary chromium in chrome platers (N=79).

The results show that generally there was good control but that there are areas where control could be improved. Exposure controls were not always in accordance with guidance, maintenance of controls was not always adequate. Improvements were seen in biological monitoring results and on site revisits following results from initial visit.

HP-13

INVESTIGATION OF SALIVA AS AN ALTERNATIVE TO BLOOD SAMPLES FOR THE BIOLOGICAL MONITORING OF INORGANIC LEAD

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Although environmental blood lead levels have dropped dramatically there are still concerns that lead exposure is a contributor to intellectual impairment in children and a contributing factor for other diseases. Blood is the preferred matrix for inorganic lead exposure however the invasive nature of blood sampling and many other factors make blood far from ideal for environmental public health sampling. Salivary lead is a potential non-invasive alternative although literature reports are conflicting.

This study aims to collect paired samples of blood and saliva from workers occupationally exposed to inorganic lead.

Twenty-two workers provided a saliva sample, using a Statsure sampling device, at the same time as a routine blood sample (provided under the Control of Lead at Work Regulations, 2002 as amended).

Prior to analysis, each sampling device was vortexed for 10 seconds. An aliquot of sample (0.5 mL of the saliva/buffer mixture) was hydrolysed for 1 hour at $100^{\circ}C$ using 0.5 mL concentrated nitric acid. After cooling, the mixture was diluted ten-fold in diluent (1% nitric acid, 10 $\mu g \cdot L^{-1}$ Pt internal standard), resulting in an overall dilution of saliva of 1 in 40. Spiked saliva quality control material (2 $\mu g \cdot L^{-1}$) was prepared and an aliquot extracted through a sampling device prior to analysis.

Analysis was by inductively-coupled-plasma mass spectrometry (ICP-MS, Thermo X7 Series 2) in normal mode measuring ^{208}Pb and using ^{195}Pt as an internal standard.

Recovery of lead from spiked saliva using the sampling device varied from 102% (2 $\mu g \cdot L^{-1}$ spike) to 105% (20 $\mu g \cdot L^{-1}$ spike). Quality control material showed intra-assay variation of 5.4% (n=6).

Blood samples from workers showed lead levels ranging from 1 to 25 $\mu g \cdot dL^{-1}$ (all below the UK suspension limit of 60 $\mu g \cdot dL^{-1}$). The paired saliva samples showed lead levels between 6 and 398 $\mu g \cdot L^{-1}$. A weak ($p=0.065$), but positive, correlation was seen between blood and saliva lead measurements. Two outliers in particular were noted where one matrix had an elevated level of lead whereas its pair did not. Excluding these two samples improved the correlation to $r=0.68$ with a 1:1 relationship between blood and saliva.

The initial data suggest a positive correlation between blood and salivary lead levels with roughly a 1:1 relationship. This is in agreement with the previous work of Coventry Diagnostics. The data presented here show quite a weak correlation with significant variability – there may be a number of reasons for this including kinetic differences between blood and saliva. Whereas the initial work by Coventry Diagnostics was on environmental exposures (where participants might reasonably be expected to be at a steady-state regarding lead exposure) the data presented here are from workers. Depending on their working history, these workers may not be at steady-state with regard to lead exposure. The differences in lead absorption and elimination kinetics in blood and saliva would therefore potentially have an influence on the correlation in these samples. These variables are currently being investigated, with further recruitment and analysis also taking place.

URANIUM MEASUREMENT IN URINE WITH AGILENT 7700X ICP-MS

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Biological fluids can be used as a good indicator for human exposure to certain kind of pollutants. As an example, the evaluation of their elemental composition is a good indicator that workers has been in contact with toxic metals. In particular in the nuclear industry, human exposure to uranium can be traced by measuring its elemental concentration in the urine.

The analysis of such samples can present some difficulties in relation to the heavy sample matrix. Therefore, high level of sample dilution is applied prior their analysis which is often incompatible for the detection of low concentration. In addition, the high dilution of sample tends to increase the impact of contamination leading to erroneous final results.

In the present works, two analytical strategies have been compared for the assessment of uranium in urine samples using Agilent 7700x ICP-MS. First, the urine samples have been diluted and the sensitivity of the system has been maximized for the determination of high mass elements. Second the direct analysis of urine samples has also been tested thanks to the use of the High Matrix Introduction (HMI) technology. When conventional introduction systems are limited to a total dissolved solid (TDS) of 1 $g \cdot L^{-1}$, the use of the HMI enables the direct introduction of solution containing up to 10 to 20 $g \cdot L^{-1}$ of TDS. This approach was compared with the conventional one to underline benefits of the new methodology.

HP-15

QUANTIFYING POTASSIUM IN ULTRA HIGH PURITY SODIUM SALTS BY SECTOR FIELD ICP-MS

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Sodium iodide crystals doped with thallium is one of the most common materials used to make scintillation detectors. The sodium iodide used to make the crystals must be extremely pure. One of the common impurities in sodium salts is potassium. The decay of naturally occurring K-40 in the sodium iodide crystals is often the limiting factor to measuring low level gamma radiation for nuclear physics and nuclear medicine applications.

Quantifying low ppb concentrations of potassium in sodium salts is challenging. A robust method was required to analyze the starting materials, reagents, intermediates and final product in the production of ultra high purity sodium iodide. The high sensitivity and resolving power of Sector Field ICP-MS is ideal for this application. Results will be reported from an Element2 SF-ICP-MS combined with an ESI microFAST continuum system.

ICP-MS TECHNOLOGY – A PERFECT SOLUTION FOR ENVIRONMENTAL CHALLENGES

Ewa PRUSZKOWSKI, **Cynthia BOSNAK, Stan SMITH**
PerkinElmer Inc., Shelton, USA

The objective of this poster is to investigate the capability of the current ICP-MS technology for environmental analysis.

It would be shown that the ICP-MS is a perfect technique not only for analysis of drinking water, soils and sediments but also for such challenging matrices as Flue Gas Desulfurization wastewaters (FGDWW). The US EPA methods 200.8, 6020a and a proposed SOP for analysis of FGD wastewaters would be discussed.

ICP-MS TECHNOLOGY – CLINICAL ANALYSIS MADE EASY

Ewa PRUSZKOWSKI
PerkinElmer Inc., Shelton, USA

The objective of this poster is to demonstrate the capability of the current ICP-MS technology for trace element analysis in clinical samples.

It would be shown that the ICP-MS in combination with an optimized sample introduction system is a perfect technique for analysis of diverse types of clinical matrices including urine, serum and blood. One simple sample preparation technique, appropriate diluent and panels or individual analytes can be measured fast and precise. Results in reference materials would be shown and discussed.

DETERMINATION OF TRACE RARE EARTH ELEMENTS IN HIGH PURITY RARE EARTH COMPOUNDS BY ICP-QQQ (ICP-MS/MS)

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High technology industries such as electronics, optoelectronics, glass, medical and nuclear applications have been increasing their use of high purity rare earth elements (REEs). In these applications, high purity REE metals and their compounds require strict quality control.

Inductively coupled plasma mass spectrometry (ICP-MS), a powerful technique for fast and accurate elemental analysis, is commonly used for the determination of trace level REE impurities in high purity materials.

However, accurate analysis of low-level REE impurities with conventional ICP-MS have been traditionally been challenged by interferences due to spectral overlap of oxides of low mass lanthanides on higher mass lanthanides.

Trace impurity REEs in high-purity REE material, such as La_2O_3 and Gd_2O_3, etc., were determined using a newly developed inductively coupled plasma triple quadrupole mass spectrometer (ICP-QQQ). ICP-QQQ features a new generation reaction cell that far outperforms any existing reaction cell ICP-MS in interference removal capability.

In this study of Gd matrix samples, interference problems arising from GdO and GdOH on Yb were overcome using NH_3 in a ICP-QQQ reaction cell. With ICP-QQQ, the background equivalent concentration for Yb was significantly improved by 4 orders of magnitude compared to that of a conventional cell.

SIMULTANEOUS DETERMINATION OF TRACE ELEMENTS IN HIGH PURITY STEEL BY TRIPLE QUADRUPOLE ICP-MSMS (ICP-QQQ)

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Steel manufactures require an analytical technique that is rapid, accurate, and sensitive in order to determine and reduce any possible impurities in their final product, high purity steel.

Although Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is the analytical technique of choice for analyses of trace elements in steel, the sensitivity of single quad ICP-MS is not sufficiently high to allow for determination of difficult analytes such as phosphorus and sulfur.

Moreover, determination of manganese in an iron matrix is extremely challenging for single quad ICP-MS due to the very high iron (^{54}Fe and ^{56}Fe) signal that overlaps the mono-isotopic signal of manganese at m=55. As such, successful analysis of trace analytes in steel by single quad ICP-MS requires a very time consuming and labor intensive matrix separation.

Triple quadrupole ICP-MSMS (ICP-QQQ) allows for a more effective removal of polyatomic interferences, such as $^{14}N^{16}OH$ on ^{31}P and $^{16}O_2$ on ^{32}S, using controlled chemical reaction. Furthermore, the superior abundance sensitivity of the ICP-MSMS can successfully resolve the Mn signal from the very intense overlapping Fe signal in this extremely high iron matrix.

Here we will report our analytical results for determination of minor to trace elements in high purity steel, including difficult elements such as sulfur, phosphorus and manganese using ICP-QQQ.

THE DETERMINATION OF MAJOR AND TRACE ELEMENTS IN MILK USING ICP-Q-MS

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Milk and milk products form a major part of a healthy diet. FDA recommended daily consumption of milk for children and adults is two and three cups daily respectively. As well as being a high source of calcium and potassium, milk contains a number of essential elements such as iron, copper and zinc. Multi-elemental analysis of milk can determine whether milk is meeting the expected nutritional requirements or is lacking either due to regional soil deficiencies in the case of cow milk or poor diet in the case of breastmilk. Alternatively, the analysis of trace elements that are toxic in nature can alert us to the possible risk of contamination in milk.

As the sole source of nutrition for young babies and as a major constituent of the diet for older babies and toddlers, nutritionists are also eager to investigate the differences in bioavailability of some of the essential elements. As the bioavailability is dependent on the chemical form of the element, speciation analysis is perceived as the most promising approach to identifying differences between baby formulas and breastmilk for example.

The new quadrupole ICP-MS system, the Thermo Scientific iCAP Q, was used for the analysis of cow milk, breastmilk and powdered baby formulas. New technologies introduced in the iCAP Q such as skimmer inserts for improved matrix tolerance and flatapole technology in the cell that enables full mass range KED analyses were exploited for the accurate and robust analysis of over 30 elements in the different milk samples. Speciation methodologies were also investigated for feasibility of determining certain components of the milk samples.

DETERMINATION OF SELECTED METALS IN CLINICAL SAMPLES IN CONNECTION WITH ARTICULAR REPLACEMENTS

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Articular replacements can prolong active life of many patients, whose joints are damaged or affected by inflammation. Metals are one of materials, from which are replacements made. The most frequently used are bio-inert metals or their alloys, which contained titanium, cobalt, nickel, chromium and vanadium. Unfortunately, these metals can be released to tissues and body fluids and then they can cause additional health problems or internal organs damage. From those reasons it is necessary to watch over levels of these metals in human body. In this contribution we describe the development and verification of method for the determination of selected metals (Al, Ti, V, Cr, Co, Ni, Nb, Pb) in clinical samples by inductively coupled plasma mass spectrometry.

Analyzed samples were joint effusions and tissues, collected during revision surgeries from patients from Department of Orthopedics of University Hospital in Olomouc. Samples of joint effusions and tissues were digested in microwave system with HNO_3 and H_2O_2. Samples of tissues were previously lyophilized. The determination was performed by inductively coupled plasma mass spectrometer (Agilent 7700x, JAP), equipped by Octopole Reaction System in helium mode to reduce spectral interferences. Certificated reference materials (CRM) Seronorm Trace Elements Whole Blood L-1 and L-3 were used for method verification.

Method was verified by the following parameters: limit of detection (LOD), linearity of calibration, repeatability, trueness and intermediate precision. We obtained very good LODs in range of 0,003–0,280 ppb. Results of repeatability (expressed as RSD) for all elements were in range 3.5–7.1%, only for aluminium was slightly higher. Regarding trueness, all results obtained from the analysis of CRM were inside expanded uncertainties presented in certificates. This contribution will show results, coming from the analysis of real samples (effusions and tissues) and its statistical evaluation and comparison.

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REMOVAL OF TITANIUM BASED INTERFERENCES ON NICKEL, COPPER AND ZINK ON ICP-QQQ WITH MS/MS BASED REACTION TECHNOLOGY

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Molecular based interferences are major thread for the analysis of materials by ICP-MS.

Titanium will, due to its multi isotopic nature, generate oxide interferences on Nickel, Copper and Zink. Titanium dioxide is widely used in Food, cosmetics and materials that will have direct contact with the human body. Low level contaminations have to be monitored closely.

The Poster presents a concept to overcome those interferences by the use of Ms/Ms reaction cell technology. Various cell gasses and the optimization of other reaction cell parameters are used and will be discussed regarding their specific properties.

Detection limits and other figures of merit will be presented.

ICP-MS DETECTION OF HEMODIALYSIS INFLUENCE ON TRACE ELEMENTS CONTENT IN WHOLE BLOOD

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It is known that serum elements concentration in hemodialysis (HD) patients may be affected by several factors, i.e. by reduction of excretion in urine, by disturbed absorption by digestive systems and by effects of concentrations in dialysate. [1]. Hemodialysis patients are exposed to very high volumes of dialysate. Therefore, even minute levels of toxic substances in source water could lead to tiny concentration gradients between blood and dialysate [2]. Thus, hemodialysis patients are at theoretical risk for both deficiency and accumulation of trace elements, depending on removal efficiency by dialysis and the composition of the source water used for hemodialysis [3]. However, the incidence of abnormal trace element status in dialysis patients and contribution of dialysis methods has not been comprehensively studied [4].

Influence of hemodialysis on whole blood`s trace elements concentration was main task of present research. High sensitivity ICP-MS (Bruker, USA) was used for determination of trace elements in whole blood after microwave digestion. ICP-MS detection method for concentration of Al, As, B, Ba, Cd, Co, Cr, Cs, Cu, K, Mg, Mn, Ni, P, Pb, Rb, Se, Sr, Tl, V and Zn in whole blood of children with chronic renal failure in stage V D has been developed. Blood sampling was carried out in inlet and in outlet of dialyser. Quantity of patients that took part in the studying is 28. Average duration of replacement therapy is 2.7 years. Age of patients was varying from 8 till 15 years.

Selective detoxication features of hemodialysis were exhibiting considerable decrease of trace elements in 9 cases (particularly for B, Mg, P, K, Ni, Rb, Sr, Cs and Pb). Reliable decreasing ($p<0.05$) was registered for B, Mg, Rb and Sr elements due to very good reproducibility of the developed method. Increasing of trace elements content was registered only in case of Al.

Research showed:

a) ICP-MS can be reliably used for the hemodialysis trace elements control in whole blood.
b) hemodialysis do not result in deficiency of the majority of essential trace elements (Zn, Cu, Se, Mn, Co).
c) theoretically hemodialysis can be used for elimination of some trace elements with definite efficiency (Sr, Rb, B, Cs, Pb, Ni, P, K).
d) hemodialys can lead to definite accumulation of aluminum in spite of using high purified dialysates.

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ICP-MS TRACE ELEMENTS CONCENTRATION STUDY IN WHOLE BLOOD OF HEMODIALYSIS CHILDREN WITH CHRONIC RENAL FAILURE

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Uraemia is characterized by functional and biochemical disturbances that result primarily from the diseased kidneys diminished capacity to remove organic solutes from the body [1]. Besides it, trace elements are potentially important with both toxicology and nutritionally, in patients with uraemia [2]. Trace elements disturbances could appear both as a result of renal failure or replacement therapy. Accurate quantification of trace elements is critical in uraemia research. Because of very low concentration of trace elements in the body, extreme care must be taken in the sampling, preparation and measurements of these elements [3]. Some surveyed works had registered changes of trace elements content, but achieved data were rather multidirectional [4]. Determination

Research task of this work was blood trace element content study in whole blood samples from children with chronic renal failure. Method for trace elements determination in whole blood by ICP-MS (Bruker, USA) was developed and validated. Concentration of Al, As, Ba, Cd, Co, Cr, Cs, Cu, Mg, Mn, Ni, Pb, Rb, Se, Sr, Tl, V and Zn in blood of the control group and children with chronic renal failure in stage V D were also analysed. Before ICP-MS analysis, the whole blood samples were prepared by microwave digestion. Quantity of children that took part in the studying is 31 persons. Average duration of replacement therapy is 2.7 years. Age of patients varied from 8 till 15 years. Control group was presented by 61 healthy persons. The differences in trace elemental content between both of groups with chronic renal failure (and without) were registered. Reliable increasing of trace elements content in whole blood of patients with chronic renal failure in comparison to control group was observed for Al, Ba, Cd, Co, Cu, Pb, Sr and Tl. Reliable decreased level has been found for Cs, Mg, Rb, Se and Zn. No significant changes were observed for As, Cr, Ni, Mn and V.

Differences in trace elements content in the group with chronic renal can be characterized by trend of accumulation of trace elements with toxic features (Al, Ba, Cd, Co, Cu, Pb, Sr and Tl). Besides it, decreasing of essential trace elements (Mg, Se, Zn) and Rb and Cs content is admitted in child patients with chronic renal failure.

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HP-26

DETERMINATION OF TRACE METALLIC IMPURITIES SUCH AS PHOSPHORUS AND TITANIUM IN HIGH PURITY SILICON MATERIALS BY ICP-MS/MS

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As it is well known, monitoring metallic impurities in high purity silicon materials is very important for semiconductor device manufacturing. Particularly impurities on silicon wafer must be routinely analyzed by VPD (vapor phase decomposition) combined with ICP-MS. Most device manufacturers' analysts spend a lot of their time on this kind of analysis. Moreover, the recent demand for development and manufacturing of highly efficient solar batteries requires high level quality control for impurities such as phosphorus, boron and transition metals in bulk photovoltaic silicon.

Most trace metals can be determined by conventional ICP-MS equipped with collision reaction cell. Cool plasma also works well for ultratrace determination of K, Ca and Fe in low Si concentration samples. However, some samples containing high concentration of Si shows significantly strong spectral interferences. A typical example is ^{31}P which suffers from ^{30}SiH interference with $^{15}N^{16}O$ and $^{14}N^{16}OH$ interferences. Si and co-present hydrofluoric acid also creates $^{29}Si^{19}F$ ion which makes it difficult to determine trace ^{48}Ti. So the use of high resolution ICP-MS has been the only one technique to overcome such spectral interferences. Agilent 8800 ICP-MS, recently developed in Japan, utilizes MS/MS technology and improves performance of conventional collision reaction cell technology. The 1st quadrupole mass filter placed before the reaction cell allows only the analyte and interfering ions come into the cell. Those ions react with gas molecules such as oxygen or ammonia to produce ions with different mass from the original ions. The 2nd quadrupole mass filter selects only product ions of the analyte, and the interfering ions which do not create product ions are excluded.

The Agilent 8800 model is a Q-pole based ICP-MS. The mechanical structure and operation are simple and its productivity is very high. Some preliminary applications such as Ti determination in 9.8% sulfuric acid were shown in the previous Winter Conference on Plasma Spectrochemisty. In this report, trace impurity analysis of high purity silicon materials by ICP-MS/MS is explained in detail. Bulk silicon samples of single crystal, polysilicon and silicon wafer were analyzed.

Agilent 8800 ICP-MS (high sensitivity model) was used with hydrogen, ammonia and oxygen gases. By considering that VPD sample volume is generally as low as 0.2 mL and some samples contain as high as 2000 ppm Si, ultra low flow uptake nebulizer C-flow 50 was used. Silicon samples were dissolved with mixture of HF and HNO3 and solution samples were prepared by appropriate dilution. For 30 ppm Si sample (pseudo sample of naturally oxidized Si wafer VPD), high sensitivity tuning including cool plasma was applied. For 2000 ppm Si sample (thermally oxidized Si wafer VPD or bulk silicon material), robust tuning was used. Phosphorus was determined as $^{31}PH_4$ by H_2 reaction and titanium was determined as $^{48}Ti_{16}O$ by O_2 reaction.

Basic performance of ICP-MS/MS such as BEC, DL and long term stability was examined. Analytical result for real samples will be shown.

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ICP-MS ANALYSIS OF ENGINEERED NANOPARTICLES - FUNDAMENTAL CHARACTERIZATION AND SAMPLE PREPARATION STRATEGIES

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Due to a strongly increasing use of engineered nanoparticles (ENPs) in numerous products and applications, questions about the toxicological and environmental impacts need to be addressed. Although several analytical methods are available, the detection, characterization and quantification of ENPs is still a challenging task and universally applicable analytical concepts are missing. However, environmental and toxicological risk assessments require the characterization of the nanomaterials in different and often complex matrices which is (among others) hindered by the heterogeneity of the ENPs among each other, physicochemical differences between nano- and bulk-material as well as transformation processes caused by variable environmental conditions. Even though results of numerous scientific studies are already available, the characterization of nanomaterials themselves is still a neglected aspect. To provide a basis for further experiments, we conducted a comparison of different methods to determine (i) the concentration of different nanoparticle suspensions and (ii) to quantify the respective percentage of the dissolved (ionic) fraction.

A commonly applied technique for the quantification of elemental concentrations of ENP suspensions is inductively coupled plasma-mass spectrometry (ICP-MS). Since it is questionable if the (elemental) concentration of the ENP suspensions can be determined precisely if the (aqueous) suspensions are directly introduced into the system, the obtained results were compared after microwave digestion or acidifying of the respective ENP suspensions. As a result the nanomaterials tested (Ag, TiO_2, CeO_2 and Au) require different sample preparation methods: in some cases simple acidification of the suspensions seems to be sufficient (e.g., Ag, CeO_2), whereat other ENPs need to be digested via microwave assisted methods. Moreover, our results indicate that not only the properties of the different materials but also the size of the particles determine the sample preparation needed.

Next to “particle” fraction (>1nm) within a given suspension a “dissolved” (ionic) fraction is present, which needs to be kept in mind during ENP quantification - hence, we further characterized the ENP suspensions and the percentage of the dissolved fraction was determined. Therefore, different off-line fractionation methods were set in contrast to each other (e.g. ultrafiltration, ultracentrifugation, dialysis, cross flow filtration, cloud point extraction); afterwards the ionic species were analyzed by means of ICP-MS.

The results of the experiments highlight the importance of an thorough sample characterization and preparation of ENPs previously to any further experimental work or measurement. The increasing use of nanomaterials with new and unknown properties demands for further scientific research and requires for the adjustment of commonly applied methods, e.g. ICP-MS especially with respect to sample preparation.

THE DETERMINATION OF TITANIUM IN HUMAN SERUM BY ICP-MS USING DYNAMIC REACTION CELL TECHNOLOGY

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Titanium is commonly used in metallic hip replacement joints. Owing to wear and tear or different types of electrochemical processes that could take place in the body, there is a serious potential of leakage of titanium into the surrounding tissues. As a result it is important to monitor the titanium serum levels in patients that have undergone or are due to undergo a hip replacement surgery. The analysis of titanium in serum by ICP-MS is fraught with difficulties due to significant spectroscopic interferences from calcium on the major isotope of titanium (m/z 48) and other molecular ions such as PO, SO, CO_2, ArC and NO_2.

The NexION® 300D is a robust, highly innovative cell-based inductively coupled plasma mass spectrometer benefitting from three quadrupoles with the middle one acting as a universal cell. This cell can be used both as a collision cell using inert gases such as helium and as a true dynamic reaction cell with the benefits of using the most appropriate reactive gas for the efficient targeting of any spectral interference. In this work we describe a method to shift the titanium ions away from the interferences using dynamic reaction mode with ammonia as the reaction gas to determine the concentration of titanium in Serum.

This poster will highlight the potential of NexION® for the routine analysis of titanium in serum. Using ammonia in reaction mode we successfully overcame the variety of interferences from the serum matrix and were able to determine the concentration of titanium in serum accurately and reproducibly.

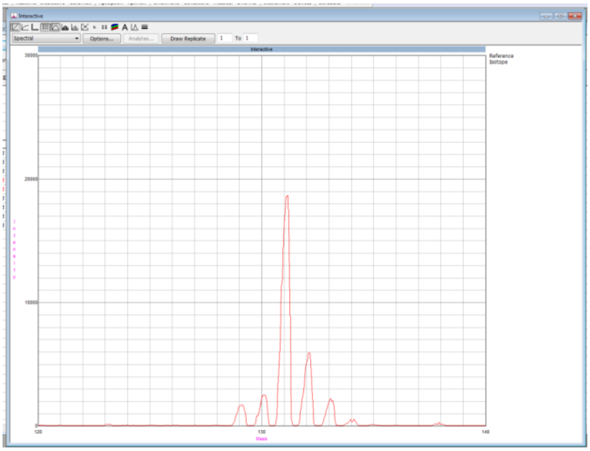

Fig.1. Spectrum for 10 ng·mL^{-1} titanium detected as $TiNH(NH_3)_4$.

EFFECT OF STORAGE TEMPERATURE AND PACKAGING TYPE ON THE TRACE METAL ANALYSIS OF WINE

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For wine makers, the determination of shelf life after bottling or filling is a crucial aspect of the final quality. However, in most cases, shelf life is outside the control of the winemaker. Factors like storage temperature and packaging type are important in determining wine shelf life [1,2]. California Chardonnay (vintage 2010) was stored at three different constant temperatures (10, 20, and 40°C) for six months in four different packaging configurations: 0.75-L glass bottles with ROTE screwcaps, natural corks, or synthetic corks and 3-L bag-in-boxes. After storage, all samples were analyzed using a generic descriptive analysis for aroma, flavor, taste, and color by 14 trained panelists. After the testing, visual damage to the screw caps were noticed. To determine which storage conditions and package types led to damage seen in some of the caps, and potential metal contamination, each wine was tested for trace metal contaminates using an Agilent 7700x ICPMS. Over 20 metals were tested, and results showed that tin was leaching into the wine under some of the conditions tested. Additional studies were conducted to determine the origin of the tin from the different packagings' used in this study.

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DETERMINATION OF SELENIUM IN BOVINE SEMEN BY ICP-MS USING FORMIC ACID FOR SAMPLE PREPARATION

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Selenium presents essential role in several biological functions of mammals. Infertility in humans and animals, including bulls, may be related to the lack of this element.

Determination of selenium by ICP-MS can be difficult due to spectral interferences. These interferences can be eliminated by using collision reaction interface (CRI) technology, but a pronounced decrease of the net signal intensities is observed [1]. On the other hand, the presence of carbon in the argon plasma increases the ionization efficiency of high ionization energy elements, such as selenium, due to carbon charge transfer reactions [2].

In general, sample preparation is the most critical step in an analytical sequence. The development of faster, simpler, cheaper and greener procedures is required. Formic acid has been reported as an effective reagent to solubilize solid biological samples for the determination of trace metals by ICP-MS [3].

A simple and fast method for determination of Se isotopes in bovine semen by ICP-MS after sample solubilization with diluted formic acid is here proposed.

Approximately 200 mg of bulk freeze-drying of sample were mixed with 20 mL of 50% vv^{-1} formic acid, kept at 90 °C for 1 h. After 30 min, it was added 1 mL of 30% vv^{-1} H_2O_2. Different formic acid concentrations (0, 1, 2, 4, 6, 8, 10, 12, 14, 16, 18 and 20% vv^{-1}) were used to investigate the effect of this reagent on selenium signal intensities. The interference by double charged ions and oxides were verified using solutions containing 5 $\mu g \cdot L^{-1}$ of Ba and Ce in formic acid medium. The formation of poliatomic ions were investigated using increasing formic acid concentrations with 2% vv^{-1} HCl. The nebulizer gas flow rate and RF applied power also were evaluated. All these experiments were performed without using CRI or with the introduction of 60 $mL \cdot min^{-1}$ of H_2 through the skimmer cone.

The formic acid causes an increase (ca. 50%) of the Se net signals and the maximum gain was obtained at 10% vv^{-1} formic acid. The formic acid had no significant effect on oxides and double charged ions formation that remained below 1% and 3%, respectively, for all studied formic acid concentrations. The polyatomic interferences formation was also negligible. The optimized and adopted nebulizer gas flow rates were 1.05 $L \cdot min^{-1}$ and 0.95 $L \cdot min^{-1}$ and RF applied power were 1.3 kW and 1.4 kW without and with CRI, respectively. For comparison purposes the solubilization of bovine semen with formic acid was compared with microwave-assisted digestion. No statistical differences between these sample preparation strategies at the 95% confidence level (t-test) were obtained for $^{77}Se^+$, $^{78}Se^+$ and $^{82}Se^+$ without using CRI and $^{82}Se^+$ with CRI.

Acknowledgement

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HP-31

ATTENUATION OF INTERFERENCES IN COLLISION/REACTION CELL INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY, USING HELIUM AND HYDROGEN AS CELL GASES – APPLICATION TO MULTI-ELEMENT ANALYSIS IN MASTIC GUM

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A collision/reaction cell ICP – MS was used to develop a method for the simultaneous determination of Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Nb, Mo, Ag, Cd, Sb, Cs, Ba, Hg and Pb in mastic gum. Evaluation of helium and hydrogen as cell gases took place and their ability to reduce several interferences arising from Si, S, P, C, Cl and F based matrix was investigated. Likewise, much polyatomic interference was attenuated efficiently by the effect of kinetic energy discrimination. Moreover, a study of stopping curves measurements was performed. Thus, measurements of the ion loss caused by collisions, reaction cross sections given by the Langevin – Gioumousis – Stevenson model and collision cross sections were carried out.

In addition, a full factorial design of 25 experiments was initially performed, in order to screen the factors that affect the microwave digestion of mastic gum. The screened factors were the volumes of HNO_3, HF and HCl, temperature and hold time. The critical factors were temperature, hold time and HCl volume and a central composite design of 23 experiments was carried out, to fully optimize the significant factors.

The method was validated and the calculated recoveries for all elements (at three concentration levels) were ranged between 92.6% (Ti) – 105% (Ag) and the relative standard deviation (% RSD) of reproducibility were ranged between 1.6% (Co) – 9.9% (Ca). The limits of detections were ranged between 0.11 $\text{ng}\cdot\text{g}^{-1}$ (Fe) – 1.12 $\mu\text{g}\cdot\text{g}^{-1}$ (Ca). The trueness of the method was also checked by the analysis of a standard reference material (SRM, 1573a tomato leaves).

REDUCTION OF INTERFERENCES IN THE DETERMINATION OF RARE EARTH ELEMENTS BY AN OCTOPOLE COLLISION/REACTION CELL INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER – APPLICATION TO THE ANALYSIS OF CHIOS MASTIC GUM

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The aim of the present work was to investigate the molecular oxide (MO^+, MO_2^+) and hydroxide (MOH^+) interferences on the determination of rare earth elements. The capability of an octopole collision/reaction cell ICP-MS to attenuate or remove these interferences was studied. The effect of instrumental parameters on the MO^+/M^+, MOH^+/M^+ and MO_2^+/M^+ ratios was studied to ensure that observed changes in these ratios were a result of an alteration of the parameter and not due to random fluctuations. Moreover, the effect of kinetic energy discrimination to suppress these species was demonstrated. The energy losses of ions were measured from stopping curves and the estimation of collision cross sections and reaction cross sections was done. Efficiencies of He and H_2 collision gases were compared and H_2 was finally selected for all the elements.

In addition, an experimental design, as a multivariate strategy, for the microwave digestion of mastic gum was performed, since decomposition difficulties occur in such complicated matrices (i.e. resins, gums). Five factors (volumes of HNO_3, HF and HCl, temperature and hold time) were studied and optimized. Hold time, temperature and HF volume, were found to be the most critical factors, so further optimization using response surface methodology (CCD) was performed.

The method was validated and the calculated recoveries for all the elements (at three concentration levels) were ranged between 90.0% (Dy) - 104% (La) and the relative standard deviation (% RSD) of reproducibility were ranged between 4.4% (Nd)- 14% (Tb). The limits of detections were ranged between 0.024 $ng \cdot g^{-1}$ (Ho, Tm) – 2.10 $ng \cdot g^{-1}$ (Hf). The trueness of the method was also checked by the analysis of a standard reference material (SRM, 1573a tomato leaves).

ELEMENTAL ANALYSIS OF SEMICONDUCTOR GASES USING A GAS EXCHANGE DEVICE COUPLED TO HIGH SENSITIVITY ICP-Q-MS

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In the semiconductor industry, the elemental analysis of gases such as AsH_3, GeH_4, PH_3, SiH_4, SO_2 is an important step in quality control of the manufacturing process. For example, in semiconductor manufacturing AsH_3 is used in MOVPE (Metal Organic Vapor Phase Epitaxy), while PH_3 is the raw material in production of the doping gas.

This presentation describes the direct measurement of semiconductor gases using a new high performance quadrupole ICP-MS system, the Thermo Scientific iCAP Q, coupled with a Gas Exchange Device (J-SCIENCE LAB, Kyoto, Japan). The Gas Exchange Device consists of two concentric glass tubes with pores of 0.1 µm in diameter. By passing semiconductor gases through this device, gas molecules (e.g. N_2, O_2, CO_2 and H_2O) in the sample are exchanged and thus only the nanoparticle element impurities are passed to the ICP-Q-MS for quantification.

For example, O_3 and NH_3 are used in a gas reaction cell before the Gas Exchange Device:

$$2AsH_3 + 2O_3 \rightarrow As2O_3 + 3H_2O$$
$$2NH_3 + 4O_3 \rightarrow NH4NO3 + H_2O + 4O_2$$

AsO_3 and NH_4NO_3 existing as nanoparticles, as well as other molecules, are then passed as a gas into the reaction device. After online gas reactions, As_2O_3 and NH_4NO_3 particles are gathered by the Gas Exchange Device to provide a stable signal for subsequent ICP-MS measurement.

In this presentation results from the analysis of real samples will be provided, showing fully quantitative calibrations (from 5 ppt to 1 ppb) and sub ppt detection limits for AsH_3.

The application of a Gas Exchange Device coupled to high sensitivity ICP-MS iCAP Q is not limited to just the semiconductor field. Additional applications for the monitoring of a range of gas samples (e.g. nuclear, engine exhaust and tobacco smoke etc) will be discussed.

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HP-34

INVESTIGATIONS ON THE MECHANISM OF MANGANESE-INDUCED INJURY OF DOPAMINERGIC NEURONS

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Being an essential trace element, a sound body requires a certain amount of Manganese (Mn) to ensure a variety of physiological processes like protein and energy metabolism, bone mineralization as well as normal brain and nerve functions [1]. Therefore, Mn serves as a cofactor of several enzymes, among others the acetylcholinesterase (AchE). Accumulation of Mn in the body leads to a neurodegenerative disease called manganism. Diederich et al. could show in a rat model by i.v. and i.t. application of Mn that mainly Mn-citrate crossed the blood-brain-barrier [2]. Based on these results, we now want to investigate the relation between Mn-species and neurotransmitters, acetylcholinesterase activity and misbalances between other trace elements (like Fe, Cu or Zn) to clarify the mechanism which is leading to the Mn-dependent neurodegeneration.

Therefore, we wanted to cause a chronic Mn overexposure in rats with a feeding trial. In a feeding pretrial control rats were fed with standard chow whereas test rats were supplemented with Fe-deficient and Mn-high chow for 1 month. Brain, liver, kidney and serum were analyzed by ICP-AES or ICP-MS and Mn speciation was performed by SEC-ICP-MS. Therefore, both chemical digestion and extraction of brain, liver and kidney [2] were carried out for determination of total contents of Mn, Fe, Cu, Zn, whilst extracts or serum were used for Mn-speciation and determination of AchE activity.

As the results showed significant differences between control and test rats for Cu and Zn, but only little for Mn (concentration in brain was only 7% higher in test rats) a further feeding trial was established to enforce these first indications.

Here, Mn concentration in test rats chow was elevated and feeding time was extended to 2 month. In parallel, a trial with i.v. application of $MnCl_2$ according to Diederich et al. [3] was carried out. Evaluating the results of those trials, prediction about a possibly Mn intoxication via the oral route in comparison to the systemic application can be made. Furthermore, the organs and serum of i.v. treated rats will serve for the intended analysis of the Mn-dependent mechanism of neurodegeneration as adequate concentrations of Mn in organs are ensured according to [2]. Further, the brain will be examined by FT-ICR-MS to see which other neurotransmitters (i.e. glutamine) are involved and by LA-ICP-MS of brain sections to localize trace elements in the brain.

After all, deciphering the mechanism of Mn-induced injury of dopaminergic neurons might help for a better understanding of manganism to show risks and chances of preventing this disease and might contribute to find biomarkers in samples before the ongoing of injury.

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HP-35

ESSENTIAL METALS PROFILE IN HAIR AND NAILS OF PATIENTS WITH LARYNGEAL CANCER

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Dynamic equilibrium of an organism is determined by a number of factors both internal and extracorporeal, e.g the presence of micro- and macroelements [1]. The most dangerous consequence of their imbalance may be carcinogenic processes related with disturbance of homeostasis. All changes connected with its disorder are difficult to be revealed basing only on detection of elements in physiological fluids. However, despite of unseen changes in elements content in human blood, so called alternative materials such as hair and nails may serve as indicator of disorders in microelements management [2].

The aim of the study was examination of changes in essential metals content in human serum and alternative materials, i.e. hair and nails, in case of patients with laryngeal cancer. Hair and nails, collected from patients and a group of healthy volunteers, were subjected to analysis for calcium, copper, iron, magnesium, manganese and zinc. Mineralization was conducted with the use of a MARS 5X multiposition microwave digestion system. Inductively coupled plasma mass spectrometer (ELAN DRC-e Axial Field Technology) and inductively coupled plasma optical emission spectrometer (Optima 2100DV), both by Perkin Elmer, were employed for metal analyses.

In the case of hair samples collected from the control group the highest mean concentration among the elements of interest was registered for calcium (9748 $\mu g \cdot g^{-1}$), the lowest for manganese (11.3 $\mu g \cdot g^{-1}$). In the case of nails collected from the control group again the highest mean concentration was noted for calcium (3422 $\mu g \cdot g^{-1}$), the lowest for manganese (5.03 $\mu g \cdot g^{-1}$). Similarly as in hair, in nails the highest concentration was show for Ca (1399 $\mu g \cdot g^{-1}$), and the lowest for Mn (1.94 $\mu g \cdot g^{-1}$). The performed statistical analysis enabled to conclude that in the case of the control group concentrations of essential metals in both hair and nails were significantly higher than in the group of patients with laryngeal cancer. Further analysis of the obtained data should prove whether determination of essential elementsin hair and nails may be exploited in diagnosis of laryngeal cancer and in the case of necessityof supplementation with these elements.

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HP-36

VARIATION OF CONCENTRATION OF SELECTED ESSENTIAL AND TOXIC METALS IN SALIVA OF PEOPLE WITH PERIODONTAL DISEASE

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Mineral deficiencies bring about specific *human body dysfunctions*. At the same time accumulation of or exposure to toxic or essential metals may also lead to serious health problems or even to death [1]. In recent years, many researchers have investigated the relationship between *concentration* levels of metals in the body and different diseases [2-4]. Various chemometric methods, such as correlation analysis [2-4], principal component analysis [2-4] and cluster analysis [4] have been implemented as *useful tools* in discovering and elaborating the models of the above-mentioned relationships.

The goal of the study was to examine possible influence of periodontal disease on concentration of selected metals in saliva. Saliva samples from examined groups (patients and controls) were digested with nitric acid in closed vessels in accordance with the optimized pressure and temperature program at the power of 1200 W. The saliva samples were analyzed for 10 metals: Cd, Co, Cr, Ca, Cu, Fe, Mg, Mn and Zn with use of inductively coupled plasma mass spectrometry (ICP MS) and inductively coupled plasma optical emission spectrometry (ICP OES) under optimum analytical conditions. Subsequently, statistical analysis of the obtained data was carried out. The highest mean concentration levels were observed for Ca (39.22 mg·L^{-1}), followed by Mg (9.92 mg·L^{-1}), Fe (984.91 µg·L^{-1}) and Zn (79.11 µg·L^{-1}) in the saliva of the examined patients. Similarly, the dominant metal levels in the saliva of the controls were Ca (34.97 mg·L^{-1}), next Mg (6.04 mg·L^{-1}), Fe (933.24 µg·L^{-1}) and Zn (75.25 µg·L^{-1}). Significantly higher concentrations of Cr, Cu, Mg and Mn ($p<0.05$) in saliva were observed for patients with periodontitis in comparison with the control. Weaker correlations between metals were found in biological fluids of patients than of healthy donors. The employed Cluster Analysis was able to distinguish saliva samples of patients and healthy individuals correctly.

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HP-37

COMPARISON OF RESULTS FOR MANGANESE OBTAINED BY GF AAS AND ICP-MS METHODS IN URINE COLLECTED FROM PATIENTS ADDICTED FROM EPHEDRONE AND HEALTHY VOLUNTEERS

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In recent years many cases of poisoning with manganese have been reported for patients taking ephedron. This substance is popular among drug addicts and its action is similar to the one of popular psychoactive substances, e.g. amphetamine. Ephedron, when synthesized with the use of potassium permanganate as an oxidant gets contaminated with manganese compounds [1]. Excessive concentration of manganese in a human body may cause pneumonia, along with disorders in the central nervous system, and as a consequence may result in a disease resembling Parkinson's disease [2].

The aim of the study was to develop and optimize methodology for determination of manganese in urine with the use of GF AAS and to apply the method to determine its levels in urine collected from patients treated with ephedrone and a group of healthy volunteers. In the first stage of the experiment, urine mineralization process was optimized with the use of a certified reference material (selected power of mineralization: 1200 W) which was followed by optimization of pyrolysis temperature and atomization temperature and subsequently the best modifier was selected ($Mg(NO_3)_2$ and $Pd(NO_3)_2$ in appropriate ratio). This step allowed to achieve good accuracy. Afterwards, validation process was performed - analytical parameters, such as: limit of detection (0.0037 $\mu g \cdot L^{-1}$), limit of quantification (0.0125 $\mu g \cdot L^{-1}$), sensitivity, calibration range, method linearity, accuracy (0.10%), and precision (<10%), were estimated.

When the results from patients were compared to the healthy subjects, significant increase in Mn concentration was observed, probably due to the intake of ephedrone.

In order to verify the GF AAS method the ICP-MS technique was used. A urine reference material was used to calculate of the accuracy. Results shown on the poster will present data, analysed applying techniques mentioned above, obtained from both subject groups.

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HP-38

HUMAN HAIR ANALYSIS IN RELATION TO SIMILAR ENVIRONMENTAL AND OCCUPATIONAL EXPOSURE

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Over the last decades, there has been an increasing awareness of environmental and occupational exposure to toxic or potentially toxic trace elements. Environmental biomonitoring may be done by using different kinds of body tissues such as blood or urine for acute exposure or hair or nails for long-term exposure. However, determination of minerals in blood does not necessarily reflect the current organism status, because of homeostatic mechanisms and the fact that urine represents the amounts of elements eliminated from the body. What is more, hair is a highly mineralized tissue, which means that concentration of elements is higher than in blood or urine [1,2]. Hair is a biomarker, which has been used preferably because the elements are permanently deposited in hair shaft as it grows and are supplied by blood [3]. Hair analysis can provide retrospective information on the level of both essential and toxic elements in the organism [2]. Besides the possibility of (I) long-term exposure and (II) higher concentrations of elements in hair than in other tissues, there are other advantages such as (III) non-invasive sampling and (IV) no problems with storage and transport [1-3]. Hair mineral analysis is a very useful tool in the investigation of the mineral status of human organism, which gives information on the diet, environmental exposure, health problems, medicines or supplements taken. The composition of human hair depends on different factors such as age, sex, cosmetic treatment (coloring, perming, bleaching, frequent washing), dietary and living habits, geographical region and individual physiological differences [2]. Because there may be some problems in interpreting the results, every volunteer should fill a questionnaire before the analysis (questions about diet, age, gender, etc.) [3].

The aim of this work was to assess the influence of various factors on the elemental composition of the investigated hair samples. The studied population consists of students of Faculty of Chemistry at Lodz University of Technology and included 100 subjects (75 females and 25 males, aged 19-26). The volunteers were asked to fulfill a questionnaire concerning questions about their dietary habits (which can be helpful in the identification of sources of exposure from the diet), sex, properties of hair (color, hair treatment), amount of fish consumed, etc. We assume that the participants are exposed to similar environmental and occupational factors. The samples were cut from the nape of the neck (up to 5-6 cm long), which corresponds to the period of the past 3-4 months of exposure. The concentration of chosen toxic and essential elements in human hair samples was determined using the inductively coupled plasma mass spectrometry technique with the quadrupole analyzer, ICP-QMS (X-Series, Thermo Electron Corporation). The samples before the elemental analysis (about 0.2 g) were solubilized with concentrated nitric acid (Baker) and digested in the microwave oven Milestone 1200 MEGA. The analysis of mercury concentration was performed using Automatic Mercury Analyzer SP-3D, Nippon Instrument Corporation. The analytical procedure was verified by the analysis of certificate reference material of Human Hair NCS ZC81002. The obtained results were elaborated using the *Statistica* software. The existence of the statically significant differences in the concentration of analyzed elements in relation to the studied factors were pointed out.

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HP-39

THE RELEASE OF METAL IONS FROM SILVER-MODIFIED DENTAL MATERIALS INTO ARTIFICIAL SALIVA MEDIUM

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Nowadays, depending on different requirements for a wide range of applications, dental material market offers a large variety of products. It is well-known, that all dental materials release ions into the oral environment, having the potential to interact with the oral tissues. Many cases of such oral tissue reactions have been reported in literature. Some metals, in particular Ni and Cu, are thought to be toxic and cause some adverse effects i.e. gingival inflammation, while others like high noble and noble alloys are supposed to be responsible for discoloration and hyperplasia of the adjacent gingiva. The comparatively high allergy towards some components of dental filing should result in replacement of those materials by some suitable alternatives [1]. During the last 15 years some remarkable changes in restorative dentistry have occurred. The employment of amalgam and different kinds of alloys has dropped dramatically. The main reasons were connected with the aesthetic aspects, the controversial discussion about the amalgam employment and metal toxicity, but also environmental pollution by mercury waste. The increasing restrictions in many countries have resulted in the development and application of composite resin and ceramic materials in the last two decades [2]. Recently, the addition of silver nanoparticles to a resin composite material in order to increase the surface hydrophobicity and reduce the number of adhering bacteria has been investigated. Silver has already been proved to be effective against human streptococci and periodontal pathogens. Thus, it can be potentially useful as an antibacterial additive to dental materials [3] provided that the modified dental materials release Ag ions with time and preserve good performance.

The aim of this work was to evaluate the influence of the type of the studied composite material (modified and non-modified) compared to cement resin material (modified and non-modified) on the process of the metal ions release into the artificial saliva solution (0.9% NaCl). The studied samples consisted of composite materials SDR (Dentsply), a low viscosity, bulk-fill flowable base composite for posterior restorations. Cement resins Accolade PV (Danville) and Variolink II (Ivoclar-Vivadent) were analyzed for comparison purposes. In order to modify the composite material fumed silica Arsil (Z.Ch. Rudniki) and Areosil (Degussa) with a layer containing silver or in a nanosilver dispersion of different concentration were used. Cement resin samples were modified only with Arsil fumed silica containing a nanosilver layer. A silica-bead moiety was then filled with a three-dimensional cross-linked hydrophobic polymer. Composite samples were stored in 37°C for a week, 1 and 3 months in order to assess the short and long-term corrosion resistance. The amount of the metal ions release into the 0.9% NaCl solution was determined using the inductively coupled plasma mass spectrometer with the time-of-flight analyzer, ICP-ToF-MS (OptiMass 8000, GBC).

Acknowledgement

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ANALYTICAL PROBLEMS OF DETERMINATION OF RARE EARTH ELEMENTS IN NATURAL WATERS

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More frequent application of rare earth elements (REEs) in the industry has led to increased releases of REEs to the environment and has raised growing interest in the investigation of their content in the environmental samples.

As the natural water samples contain very low concentration of REEs, it is necessary to apply the most sensitive measurement techniques. Inductively coupled plasma mass spectrometry (ICP-MS), which characterizes low quantification limits at level a few $ng \cdot L^{-1}$, has become the most often used technique for REEs determination [1-3]. The main advantage of this technique is quick, simultaneous measurement of all elements from the REE group directly in the most of the water samples.

In this study REEs were determined in the water samples (ground and surface) originating mainly from the monitoring carried out in Polish Geological Institute. About 300 water samples were analyzed by ICP-MS (Elan DRC II, Perkin Elmer Sciex) equipped with the standard introduction system (cross flow nebulizer and Scott double pass spray chamber).

Verification of the obtained results and method validation were done via analysis of the available reference materials (SLRS, SERMIN1 and VIDAC18), using the standard addition method and estimation of spike recovery for selected water samples. Moreover, the long term repeatability and reproducibility for the natural samples and the selected reference materials was investigated.

Nevertheless, the certified reference materials (CRM) are needed to meet method validation requirements and improve inter-laboratory consistency and accuracy.

Low content of REEs in the water samples effects the worse measurement precision and contributes to the higher combined standard uncertainty. Occurrence of the spectral interferences, especially form BaO is the second main contribution to the total uncertainty in case of samarium and europium. The contribution from BaO interferences depends on the barium concentration in the samples, which is quite variable (from a few $\mu g \cdot L^{-1}$ till 500 $\mu g \cdot L^{-1}$) and for this reason samples with very high content of Ba should be treated more carefully. In this work mathematical corrections were applied for minimizing spectral interferences and rhenium was used as an internal standard.

The advantages of determination of REEs in comparison with the other trace elements (e.g. Cu, Pb, Ni, Al) are obtaining clean blank samples (no contamination problem) and lack of memory effects during measurements.

Investigation of rare earth elements content in the water samples carried out in the Central Chemical Laboratory Polish Geological Institute – National Research Institute has aimed at preparation of a method which enables quantitative determination of these elements in natural waters. In the analysed sample population REEs were present at very low concentrations. Despite the fact that very sensitive method was applied (ICP-MS), it was possible to obtain quantitative results only for about 20% of the population. About 80% of the results was below the limit of quantification (below a few $ng \cdot L^{-1}$). The highest concentrations were found for Ce, La and Nd (about 8 $\mu g \cdot L^{-1}$, 5 $\mu g \cdot L^{-1}$ and 4 $\mu g \cdot L^{-1}$, respectively).

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HP-41

ELEMENTAL ANALYSIS OF HUMAN ORIGIN SAMPLES BY ICP MS AND HG AFS FOR MEDICAL DIAGNOSTICS SUPPORT

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Atomic spectrometric techniques are commonly used in elemental analysis of different materials. The particular techniques differ in sensitivity and analytical capabilities (e.g. multielemental analysis, matrix effects). Hence, to the general trace elements determination ICP MS is used, however HG AFS is recommended for determination of trace elements forming volatile hydrides difficult to determine by previous technique because of isobaric effects [1-3] .

Inflammatory Bowel Disease (IBD) is a group of chronic diseases of the alimentary canal of unknown reason, different pathogenesis and different clinical symptoms. One of the factor that could affect the development of IBD disease is a disbalance of several elements contents in the body. Thus, determination of zinc, manganese, cooper, lead, selenium and iron in chosen clinical or alternative samples could be helpful in discovering the impact of these elements on the development of the diseas and, later , in selecting of an appropriate diet and treatment [4].

In this work, procedure of hair samples preparation for the determination of Mn, Fe, Cu, Zn, Pb using ICP MS and Se using HG AFS technique, was tested and optimized. Preliminary study for assessment of sample preparation on result of determination were conducted with the use of laboratory sample of hair. An assessment of the impact of kind of solvent for washing hair, drying temperature and the conditions of digestion was accomplished. Trueness of the total procedure was confirmed analyzing reference material of hair GSH-1. The detection limits of Zn, Mn, Cu, Pb and Fe determination in digest by ICP MS equate: 0.96, 0.10, 0.076, 0.46 and 1.66 μg/L, respectively, it correspond to: 0.062, 0.0065, 0.0049, 0.030 and 0.108 μg/g. Because of expected interferences in determination of selenium in biological samples by ICP MS, HG AFS was used. Obtained results were compared, it was found that only determination of Se by HG AFS gave correct value of concentration for reference material. The detection limit of Se determination in digest by HG AFS equates 0.18 μg/L (0.011 μg/g). The developed procedure was applied for the hair samples analysis of children with IBD from Clinic of Pediatrics, Gastroenterology and Nutrition University Children's Hospital in Krakow and control hair samples of healthy children. Hair from patients were sampled directly after disease recognition and second time after one year of therapy. Digestion of sample was carried out in nitric acid (Merck) with microwaves. The changes of some trace elements contents were observed.

Acknowledgement

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DETERMINATION OF ^{99}Tc IN PEAT BY FI-ICP MS WITH RECOVERY EVALUATION ON THE BASE OF ^{95m}Tc MEASUREMENT

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The ^{99}Tc long lived technetium isotope is present in environment generally as sum of a global, or in Europe, as a Chernobyl fallout. Also development of nuclear medicine influence the increase of long-lived ^{99}Tc concentration in biosphere. Nevertheless, there is very low final concentration of ^{99}Tc in environment and the most sensitive analytical techniques should as ICP MS be applied for monitoring. But, even for peat analysis which could accumulate technetium, careful its extraction, separation and preconcentration prior to determination by ICP MS is recommended.

In the analytical procedure of peat analysis three steps are crucial: gentle but efficient digestion, selective separation – both with effective recovery evaluation, and accurate determination – without isobaric effects.

For analysis peat samples were soaked with ammonia and ashed at 400 °C, the residue was leached using conc. HNO_3. After few steps of main matrix removal solution undergoes analysis.

Separation and preconcentration if carried out on-line by FIA technique can not only improve method sensitivity but also can eliminate or at least minimize some interferences. In presented research as a SPE sorbent TEVA resin was applied.

Because in previous examination two markers were tested to evaluate recovery: ^{95m}Tc (produced by us at Krakow's cyclotron by irradiation of ruthenium compounds with protons) and stable rhenium - but both not met our requirements (^{95m}Tc was contaminated with ^{99}Ru and Re as was not quantitatively separated by TEVA). In presented research ^{95m}Tc (free of ruthenium traces) produced from molybdenum compounds was applied.

Herein data obtained by ICP MS determination after ^{99}Tc preconcentration realized on-line by flow injection system are presented.

For determination ICP MS Elan DRC-e spectrometer coupled with FIAS system both from Perkin Elmer, USA was used. Results of the recovery evaluation were controlled by parallel LSC ^{95m}Tc determination using Liquid scintillation β spectrometer Wallac 1414-003 Guardian and Pro Safe HC cocktail (Meridian).

Acknowledgement

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TRIPLE QUAD ICP-MSMS: ILLUMINATING THE CHALLENGES IN CLINICAL ANALYSES

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While ICP-MS is an immensely powerful multi-element analytical technique, it does suffer from some well-documented spectral interferences. Achieving low detection limits is limited by background signal from low level impurities and the presence of polyatomic interferences. In the last decade nine out of ten laboratories have been switching to collision/reaction cell (CRC) instruments as they presented a much simpler to use and improve results alternative for a wide range of complex matrices.

Today many of the challenges in ICP-MS analyses have been conquered yet, achieving low detection limits via single quad ICP-MS in clinical applications still presents many obstacles to existing CRC instrumentation. In single quad ICP-MS the entire ionized matrix and sample analytes enter the cell. This makes it impossible to perform targeted chemical reactions for interference removal. The ability to restrict the entrance of unwanted analytes precludes the formation of cluster ions or new polyatomic interferences, which result from matrix components reacting with the cell gas.

Triple quad ICP-MS with MSMS capability restricts what enters the collision/reaction cell. This capability is controlled by the first quadrupole, which controls entry into the CRC of either a selected mass-range or a single AMU. This level of control provides the necessary knowledge of what enters the cell. Knowing what enters the cell, allows us to perform targeted chemical reactions thus removing all polyatomic interferences while achieving low detection limits and unbiased, accurate analyses.

Here we present a comparative study between single quad and triple quad analysis of both urine and whole blood samples. The data clearly indicates the superior interference removal of the triple quad ICP-MSMS.

TRACE METAL DETERMINATION IN HEAVY AND EXTRA HEAVY CRUDE OILS BY ICPMS: COMPARISON OF DIFFERENT METHODS FOR ACID DIGESTION

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In spite of developments in analytical chemical techniques, sample preparation for metal determination in crude oils and by-products is still a challenge, due to the high organic nature of the matrix.

In this work, four microwave conditions (including a combustion device) and a High Pressure Asher (working each one at different temperature and pressure) were compared for the digestion of heavy and extra heavy crude oils. From a quantitatively point of view, similar results were obtained. All the procedures evaluated showed recoveries between 80–100%. However, from a qualitative point of view, differences in the degree of decomposition of the organic material were observed

HP-45

QUANTIFICATION OF PLATINUM GROUP ELEMENTS (Pt, Pd AND Rh) IN ROADSIDE SOIL WITH ICPMS

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Since the introduction of the assembly line in modern car production, the number of automobiles is increasing constantly. The drawback of the increased mobility is the massive emission of hazardous exhaust gases such as carbon monoxide, unburnt hydrocarbons and nitrogen oxides. In order to face this problem catalytic converters have been developed.

Catalytic converters containing the platinum group elements Pt, Pd and Rh (PGEs) have to convert toxic and hazardous emissions into their non-toxic forms carbon dioxide, water and nitrogen. The challenge is to find a satisfying compromise between oxidizing (Pt and Pd catalyzed) and reducing (Rh catalyzed) reactions. This compromise is depending highly on the catalytic active metals and their concentrations.

Although the PGEs are not used up chemically during the catalytic processes, they are released due to thermal stress and surface abrasion caused by exhaust fumes [1,2].The airborne particles accumulate in the environment in road dust and roadside soils, from where they might get into aquatic systems and the vegetation. Thus far, there are evidences that the complex salts of PGEs are affecting the respiratory system and that especially Pt and Pd in metallic form are potent sensitizers [3,4,5].

The present work describes the quantification of platinum group elements in roadside soil near Graz (Austria) with ICPMS. Samples were collected at intervals of 6-7 meters. After microwaveassisted acid digestion the samples were analyzed with an ICPMS. The main challenges were the low concentrations of the PGEs in the samples and spectral interferences (especially for Pd and Rh) caused by matrix elements. Even with the use of an octopole reaction/collision cell and H 2 or He as cell gases the polyatomic interferences couldn't be removed completely.

Finally, we analyzed the samples with an ICPQQQMS using several cell gases (O_2, NH_3 and H_2) for interference removal. Accurate results for the certified reference material BCR-723 Road Dust were obtained only with a He/NH_3 mixture.

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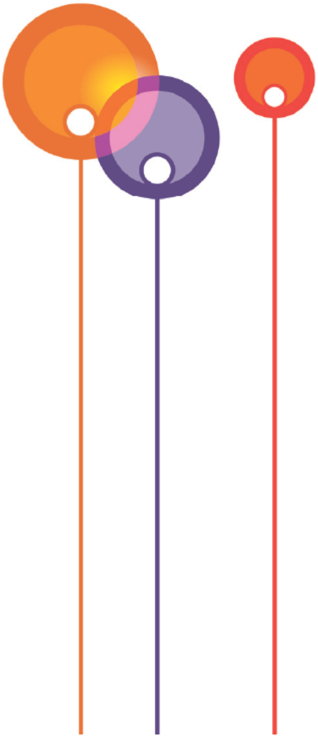
I

section

Glow discharge – poster presentations



IP-1

DEVELOPMENT OF IMAGING DETECTION TECHNIQUES IN GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY

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In the „*International Collaboration in Chemistry: Novel Instrumentation for Modern Elemental Speciation Analysis*" – project, jointly funded by the *German Research Foundation* (DFG) and the *National Science Foundation* (NSF), a novel type of a pulsed radio frequency glow discharge plasma source (pRFGD) was developed. The general aim of the project is the development of a monochromatic imaging system that provides element selective images with good spatial resolution of a large area glow discharge plasma discharge. A new highly sensitive detection method for speciation analytical investigations of metals in proteins separated by electrophoretic methods is the final project goal.

The pRFGD instrument currently installed at the University of Münster has originally been constructed at the Indiana University, Bloomington, IN, USA, before it was further improved at the Leibniz Institute for Solid State and Materials Research, IFW Dresden, Germany. The optical detection system is a monochromatic imaging spectrometer (MIS). It consists of a Czerny-Turner monochromator, achromatic lenses and an ICCD-camera. This setup allows the recording of spatially resolved images at selected wavelengths. An alternative detection system is the newly developed acousto-optical spectrometer (AOS) that also allows the detection of monochromatic images of selected element emission lines.

First approaches of quantification strategies and determination of limits of detection for selected elements will be shown.

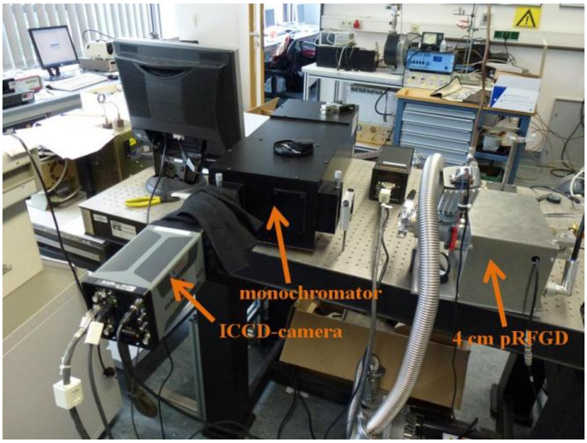

Fig.1 Technical setup of the pRFGD-MIS system.

GLOW DISCHARGE AS A TOOL FOR THE PREPARATION OF SAMPLES FOR ELECTRON MICROSCOPIC MEASUREMENTS

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The presentation is dedicated to a possibly new application of the glow discharge sputtering. Those people who deal with electron microscopic (e.g. Scanning Electron Microscopy or Transmission Electron Microscopy) know that existing sample preparation methods such as polishing, chemical etching, and ion beam etching are laborious and time consuming. Sputtering in the glow discharge has a great number of attractive features and thus lends itself to a fast and simple sample preparation. As the glow discharge is not often used for sample preparation, the influence of the glow discharge sputtering on the sample surface was systematically investigated. The results may by crucial for the analytical glow discharge as well. The study is a part of a research project at IFW Dresden in collaboration with the company Spectruma, which is funded by ZIM ("*Zentrales Innovationsprogramm Mittelstand*" – KF2466403AB0).

IP-3

QUANTITATIVE DEPTH PROFILE ANALYSIS OF AMORPHOUS SILICON THIN FILM SOLAR CELLS BY PULSED RADIOFREQUENCY GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY

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Over the last decade, the development of thin film solar cells (TFSC) has undergone a great expansion. Photovoltaic (PV) technology based on hydrogenated amorphous silicon (a-Si:H) thin films offers several advantages compared to traditional crystalline silicon solar cells, including a low manufacture cost, the possibility to use cheap and flexible substrates and easiness to structural integration [1]. The main limitation of a-Si:H solar cells is, however, their lower conversion efficiency (7–12%) and, therefore, increasing research efforts are currently directed towards a-Si:H final efficiency enhancements. As a result, cost effective analytical techniques with high sensitivity and depth resolution as well as with high sample throughput are needed.

Glow discharge optical emission spectrometry (GD-OES) provides an alternative technique for fast direct solid analysis of conducting and non-conducting materials with high depth resolution of comparatively large sample areas (~mm^2) [2]. Large area depth profiling is a significant advantage in analysis of heterogeneous bulk and thin film samples such as TFSC, because the scanning mode when using highly focused probes is required, further lowering throughput. Additionally, GD operates at moderate low pressure conditions (~torr), eliminating costly and time consuming ultra-high vacuum requirements. The low Ar^+ ions energy employed ensures that sputtering proceeds without significant formation of altered layers, an important prerequisite for successful depth profiling analysis. Moreover, the atomization and ionization processes in GD plasmas are temporally and spatially separated, reducing the matrix effects.

In this communication, the analytical potential of radiofrequency pulsed glow discharge optical emission spectrometry (rf-PGD-OES) is investigated for fast quantitative depth profiling analysis of thin film solar cells based on hydrogenated amorphous silicon. Determination of compositional depth profiles of a-Si:H TFSC was performed by resorting to a simple multi-matrix calibration procedure. For this purpose, certified reference materials as well as laboratory standards based on individual layers of doped a-Si:H were simultaneously employed in calibration curves. Results show that rf-PGD-OES allows to discriminate the different parts of the photovoltaic devices: the front contact composed by $ZnO{:}Al_2O_3$ (AZO), the a-Si:H layer (where it can be distinguished between the B doped, the intrinsic a-Si:H and the P doped films), the AZO/Al back contact and the stainless steel substrate. A good agreement with the nominal values for elements concentration and layers thicknesses was obtained, demonstrating the ability of rf-PGD-OES for the direct, sensitive and high depth resolution analysis of PV devices. Moreover, diffusion processes between the coating layers, which could have an important influence on the final efficiency of TFSC, can be identified. Hence, the findings support the use of rf-PGD-OES as an analysis technique in the development of PV thin films.

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IP-4

THE EVALUATION OF THE ANALYTICAL PERFORMANCE OF ATMOSPHERIC PRESSURE MICRODISCHARGE GENERATED BETWEEN MICROJET AND A LIQUID CATHODE

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Atmospheric pressure microdischarges generated in contact with liquids are alternative analytical atomic emission spectrometric methods for the elemental analysis of liquid samples [1]. They may be operate at the atmospheric pressure in the open to air atmosphere as inductively coupled plasma (ICP) and microwave induced plasma (MIP) very widely used in analytical measurements. What is also important, it is not necessary to introduce analyzed liquid samples to this excitation source using pneumatic nebulizers [1,2].

The main aim of this work was to evaluate the analytical performance of a new excitation microsource and its suitability for the determination of metals in different samples.

A direct current (dc) microdischarge was ignited between a miniature Ar/He microjet (diameter 700 μm) and a flowing liquid cathode of a new construction (see Fig. 1) [3]. The discharge was operated in the open to air atmosphere. Discharge current and voltage were 20-60 mA and 700-1500 V, respectively. A ballast resistor in the anode circuit was used to stabilize the discharge current. A grounded platinum wire was used as an electrical contact with the liquid cathode. A quartz-graphite tube (ID 2 mm) was applied to deliver solutions to the discharge zone by means of a peristaltic pump. The conductivity of solutions was provided by their acidification with HCl at 0.1 mol·L^{-1}. The flow rate of solutions was maintained at 0.6-3.2 mL·min^{-1}. One- or multi-element water solutions were analyzed.

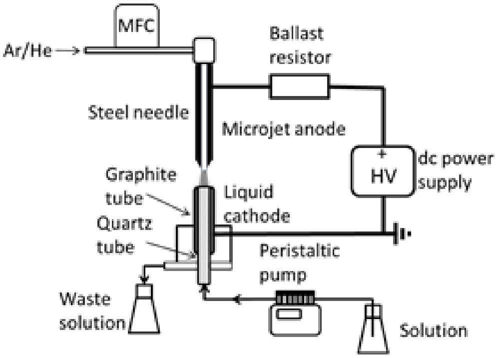

Fig.1 A schematic diagram of the investigated microdischarge (not to scale).

For selected elements, their detection limits, dynamic linearity ranges and the signal reproducibility were evaluated to ascertain the analytical performance of this excitation microsource. Additionally, its application in the trace element analysis of tap water samples was tested.

Finally, results presented here demonstrate that the atmospheric pressure microdischarge may be successfully applied as a simple and low cost atomic emission microsource for on-line determinations of trace levels of metals in different water samples.

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THE EFFECT OF THE ADDITION OF NON-IONIC SURFACTANTS TO THE SOLUTION ON THE ANALYTICAL PERFORMANCE OF THE MINIATURIZED ATMOSPHERIC PRESSURE GLOW-DISCHARGE GENERATED IN CONTACT WITH A LIQUID CATHODE

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The study of atmospheric pressure glow discharges (APGDs) generated in contact with a liquid cathode is of a great importance due to their application in analytical atomic spectrometry as a simple, low cost and low power consumption miniaturized excitation source [1-3]. So far, different constructions of liquid cathodes were employed to improve the analytical performance of APGD sources [2-6]. However, it is also possible to modify the composition and physicochemical properties of electrolyte solutions, e.g., by the addition of low molecular weight organic compounds [7], in order to enhance the sensitivity of the APGD source.

The main aim of this work was to elucidate the effect of the addition of non-ionic surfactants to electrolyte solutions served as the liquid cathode on the analytical characteristic as well as spectroscopic properties of a miniaturized direct current (dc) APGD source generated in open to air atmosphere. Two non-ionic surfactants, i.e., low weight Triton X-45 and high weight Triton X-405, were selected. The emission intensity of different molecular and atomic species as well as the background level were measured in the dc-APGD source generated in contact with solutions containing non-ionic surfactants. The amplification factor of the intensity of atomic emission lines of different metals, detection limits of these metals and the precision of measurements were calculated. Additionally, the most important spectroscopic parameters, i.e., excitation and rotational temperatures, the electron number density and the intensity ratio for Mg II to Mg I lines were determined in the near-cathode zone of the discharge as a function of the concentration of both surfactants. Possible processes responsible for changes in the excitation conditions of species in the APGD source were also discussed.

Results of experiments undertaken indicate that the addition of surfactants to electrolyte solution is very advantageous in reference to the sensitivity and the stability of the investigated dc-APGD source.

Finally, the proposed method was applied for the determination of metals in selected environmental samples, i.e., lake waters, extracts of soil and pine needle samples, coming from a mining lake area in Rudawy Janowickie mountains (the Lower Silesia region, Poland).

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IP-6

A NEW CATALOGUE OF GLOW DISCHARGE SPECTRA – THE CURRENT STATE

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The first part of a new catalogue of glow discharge spectra was completed, involving iron (2554 lines), copper (315 lines) and zinc (85 lines) in argon and neon discharges, in the range from 155 nm to 540 nm. Strengths of emission lines are expressed by emission yields [1]. They are corrected for the instrument function and are proportional to true intensities, with proportionality factors reflecting the sputtering rates of the respective pure metals in the given gas. Intensities of emission lines presented in the catalogue are consistent over the whole spectral range, between the three elements and between both discharge gases. Emission lines are classified by type (atomic/ionic) and the energy of the upper level of the corresponding transition is given.

The data for this catalogue were collected largely using the vacuum high resolution UV-VIS Fourier Transform spectrometer FT500 at Blackett Laboratory, Imperial College, London [3]. Supplementary information was obtained using two CCD spectrometers and a scanning mono-chromator. Intensity calibration was performed by standard lamps, the tungsten-halogen lamp and the deuterium lamp, and checked using the 'branching ratios' method, based on the fact that the ratios of intensities of lines originating at the same upper level do not depend on the excitation function (populations at individual levels). For this purpose, the spectrum of iron was used. Accurate transition probabilities for a number of Fe I and Fe II lines were taken from literature [4,5].

From the catalogue data, it is possible to draw a wealth of information relevant both to practical analytical work (selection of analytical lines, magnitude of line interferences) and fundamental studies (populations of individual excited levels, selection of lines for particular investigations, excitation mechanisms). Also, when planning experiments, it may help to be aware of prospective overlaps of lines observed at certain resolution, and, for measurements with a Fourier transform spectrometer, it is good to know where the strong lines in the spectrum are, so that the bandwidth can be prospectively limited by suitable filters, in order to enhance the signal-to-noise ratio in the spectral region of interest.

The work on the catalogue proceeds, raw data for a number of other elements are available.

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MATRIX EFFECTS IN GLOW DISCHARGE EMISSION SPECTROSCOPY CAUSED BY HYDROGEN

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Hydrogen is known for affecting emission spectra of many other elements in Glow discharge emission spectroscopy (GDS) [1], causing violations of the standard calibration model, i.e. matrix effects. If a matrix M is analysed, direct proportionality is assumed in most cases between intensity $I_{\lambda(E),M}$ of certain line of an element E and the product ($c_{E,M}\ q_M$) of concentration $c_{E,M}$ of that element in the matrix M and the sputtering rate q_M of that matrix:

$$I_{\lambda(E),M} = R_{\lambda(E)}\ c_{E,M} q_M \qquad (1)$$

The corresponding proportionality factor $R_{\lambda(E)}$, called emission yield, expresses intrinsic strength of the line $\lambda(E)$ in glow discharge excitation. In analytical work, emission yields of selected lines are established by calibration, so that relation (1) constitute a set of equations for different elements, that is subsequently used to interpret (quantify) measurements of unknown samples. To correct for the matrix effects caused by hydrogen, a multiplicative correction can be introduced, of the type

$$R^H_{\lambda(E)} = R_{\lambda(E)}\ f\left(n_H\right) \qquad (2)$$

where $R^H{}_{\lambda(E)}$ is emission yield of the line $\lambda(E)$ in the presence of hydrogen and $f(n_H)$ is a function of the number density of hydrogen atoms in the discharge. In practice, intensity of a hydrogen emission line is taken instead of n_H, as it is a directly measurable quantity, proportional to the number density of *excited* hydrogen atoms.

Effects of hydrogen on GDS spectra are complex and not yet fully understood. Some mechanisms responsible for these effects described so far are e.g. charge transfer excitation of certain ionic levels of an analyte by hydrogen ions (iron and titanium [2]) and effects related to the ions and metastables of the working gas (usually argon) in the plasma, such as Penning processes and charge transfer reactions between argon ions and the analyte atoms [3]. Hydrogen diminishes the number densities of both argon ions and argon metastables in the discharge, and, consequently, causes a decrease of populations of such levels of the analyte atoms and ions that are excited by these species or that are involved in their cascade deexcitation. Moreover, presence of hydrogen in the plasma reduces sputtering rates. Common quantification algorithms take variable sputtering rates of unknown samples into account and the modified sputtering rate itself virtually does not affect analysis of unknowns.

Examples will be given of applications in bulk analysis and depth profiling by GDS in which hydrogen plays a significant role. Effects of hydrogen on some analytically important emission lines of different elements will be described.

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DEVELOPMENT OF NEW IONIZATION SOURCES FOR DMA: COMPARATIVE STUDY OF PHOTOIONIZATION AND APGD SOURCES

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Differential mobility analysis (DMA) and other techniques based on ion mobility measurements are becoming powerful alternatives for analysis in fields where chromatography and mass spectrometry have been traditionally used. These techniques have several advantages compared to chromatography or mass spectrometry, since measurements are faster than chromatography and they work at ambient pressure. The ion mobility has mainly been associated with the analysis of volatile compounds for homeland security [1] as well as environmental and biological applications, such as explosives, chemical warfare agents or drugs detection [2].

The DMA technology can work at ambient atmosphere with air as carrier gas. The ion mobility is given by the acquired velocity of a particle (or molecule) charged at ambient pressure when an electric field is applied [3]. The ion mobility depends on several parameters such as ion charge, number density of neutral-gas molecules, effective temperature, etc.

The ion sources employed in ion mobility can be based on many different operation principles, such as: 1) radioactivity-based ionization; 2) electrospray ionization (ESI) and secondary electrospray (SESI); 3) surface ionization; 4) matrix-assisted laser desorption/ionization (MALDI); 5) photoionization; 6) flame ionization; 7) corona discharge (CD), and 8) soft X-rays. While radioactive sources are used in many IMS instruments, the interest in nonradioactive sources have been steadily growing.

Atmospheric pressure glow discharges (APGDs) have been used as reliable ionization sources in mass spectrometry [4], so they could be a new potential source for mobility analysis. The DMA equipment used in our studies is a prototype developed by IONER (www.ioner.eu) and based on a special IMS, with a UV lamp (10.6 eV) as ionization source. This communication compares the ionization capabilities of this source with a new APGD under development in the University of Oviedo for the analysis of volatile organic compounds.

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APPLICATION OF PULSED GD-TOFMS AS A POWERFUL SCREENING TOOL FOR CONDUCTIVE POLYMERS CHEMICAL IDENTIFICATION

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Nowadays it is known that polymers (plastics) have good insulating properties and are among the most used materials. However, it has been developed certain polymers with conducting properties: they are able to combine the electrical properties of metals and the high flexibility and low density of plastics. Conductive polymers can be used in a wide varitey of applications, including those that exploit the specific physical properties of the polymer (e.g. in the manufacture of conductive layers, fibers, antistatic coatings, and transparent electrodes and light emitting diodes) and those which include changes in the physical properties of polymers as are chemical and electrochemical sensors. Their most spectacular applications are in the field of biomedicine and biotechnology, for example, in the manufacture of artificial muscles and nerves.

In this communication, the analytical potential of pulsed radiofrequency glow discharge with detection by time of flight mass spectrometry (rf-PGD-TOFMS) is investigated for the analysis of such type of samples. This combination permits the quasi-simultaneous detection of ions along the GD pulse period and, thus, the observation of the time domains with different ionization mechanisms in the formed plasma (denoted as pre-peak, plateau and after-peak regions [1]). Aiming to search for sensitive molecular information, different glow discharge chamber designs were investigated (e.g. with different distance from sample to MS interface, or with different configuration for Ar entrance) in our experiments.

A polymer containing poly (phenylene sulfide) (PPS) was used first for the optimization of the experimental conditions, working in millisecond pulse regime. Subsequently, differentiation and identification of two conductive polymers, PPS and polyaniline (PANI), and two non-conductive polymers, poly (methyl methacrylate) (PMMA) and polystyrene (PS), was investigated through their fingerprinting spectra in plateau and after-peak regions.

On the other hand, it was observed that some of the polyatomic ions were formed by external compounds of the sample (e.g. due to vacuum microleaks). The use of a prechamber with an argon flow was here investigated trying to minimize or avoid the presence of this type of interference [2]. The role of this external argon flow is to displace the possible air entering the chamber, preventing it from reaching the plasma and from forming recombinations with sample constituents. The successful combination of a proper GD design with the use of the argon prechamber has allowed us to discriminate the polyatomic ions and identify those that are characteristic of each polymer.

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FULL SURVEY CHEMICAL ANALYSIS OF THIN FILMS WITH PULSED FAST FLOW GLOW DISCHARGE MASS SPECTROMETRY

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Sector field or high resolution glow discharge mass spectrometry is broadly recognized as one of the most sensitive and robust analytical techniques for direct bulk trace element determinations. However, due to the nature of the magnetic sector field, scan speed is considered to be a limiting factor for depth specific measurements and practically this technique is not considered to be suitable for thin film analysis.

The fast flow ELEMENT GD instruments equipped with a microsecond-pulsed DC ion source provide the means to overcome these limitations for elemental analysis of thin films. In pulsed mode, the source of the ELEMENT GD is running at much lower nominal power conditions (typically 3–4 W) as compared to standard continuous DC modes, whilst not compromising on the high instrumental sensitivity. The combination of significantly reduced sputter rates with still very high sensitivities and an intelligent way to sputter only during the acquisition of data provides the analytical conditions of performing full survey analyses even with nanometer scale depth resolutions.

In fast flow glow discharge source (Fig. 1) with microsecond pulsed modes it is possible to achieve a depth resolution of <10 nm while still achieving trace to ultra-trace level detection power. For the analysis of major components in layered systems, the GD power can be further decreased to achieve even better depth resolutions at a lower overall sensitivity.

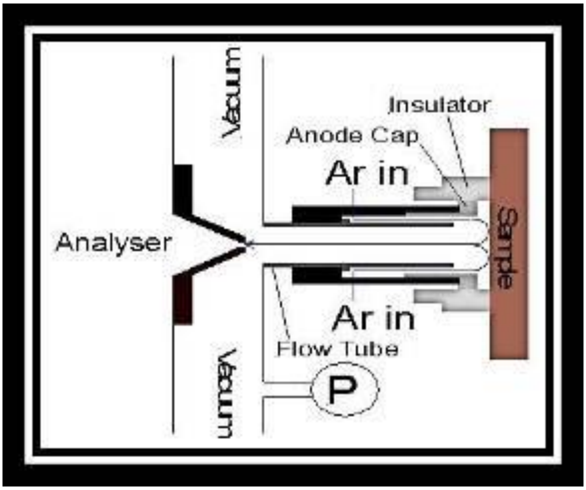
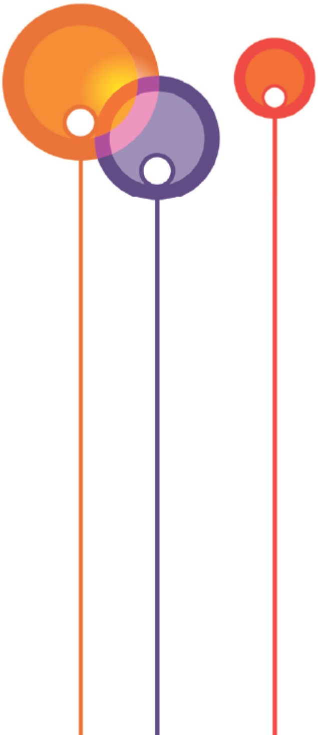


Fig.1. Schematic of the fast-flow glow discharge source

J section

Atomic emission spectroscopy



ULTRASOUND FOCUSED EXTRACTION AND ELEMENT QUANTIFICATION IN MIDDLE LIGHT PETROLEUM DISTILLATES BY ICP-AES AND ICP-MS

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Ultrasound extraction (UE) is more and more used as a preparation procedure in analytical chemistry and it was recently reviewed [1-3] in comparison with other techniques.

The main advantage of the preparation is the simplicity so that everyone can perform it [4].

The application of UE to petroleum distillates was not carried out so far.

A method for the quantification of Zn in middle distillates (200-400°C) by ICP or ICP-MS was assessed.

The preparation of the samples consisted of a quick extraction in acidic aqueous solutions by means of an ultrasound focused probe: the low acidic concentration of the extracting solution (just 1% nitric acid and 1% hydrochloric acid) and the total absence of solvents make this application compliant to analytical green chemistry [5].

The cleanness of the procedure holds both contamination and matrix interferences for instrumentation at a minimum.

The results of quantitative determination of Zn in different samples were compared to those obtained with the application of the official method ASTM 7111-11 to value the recovery and the effectiveness of the extraction.

The repeatability of the procedure was assessed for a content of 1 mg/kg of Zn: it was comparable to that of the official method (relative standard deviation or coefficient of variance: 2%).

A very conservative limit of quantification of the method was estimated to be 0.03 $mg \cdot kg^{-1}$ (by ICP-AES).

The procedure can be easily extended to other elements that were also tested as Na, Ca, Mg and more other elements could be tested by ICP-MS.

The blank extraction was evaluated for some elements; the only draw-back was contamination of Ti (and to a lesser extent of V) coming from the probe.

We tried to coin an easy acronym for the proposed preparation: I.R.E.N.E. (innovative, rapid, effective, no organic solvent extraction).

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SILICON DETERMINATION IN DIESEL AND BIODIESEL BY MICROWAVE-INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY

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Recently, a microwave-induced plasma optical emission spectrometer (MIP OES) has been made commercially available. One of its main advantages is that it runs on nitrogen gas, so an air compressor and a N_2 generator are sufficient to maintain a stable plasma, which reflects in significantly lower costs. The MIP tolerate high organic solvent loads and high dissolved solid contents [1]. In the present work, silicon determination in diesel and biodiesel samples by MIP OES with a flow blurring nebulizer (FBN) is evaluated. Three sample preparation procedures were applied: a) microwave-assisted acid digestion in closed vessels (Ethos 1600, Milestone, Sorisole, Italy) using HNO_3 7 $mol\cdot L^{-1}$ and H_2O_2 30% m/m; b) microemulsion in n-propanol [2]; and c) direct dilution of samples in ethanol 90 % v/v. The Agilent Technologies 4100 MP-AES was employed in all determinations. It was operated at 1.0 kW of applied power, with 100 – 160 kPa nebulizer pressure, – 30 to 0 mm of viewing position, and 10 s of signal integration time. An external gas control module (EGCM) was used to inject air into the plasma and prevent carbon deposition on the torch and the optical components. This device contributes for plasma stability and reduction of background emission from organic matrices. Limits of detection (LOD) varied from 5 to 240 $\mu g\cdot L^{-1}$ and relative standard deviation (RSD) values were lower than 2% in all procedures. The accuracy was evaluated by spike experiments and recoveries were between 80 and 102%. The influence of Ca, K, Mg and Na as concomitant ions on silicon determination by MP AES was investigated and neither each single element nor their combination in the same solution affected Si emission signal. Sample dilution in ethanol is recommended since it presents a higher sample throughput and the possibility of using external calibration with inorganic standards in aqueous solution. Despite the lower temperature of the N_2-MIP used in this work, neither carbon deposits nor loss of instrument performance were observed while introducing diesel and biodiesel microemulsions or samples diluted in ethanol 90% v/v. Considering that the 4100 MP-AES runs on atmospheric air (N_2 gas is obtained from an air compressor and a nitrogen generator), an important advantage of this instrument is its low cost of operation.

Acknowledgment

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DETERMINATION OF PALLADIUM CONTENT IN VALACYCLOVIR HYDROCHLORIDE USING INDUCTIVELY COUPLED PLASMA – OPTICAL EMISSION SPECTROMETER WITH AGM-1 (AUXILIARY GAS MODULE)

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The control of impurities (by catalysts, raw materials (plants, animal proteins, rDNA) and Excipients (stabilizers, fillers, binders, release agents, flavors, colors and coatings)) has always been a critical issue to the pharmaceutical industry. Traces of inorganic impurities can reduce the drug stability and shelf life of pharmaceutical products. The *U.S. Food and Drug Administration* (FDA) and the *British Pharmacopeia* (BP) strongly advise that contamination problems be fully investigated in a timely fashion.

In this study, the Palladium content in the *Active Pharmaceutical Ingredient Valacyclovir Hydrochloride* was determined by using Agilent's Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) equipped with the AGM-1 (Auxiliary Gas Module) accessory. The analysis was performed to the requirements of *USP 35 Official Monographs/Valacyclovir* (p.no 4983). In this experiment, 100 mg of different batches of *Valacyclovir Hydrochloride* were directly dissolved in dimethyl sulfoxide and hydrochloric acid (98:2) and made up to 10 mL in standard flask. Recoveries for spike solutions were found to be in the range 100 – 108%. Detection limit and quantification limits were found to be 1.0 and 3.5 $ng \cdot g^{-1}$ respectively. The relative standard deviation observed was less than 2%. These results demonstrate the ability of the Agilent ICP-OES to achieve excellent performance, even when analyzing challenging organics solvents.

JP-4

VEGETABLE OIL ANALYSIS FOR BIODIESEL PRODUCTION USING THE AGILENT 4100 MICROWAVE PLASMA – ATOMIC EMISSION SPECTROMETER

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The production and use of biodiesels have extensively increased over recent years because of the multiple benefits of these products: biodegradability, low toxicity, and the significant reduction of pollutants. Biodiesel is produced from vegetable oil via a transesterification reaction. The presence of elements such as Phosphorus, Calcium and Magnesium in the vegetable oil can impact the quality of the end product and must therefore be analyzed before transesterification.

The innovative Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (4100 MP-AES) has been used for this purpose. This new technology runs entirely on air, eliminating the need for expensive flammable gases. The 4100 MP-AES is able to perform fast multi-element organic analyses with the lowest running costs and analytical performance exceeding Flame Atomic Absorption. Moreover, the robustness of the plasma and the ease of use of the 4100 MP-AES make this technology ideally suited for routine analysis of complex organic matrices while ensuring maximum safety. This paper presents the analysis results of vegetable oil samples. Detection limits and stability tests are presented.

COMPARATIVE STUDY OF DIFFERENT METHODOLOGIES OF TRANSIENT SIGNAL PROCESSING FOR DETERMINATION OF CHROMIUM BY SPME-TD-PLASMA-OES

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A method has been developed for the determination of total chromium by solid phase microextraction of chromium(III) complex and subsequent thermal desorption with plasma optical emission spectrometric detection and derivative signal processing. Time-resolved spectra were registered by a CCD detector and next a transient signal at the selected wavelength was created. The signals were clearly visible, but especially when the concentration decreased, they could hardly be distinguished from noise. Particularly applying baselines in order to calculate peak heights or peak area more precisely was complicated due to baseline variations.

Numerical derivative techniques based on the Savitzky-Golay algorithm have been studied for the transient signal de-noising and baseline correction as well as for the correction of spectral interferences observed on the registered spectra by extracting useful information from overlapped spectral lines of the analyte [1,2]. In this paper we show a comparison of three methods of signal treatment for the capability of de-noising signals. An evaluation of the signal profiles obtained with and without the numerical derivatization has shown that compared to original spectrometry, the derivative spectrometry significantly improved the detection limit A more complex approach is proposed to eliminate the interference information for quantification of chromium using external calibration that includes noise, background and spectral overlapping by OH rotational lines. After numerical derivatization of selected time-resolved spectra, the transient signal is created based on processed data. The results showed that the derivative techniques not only eliminated the spectral interferences from the matrix, but also reduced the matrix effect on detection limit. Compared to original spectrometry, the derivative spectrometry significantly improved the detection limit. Thus, the detection power of the analytical method is improved and the evaluation of transient signals can be performed more comfortably and precisely.

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PROPERTIES OF A KHz FREQUENCY NITROGEN MINIPLASMA FOR TRACE ANALYSIS BY ATOMIC SPECTROSCOPY

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In this work we show the possibility of use ultrasonic frequencies for generation of low cost analytically useful nitrogen plasma by implementation of rotating field. The rotating field arrangements have been proven to exhibit high spatial and temporal stability. The additional advantage of the rotating field assembly over the stationary field multi-electrode system is that the electric field lines are all closed in a planar slice between electrodes while in average the potential at the axis of this plane is equal to zero [1].

A novel acoustically driven plasma radiation source was developed and tested. The nitrogen plasma is created by a multi-electrode system, which is excited by a 1.7 kHz acoustic wave with powers ranging from 200-300 W. Optical emission spectroscopy measurements were performed using a CCD spectrometer model AvaSpec-3648, focal length 75 mm, grating 2400 lines$\cdot$mm^{-1}. The resultant plasma shape allows easy entrainment of wet sample aerosol, and the plasma is immune to sample loading.

We employ a set of optical emission spectroscopic techniques to characterize a low power, low gas flow rate, atmospheric-pressure nitrogen plasma. The rotational temperature of the N_2 molecule was used to determine the kinetics of gas temperature. The gas temperature of the plasma could be above 1000 K. The excitation temperature was calculated from the slope of the Boltzmann plot using Fe atoms as the thermometric species. Over power range from 200 W to 300 W, excitation temperatures are up to 5000 K.

The goal of this study has been to develop a nitrogen plasma source which could offer comparable performance to commercial plasma sources along with advantages such as smaller size, simplicity and reduced running costs. The measured performance when used as a spectroscopic source in conjunction with a miniaturized spectrometer with a CCD detector showed detection limits approaching those of commercial nitrogen plasma sources [2,3]. Because of the robustness of the nitrogen plasma it is possible to use ultrasonic nebulization without aerosol desolvation as sample introduction technique. For the selected measurement conditions, the plasma was established to have the detection limit for Cu, Cr, Hg and Al below 10 ng$\cdot$mL^{-1}.

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APPLICATION OF ICP OES TO THE EXAMINATION OF POSTMORTEM MATERIAL IN A CASE OF POISONING WITH AN IODINE COMPOUND

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In toxicological examinations, in cases where the circumstances of the event do not indicate any particular kinds of compounds, detection of a poison is difficult. It seems that in this field, inductively coupled plasma optical emission spectrometry (ICP OES) can be helpful. This technique has mainly been used up till now in the toxicological analysis of biological material for metals (detection and quantification) and in some cases nonmetals (boron, phosphorus) as well.

In this work, the results of examination of postmortem material (blood, internal organs) in a case of sudden death of a 26-year-old man who had been hospitalized for 9 days due to severe headache and vertigo, in whom an autopsy did not reveal the cause of death, is presented. During the course of chemico-toxicological analysis, it was initially suspected that the man was poisoned with a selenium compound (samples of biological material digested in an Ethos 1 microwave system and in classical glass apparatus were pink). Using ICP OES and atomic absorption spectrometry with the hydride generation technique (HG AAS), such poisoning was excluded – in brain, liver and kidneys, as well as in blood, only the “normal” levels of selenium (found usually in non-poisoned people), were determined. However, ICP OES unexpectedly enabled detection of iodine in great amounts in all tissues and blood: this element was a strong interferent at one of the three emission lines characteristic for phosphorus ($\lambda = 178.284$ nm). Concentrations of iodine exceeded “normal” levels in biological material by about 200 times and were as follows: brain – 239, liver – 427, kidneys – 3333, blood – 2056 $\mu g \cdot g^{-1}$. The method achieved a limit of detection of 0.066–0.097 $\mu g\ I \cdot mL^{-1}$ of digested sample of biological material (depending on the emission line) and covered a linear range up to 3 $\mu g\ I \cdot mL^{-1}$. The recovery of spiked samples of blood and brain, and the total iodine content of reference material *NIST 1577b Bovine Liver* – which has neither certified nor informational values for iodine – were measured. The best analytical line for iodine determination in biological material was estimated as $\lambda = 183.038$ nm (without interference due to phosphorus).

The high concentrations of iodine in postmortem material taken during autopsy of a young man were confirmed using the starch-iodine spectrophotometric method.

The results obtained confirmed that ICP OES can be used for estimation of poisoning with unknown inorganic substances, particularly iodine.

MERCURY DETERMINATION IN BIOLOGICAL MATERIALS BY ICP OES IN CASES OF METALLIC MERCURY INTOXICATION

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Inductively coupled plasma optical emission spectrometry ICP OES, which enables simultaneous detection and determination of many elements in the same sample, can be a useful tool in routine toxicological analysis in the forensic laboratory. One of the advantages of this technique in such analyses is the possibility of using it for screening in cases of poisoning by an unknown compound(s). Other analytical techniques frequently used in the diagnosis of acute and fatal poisonings, e.g. atomic absorption spectrometry (F AAS, CV AAS, HG AAS) or spectrophotometry, do not allow screening analysis when looking for an unknown inorganic poison. Mercury (Hg) is considered to be one of the most toxic metals, being toxic in any chemical form: metallic, organic or inorganic compounds. Its concentrations in blood, urine and internal organs in such cases are many times higher than in not exposured persons and can be in the range of several $\mu g \cdot mL^{-1}$ or $\mu g \cdot g^{-1}$.

The aim of this study was to develop a convenient method of analysis of Hg in biological material (internal organs, urine and blood) by ICP OES at levels occurring in cases of acute poisoning. Analyses were carried out by Thermo spectrometer ICP-OES iCAP 6300 DUO with CID detector at the 194.227 nm line. Prior to analysis, samples were wet digested: (1) classically in a closed system or (2) with application of microwave energy.

The study encompassed selection of the optimal sample digestion method and calibration technique (calibration curve without internal standardization or standard addition technique), and evaluation of detection and quantification limits (LOD and LOQ), as well as the repeatability and accuracy of the method. The accuracy was assessed on the basis of a spike recovery experiment. The mean relative standard deviation (RSD) was 6.6%. The LOD and LOQ were much lower than concentrations of Hg encountered in biological material in cases of fatal poisonings.

The method was applied to the analysis of samples of blood, urine and several internal organs of a person who had died as a consequence of intravenous metallic Hg injection and to the analysis of samples of food to which metallic Hg had been deliberately added. The concentration of Hg in the analyzed material was in the range of 3.2 $\mu g \cdot mL^{-1}$ (blood) – 83.8 $\mu g \cdot g^{-1}$ (kidney). Obtained results were comparable with results by the cold vapour atomic absorption spectrometry (CV AAS) technique.

The developed method may serve as a screening method for detecting Hg and also as a method for its determination in biological material in cases of acute poisoning.

REAL-TIME RF POWER MONITORING OF PROCESS CHAMBER BY SELF-PLASMA OPTICAL EMISSION SPECTROSCOPY

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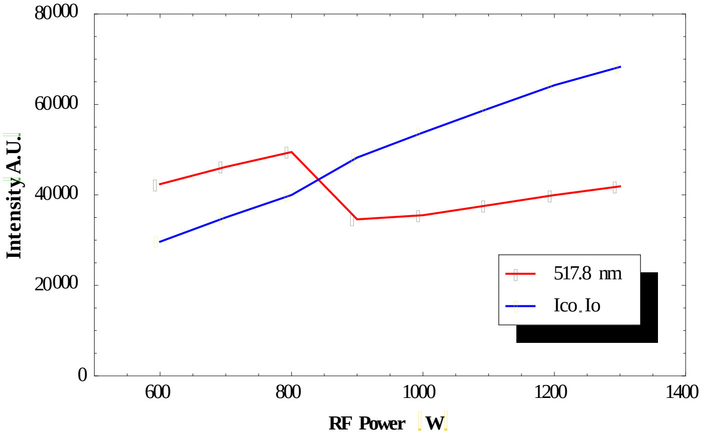
In the semiconductor manufacturing field, some unacceptable process performances by the lack of real-time control lead to significant waste and lower product yield. In order to maximize the product yield, a timely and accurately fault detection is needed. In a variety of detection methods, optical emission spectroscopy (OES) is the most common metrology in chamber monitoring and in process control. However, it is difficult to select the wavelength to monitor an abnormal process and it is more difficult to predict the cause of the fault detection from the data analysis in order to quickly recover the process chamber. In this paper, we investigated the plasma optical signals to monitor the RF power fault detection of the remote plasma source chamber. Self-plasma optical emission spectroscopy (SPOES) was used in our experiment because the chamber does not emit an enough light for using a conventional OES system. In addition, we suggested the calculation based on the optical emission line of the reactant gases instead of the statistical techniques, such as principal component analysis (PCA) and partial least square (PLS). The experimental results showed that this proposal method can detect process fault in real-time and provide the information to estimate the cause of abnormal detection.



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DEVELOPMENT OF A TUNGSTEN BOAT FURNACE FOR THE SIMULTANEOUS DETERMINATION OF Ag, Bi, Pb, Te, AND Zn IN NICKEL SUPER ALLOYS USING ICP-OES

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The mechanical properties of highly alloyed steels and nickel super alloys are not only determined by the major alloy constituents but also by several other factors like the production process or the thermal treatment (hardening) of the intermediate product. The presence of trace contaminants ($<100\ \mathrm{mg{\cdot}kg^{-1}}$) such as Ag, Bi, Pb, Te, and Zn can also severely alter the mechanical properties of these technologically advanced materials [1]. Most of the analytical procedures for these elements involve an acid dissolution of the sample, followed by matrix separation as the steel matrix is of great variability and causes severe spectroscopic and polyatomic interferences in ICP-OES and ICP-MS. Clearly, an analytical procedure employing direct solid analysis seems desirable for this type of samples.

In this contribution we will present preliminary results on our ongoing work on the use of a tungsten boat furnace (TBF) for the volatilization of Ag, Bi, Pb, Te, and Zn from nickel super alloys. The TBF was constructed from a resistively heated tungsten sheet placed in a small, argon flushed glass dome. A precisely weighted sample was placed on this sheet and after few seconds of flushing with argon the outlet of the dome was connected to the ICP. By quickly heating the tungsten sheet well above the melting point of the sample volatile analytes were introduced into the ICP whereas most of the sample matrix was left behind in the melt. Contrary to previous work [2] we intended to simultaneously detect all analytes at once and thereby significantly increasing sample throughput.

By using an axially viewed ICP-OES and solid calibration standards LODs comparable to fs-LA-ICPMS [3] were obtained. The main limitation of this technique was found to be the alloying of the tungsten boat with the sample. Thereby, the electrical characteristics of the boat were altered limiting the number of subsequent “shots” to about four.

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DETERMINATION OF MAIN METALS AND CONTAMINATING ELEMENTS IN VARIOUS HIGH PERFORMANCE PASSIVATES BY MICROWAVE PLASMA ATOMIC EMISSION SPECTROMETRY

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The plating quality as well as the visual appearance of coatings achieved by using passivates is crucially dependent on the correct concentration of the active elements which are typically present in the $g \cdot L^{-1}$ range as well as the concentration of impurities like Iron and Zinc, which are present in the range of $mg \cdot L^{-1}$ to $g \cdot L^{-1}$.

This work presents a simple method for a fast quantitative determination of all relevant elements in one dilution, by using microwave plasma atomic emission spectrometry (MP-AES). MP-AES utilizes a toroidal nitrogen plasma, where samples with high concentration of dissolved solids can be introduced into the plasma by using conventional sample introduction systems. This makes MP-AES an ideal and easy-to-use multi-element technique with low running costs.

The method has been applied to various high performance passivates and has been validated using titration methods as well as established ICP-OES methods.

ANALYSIS OF LIQUID FOODSTUFFS AND BEVERAGES BY MEANS OF DRIED DROPLET LASER ABLATION ICP OES

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The accurate determination of major and minor elements in liquid foodstuffs like fruit juices, soft drinks, wine, etc. is not only of interest when assessing their respective nutritional value, but also for monitoring noxious “heavy metals” arising from natural or anthropogenic sources.

Liquid food products have generally a challenging sample matrix with high concentrations of dissolved organic and inorganic constituents that can jeopardize correct measurement due to high viscosity and plasma-load. Therefore, the direct analysis of trace elements in this kind of liquid samples using conventional sample introduction devices (i.e., various kinds and combinations of nebulizers and spray chambers) is problematic; it requires either chemical decomposition of the organic components or dilution of the entire sample [1,2]. Besides being time-consuming, both approaches have disadvantages: if the samples are digested, a large amount of extra reagents has to be added, which raises the costs per analysis and increases the risk of contamination; if samples are diluted, the sensitivity is reduced which is especially challenging when assessing trace concentrations.

To overcome the abovementioned problems associated with the liquid sample matrix, Yang et al. proposed the Dried-Droplet method [3,4]: one single droplet of a liquid sample is deposited on a solid surface, the solvent is evaporated and the remaining precipitate is sampled via Laser Ablation. Thus, only a very small aliquot of the sample is introduced into the plasma and problems associated with conventional liquid sample introduction are circumvented. Although the Dried-Droplet method is very promising, one major shortcoming prevails: the dried residue is in most cases laterally inhomogeneous due to ring formation during the drying process. This necessitates ablation of the entire dried droplet to obtain quantitative recoveries.

In this contribution, the feasibility of Dried-Droplet analysis in combination with ICP-OES will be demonstrated; to the best of our knowledge, this method has to date been used exclusively with ICP-MS instruments. The problem of inhomogeneous lateral analyte distribution will be evaluated both qualitatively and quantitatively. The addition of internal standards to the liquid sample and the use of substrate-inherent elements for internal standardization will be compared and the performance of various organic and inorganic substrates for droplet deposition will be studied as well as the influence of different drying procedures.

The use of chemical additives for improved droplet-formation will be evaluated (e.g., buffer solutions, surfactants). Additionally, the influence of parameters like diameter and shape of the dried residue obtained and its lateral homogeneity on reproducibility and trueness of the analysis will be investigated. In order to easily locate the dried droplet on the substrate, different coloring agents (e.g., methylene blue, coomassie brilliant blue, ponceau S) will be evaluated, both in terms of blank values and in terms of their influence on droplet formation. The method will be applied to the analysis of trace-metals in different liquid food products and its performance compared with Electrothermal Vaporization (ETV) ICP-OES measurements in terms of sensitivity, reproducibility and trueness.

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MATRIX EFFECT OVERCOMING IN ICP AND DCP-ARC - ATOMIC-EMISSION ENVIRONMENTAL ANALYSIS

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Environmental analysis is one of the most important fields of modern analytical chemistry due to a growing interest of a man to the transformation and transport of substances in nature. It was developed a great variety of new powerful instrumental methods for elemental analysis, nevertheless the matrix effects remains a serious problem when you need to analyze the samples of complex composition. There are a few of approaches which allow eliminating or taking into account those influences but the most often use an internal standard method. Unfortunately, in some cases this expedient doesn't work.

The goal of the present investigation was an elaboration of the approach to eliminate those effects using a successive dilution method. Earlier a similar way has been applied by Gilbert [1] for the evaluation of the results in atomic-absorption spectrometry, but no attempts have been done in AES.

The essence of this approach consists in the use successive dilution of the samples under testing. Then for each sample of n-fold dilution the dependences of $\lg C$ (or C) as a function of $\lg \frac{1}{n}$ (or $\frac{1}{n}$) is constructed, where C is an apparent element content in a probe under appropriate dilution factor n which is estimated using a calibration plot for pure analyte in the absence of matrix components. The further extrapolation of this dependence to infinite dilution of the sample gives the true value of the concentration of the analyte in the probe.

The developed method demonstrates it's acceptability for trace elements determination in the solid environmental samples using DCP-arc-AES without previous dissolving and for the highly mineralized waters elemental analysis using ICP-AES.

The main adventures of this approach are the following:

a) it allows a correct determination of analytes in any type of unknown samples without additional information about major components contents;
b) the detection limits for minor elements in the sample under analyzing may be reduced sufficiently due to the use of a series of the most suitable dilution factors.

This method have been also successfully applied for DCP-arc-AES analysis of the reference standard solid samples (grass, soils, river and lake sediments, animal tissues, et al.), the comparison of the results using independent analytical techniques also has been done to. The produced data demonstrated a good acceptability of a developed approach for environmental analysis.

The application of this approach for trace elements determination in highly mineralized waters by ICP-AES also showed its efficiency when using "added – found" method.

The major limitation of the proposed approach is that at present moment there is no suitable mathematical background of this assumption.

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JP-14

ADVANCES IN LIQUID SAMPLE INTRODUCTION IN ICP-OES: A NEW EFFICIENT PROTOTYPE FOR REDUCED SAMPLE CONSUMPTION

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Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Mass Spectrometry (ICP-MS) are highly sensitive elemental analysis techniques widely used in modern analytical laboratories for the identification, quantification and speciation of trace elements. With these techniques, samples are most commonly provided in liquid state and the usual method to introduce it to the plasma is through a nebulizer and a spray chamber. Most of the liquid sample introduction systems used in the commercial ICP spectrometers are capable of transporting only a small percentage of sample to the plasma, typically less than 5%, and therefore 95% of the sample is wasted. Therefore, extensive research on this area has been conducted over the last few decades. Micronebulizers and direct injection nebulizers have been developed in order to increase the liquid sample introduction efficiency. However, most of these devices are usually prone to clogging due to their nozzle geometry, which strongly reduces their application in real sample analysis, especially in ICP-OES. On the other hand, introduction of the cyclone spray chambers has permitted to increase the absolute amount of aerosol transported to the plasma. Nevertheless more studies are still required in this area.

Recently, the *OneNeb*® has been introduced on the market. It uses the *Flow Blurring*® nebulization mechanism which provides generation of very fine aerosols for a broad range of liquid sample flows and, due to the physical characteristics of its nozzle geometry, permits the introduction of high solid content samples without clogging (up to 25% dissolved solids and up to 75 µm particulate matter). This permits it to be used both as conventional and as micronebulizer without compromising the quality of the results obtained for a wide range of real samples.

The work presented here has been focused on redesigning the whole sample introduction system, using the *OneNeb*® as the center piece in order to obtain advantages in aerosol transport efficiency to the plasma. As a result, a new liquid sample introduction system has been developed and characterized, that delivers high instrument sensitivity, whilst simultaneously reduces significantly the sample volume needed. It consists in an *OneNeb*® nebulizer and a new design cyclone spray chamber incorporated at the base of a modified ICP torch with increased injector tube diameter.

Analytical figures of merit (i.e., sensitivity, precision, limits of detection) and certified reference material analysis results obtained with the new sample introduction system prototype in ICP-OES are presented for low liquid flows (200 and 20 µL·min^{-1}) and for a range of environmentally important elements. These are compared to those obtained with the standard sample introduction system of the spectrometer.

This new system delivers very high signal generation efficiencies in comparison with the conventional sample introduction setup, and offers similar analytical figures of merit while the liquid sample flow requirements are 10 to 100 times lower.

Acknowledgement

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DETERMINATION OF MERCURY IN SOILS AND SEDIMENTS AFTER PRECONCENTRATION OF MERCURY VAPOR BY SPME FOLLOWED BY THERMAL DESORPTION AND OES DETECTION

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A compact 6 kHz rotating field miniplasma operating with helium as working gas at ambient atmosphere has been evaluated as a spectrochemical radiation source directly coupled with solid-phase microextraction (SPME) and subsequent thermal desorption (TD), and the suitability of the system for the determination of mercury in soils and sediments has been studied by optical emission spectrometry (OES). The content of element extractable fraction was examined after recommended leaching procedures. Cold vapor generation (CVG) head space SPME was employed for the separation and preconcentration of mercury. Retained vapor is then desorbed in TD unit and transferred with He carrier gas into the plasma. A three-electrode rotating-field digitally-controlled system operating at 6 kHz frequency has been optimized and coupled with a small CCD spectrometer with the use of optical fiber.

The concentration of nitric acid and sodium borohydride for CVG of mercury has been optimized. The emission intensity of the Hg line at 253.6 nm as a function of power (50–200 W) as well as of the total gas flow rate (50-700 $mL \cdot min^{-1}$) was evaluated. It was found that an increase of power over 120 W did not lead to a large increase of the intensity for Hg line. Under these conditions (120 W) different He flow rates were tested, achieving the highest Hg emission intensity when using a carrier gas flow rate of 50 $mL \cdot min^{-1}$. The plasma gas flow rate was kept constant during all optimization experiments being of 500 $mL \cdot min^{-1}$. The sharp transient signal obtained for Hg at desorption temperature of 150°C enables the use of the peak height for the calibration instead of the peak area which simplifies the calibration procedure. The shape of the peak indicates that desorption of Hg vapor from the Carboxen/PDMS coating is relatively fast. Analytical characteristics include detection limit of 4.8 $pg \cdot mL^{-1}$, linearity of three orders of magnitude and signal stability of between 5 and 9%.

The proposed method has been applied to determining of Hg in four soil and sediment certified reference materials. The standard addition technique was used to ensure good accuracy of the results. The results obtained were typically within the 95% confidence intervals of the certified or reference values, and the precision, expressed as relative standard deviation, was between 5 and 9% depending on the material studied.

The compact combination of solid-phase microextraction, thermal desorption, low cost helium miniplasma source and the miniature OES instrument led to a cost-effective and sensitive miniaturized system for the determination of trace Hg. A significant advantage of both the sample introduction method and He miniplasma is a low associated background. Furthermore, this instrument has the advantage of being robust and easy to handle and allows fast analysis.

Acknowledgement

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INVESTIGATION OF USEFULNESS OF DIFFERENT ELEMENTS POTENTIALLY APPLIED AS INTERNAL STANDARDS IN ICP-OES MEASUREMENTS

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The matrix effects are the important problems in the ICP-OES analysis of environmental samples (stream and lake sediments, soils). In these types of samples the major elements (Ca, Mg, Fe etc.) occur in the high concentration and cause the inter-ferences during measurements.

Using the appropriate internal standard is one of the method of minimizing the matrix effects. There are a few general requirements for element used as the internal standard. The most important for the internal standards are: a very low amount in the samples, stability in solutions, high analytical sensitivity of selected lines, negligible spectral interferences and similar analytical behaviour to investigated lines of analytes.

In our study Be, Bi, Eu, Ge, Ir, Lu, Re, Rh and Ru were selected as potentially internal standards. The solution of these elements at the concentration of 1 $mg \cdot L^{-1}$ were tested. Calcium at different concentrations was added to the solutions to imitate the sample matrix. The highest content of calcium in the solution with internal standard was 4000 $mg \cdot L^{-1}$.

In the presence of the high calcium amount significantly variable behaviour of the investigated analytical lines was observed. The strongest signal suppression (22%) was observed for ruthenium (233.4 nm Ru) when Ca was present at 4000 $mg \cdot L^{-1}$. The lowest signal suppression was measured for europium (412.9 nm Eu). Similar measurements were done for the trace elements (As, Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn). Then the behaviour of the internal standards and selected trace elements in different matrices was compared and evaluation of the usefulness of the internal standard was done on the basis of the experiments. We have concluded, that in case of determination of many trace elements the best results were obtained when several internal standards were used.

The correctness of used of internal standards was showed on the example of analyses of soils and lake sediments samples.

JP-17

DETERMINATION OF SELECTED ELEMENTS IN FAME BY ICP OES TECHNIQUE USING INTERNAL STANDARD METHOD PERFORMED IN CONTINUOUS FLOW SYSTEM

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Fatty acid methyl esters (FAME), produced from natural sources like vegetable oils or animal fats [1] and commonly known as biodiesel, can be used as fuel for diesel engines alone or in a blend with petroleum diesel fuel. Determination of selected elements are of great importance for FAME quality control. The *European Standard EN* 14214 [2] defines requirements for FAME delivered on fuel market. The standard specifies, inter alia, the maximum allowed content of Ca, K, Mg, Na, P and S in FAME. The limitations of metals contents are necessary due to their ability to form undesirable compounds that can damage some pieces of internal-combustion engines and reduce time of their operation. The presence of phosphorus may be the reason of changing the fuel properties, whereas sulphur is a source of air pollution in the form of SOX. The EN 14214 standard also specifies test methods employing FAAS or ICP OES techniques for determination of alkaline metals (Na and K), ICP OES technique for determination of alkaline earth metals (Ca and Mg) and phosphorus, and XRF or UVF techniques for determination of sulphur.

The internal standard method is widely used for viscosity effects compensation in ICP OES organic samples analysis. Generally, the method is based on employing an additional element that is added to both sample and standards solutions in the same concentration during the step of their preparation. In practice, implementation of the internal standard method in manual mode is laborious and time-consuming. Therefore, an attempt has been made to improve the step of preparation solutions with the use of continuous flow technique.

In the proposed approach, an internal standard is introduced into the system in continuous way, afterwards merged with a stream of sample (or standard), and finally the mixture is directed to the detector. All measurements were performed using the Spectro ARCOS ICP optical emission spectrometer with radial plasma viewing. The flow based procedure for determination of Ca, Mg, K, Na, P and S in FAME was developed. Beryllium, cobalt, scandium and yttrium were used as internal standards. Certified reference material of biodiesel with established values of concentration of the selected elements was used for accuracy verification. The results are characterized by acceptable accuracy and very good precision. In comparison to the manual batch procedure, the developed approach makes an analyst work more convenient and shortens the time of analysis. It can be recommended for determination of the selected elements in FAME routine analyses.

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APPLICATION ICP OES AND ICP MS SPECTROMETRY FOR PLANT QUALITY EVALUATION

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The macro and trace element contents of plants are known to be affected by the cultivar of plant, soil quality, weather conditions during the growing, use of fertilizers and the state of the plants maturity at harvest. Among the elements selenium is an essential trace element for the health of humans and other animals. Deficiency of selenium in cells of living organisms have been reported in many parts of the world, where were the cause of various diseases, also cancer. To improve Se deficit Finland recommended the addition of this element to fertilizers for croplands. However, such supplementation of fertilizers can change also the micro- and macro-elements content of all vegetable foods [1]. Therefore, it is necessary to control the macro- and trace element contents, particularly in crops which are the primary source of food for humans and feed for farm animals, and which undergo Se supplemented fertilizers.

The aim of the work was to optimize developed previously procedure [1,2] including microwave assisted digestion and plasma spectrometry analysis for determination of Ca, K. S, P, Fe (Fe in roots) by ICP OES, and of Fe (in leaves) Mn, Cu, Zn, Se and Mo by ICP MS in roots, leaves of different stage of evolution and seeds (flour).

Four wheat genotypes, which were selected with the newly grown resistant lines were cultured in hydroponic conditions. Culture media contained a basic set of micro-and macro-elements (control), and an additional 5 μM or 15 μM Na_2SeO_4. The aqueous solutions were continuously aerated and each solution was changed every 2 days onto fresh medium. Analyses were performed in base seeds, 3-leafy seedlings (vegetative stage), the plants in the generative phase. Seeds and parts of plants (leaves and roots) were homogenized in liquid nitrogen and then lyophilized. Dry and weighed plant material was then put to further stage of the preparation in the assay.

Plant samples were digested in conc. nitric acid using multivessel (4) microwave system Anton Paar 3000 according to one stage program with maximum energy of 700 W and digest analyzed using either Optima 2100 or Elan DRC-e both Perkin Elmer spectrometers.

Trueness of analysis were confirmed analyzing reference materials CTA-OTL-1, INCT-OBL-5.

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DETERMINATION OF RARE EARTH ELEMENTS IN ELECTRONIC WASTE USING ICP-OES SPECTROMETRY

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Rare earth elements (REE) according to IUPAC definition are a selection of seventeen chemical elements from the periodic table. In contrast to their name the REE are much more present in the earth crust than expected, but because of their geochemical properties rare earth elements are typically dispersed and an economic treatment of rare earth minerals and ores is difficult. Nowadays the biggest ore deposits of REE are located in China (Mongolia) and China is controlling the global REE market.

As REE are required in the electro- and electronics industry the demand for special metals used in the manufacturing of “high tech” products is booming and in European countries the electronics trash could be worth to be recycled in order to be independent from expensive imports [1].

Experimental work has been done on electronic waste material such as mobile phones, notebook PC´s, electronic boards, batteries and more. Samples have been prepared using crushers and mills, homogenized and finally digested in a microwave digestion procedure.

The sample solutions have been measured using qualitative and quantitative analysis on a simultaneous ICP- OES spectrometer. The Shimadzu ICPE-9000 has been optimized for the determination of rare earth elements. Experimental data will be presented in comparison with alternative techniques.

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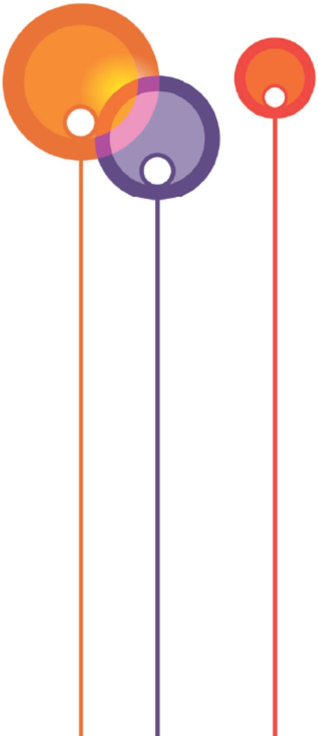
K section

Laser ablation and elemental imaging



IMAGINING AND QUANTIFICATION ANALYSIS OF THE ELEMENTS IN PEANUT SEEDS

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Laser ablation (LA) inductively-coupled-plasma mass-spectrometry (ICP-MS) is an effective approach for spatially resolved analysis of the elements in solid samples. In recent years, LA-ICP-MS has been applied to elemental imaging of plant samples such as bark [1], leaf [2], root [3], and grain [4]. It is noteworthy that most of these applications focused on the leaf and root for the uptake of nutritional elements or harmful heavy metals. The report on the elemental imaging of food samples is still scarce. Taking into consideration this background, the present authors are trying to carry out elemental imaging of food samples, e.g. plant seeds and grains, in order to provide valuable information on mineral nutrition and food safety.

In the present work, elemental imaging of peanut seeds was carried out using an LA-ICP-MS system. Furthermore, quantitation of the elements in different parts of peanut seed was carried out by ICP-MS after microwave assisted acid digestion using HNO_3, H_2O_2, and HF.

The elemental images of 11 elements, i.e. Mg, P, K, Mn, Fe, Cu, Zn, Rb, Sr, Mo, and Ba, in a peanut seed were obtained by the LA-ICP-MS measurement. It is noted that the distribution of Mo was significantly different from those of other elements such as K, P, and Mg. The enrichment of Mo was observed in the radicle of peanut seed and was further confirmed by the isotopic ratio of Mo.

Furthermore, the quantitative results of 18 elements were obtained for two parts of the peanut seed, i.e. the cotyledon part and the rest part including the radicle, the plumule, and the hypocotyl. The quantitative results were obtained for B, Cd, Na, Ca, Co, Ni, and Ga in addition to those observed by elemental imagination. The concentrations of most elements were generally equivalent in the two parts of each seed. However, the concentration of Mo in the part containing the radicle was significantly higher than that in the cotyledon by ca. 5 folds. These results confirmed the relative enrichment of Mo in the radicle of peanut seed as observed by elemental imagination.

The information of relative Mo enrichment in the radicle of peanut seed might help to prepare nutrient-enriched food.

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ELEMENTAL MAPPING USING THE SIMULTANEOUS DP-LIBS AND LA-ICP-OES SETUP

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The main advantage of DP-LIBS for surface analysis is not the quantitative accuracy of the obtained chemical information but the fact that each sampling position in DP-LIBS is analyzed individually. On the other hand, the approaches used for surface investigation based on laser ablation in which the ablated material is transported to a second excitation/ionization source (LA-ICP-OES or LA-ICP-MS) are generally characterized by lower matrix effects and higher accuracy of quantitative results. The aim of this study was focused on the development of analytical methods for the spatially resolved elemental mapping using both approaches simultaneously.

The special DP-LIBS and Laser-Ablation ICP-OES setup was designed by utilizing a modified commercially available laser ablation system UP 266 Macro (New Wave). The new ablation chamber was designed to be compatible with the UP 266 Macro laser ablation system and to fulfill all demands for simultaneous measurements utilizing both above mentioned techniques. The first ablation laser is used without any modification of the original optic. Therefore, it is possible to use all comforts of original UP-266 arrangement including sample illumination, sample surface monitoring by internal CCD camera and settings of laser ablation parameters. The second re-heating laser pulse with fundamental wavelength 1064 nm (Quantel, Brilliant) is focused parallel to the sample surface by 80 mm focal length glass lens through the second window from right side. For collection of laser induced plasma emission the window at the front side of the ablation chamber is used. For transport of ablated aerosol to ICP-OES spectrometers the carrier gas is used and ablated material is transported along polyamide tubing into the ICP-OES spectrometer.

One part of this study was focused on the development of analytical method for the spatially resolved elemental profile determination through the growth zones of urinary stones. The knowledge of the spatial distribution of major and minor elements in urinary stones is important for comprehension of the mechanism of its formation and for prevention and medical treatment of this disease.

Acknowledgement

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KP-3

BIOIMAGING TECHNIQUES OF METALS BY LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR DIAGNOSIS OF FIBROTIC LIVER DISORDERS

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Unbalance of metals may play an important role in the development of liver diseases. LA-ICP-MS is a highly accepted technique, widely used method for the determination of major, minor and trace metals. This work demonstrates the potential for the distribution analysis of metals (Mn, Fe, Cu, and Zn) in healthy and diseased (fibrotic/cirrhotic) human liver tissues using LA-ICP-MS. The trace metal concentrations in the samples were determined by single point calibration using NIST SRM 1577c (bovine liver) standard reference material. The results show that the metal distributions are homogeneous within the control tissue, while they are redirected within diseased livers resulting in significant metal deposits. Moreover, total iron and copper concentrations in diseased liver were found about 3 and 5 times higher than in normal liver samples.

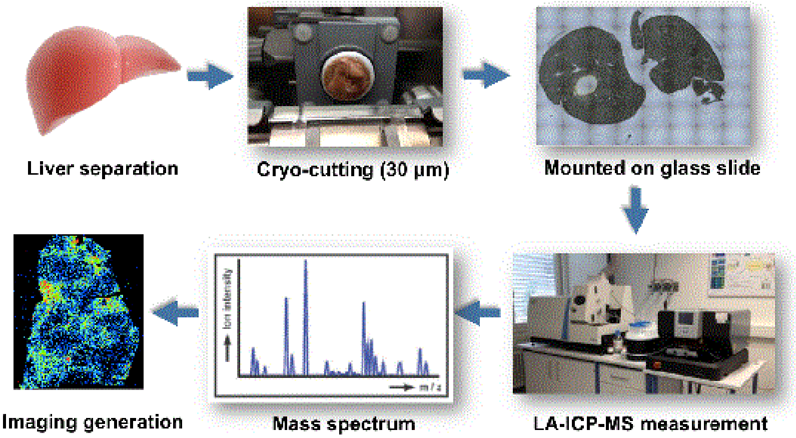

Fig.1 Workflow of imaging mass spectrometry from sample preparation of thin section by cryo-cutting, via the measurement procedure by scanning of thin tissue section (line by line), acquisition and evaluation of analytical data including quantification using single point calibration (NIST SRM 1577c bovine liver).

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KP-4

CHALLENGING THE SPATIAL RESOLUTION LIMITS OF HIGH-RESOLUTION MAPPING IN LASER ABLATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY USING ACTIVE 2-VOLUME CELLS

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Achieving the best spatial resolution (<10 µm) in laser ablation (LA) mapping experiments requires a high performance, quick washout sample cell. Historically this required a small volume sample chamber which in turn limited the physical size of samples that could be analyzed. Recent developments have given us 2-volume cell technology that can be employed to house large samples in an outer cell, but only ablate in a small volume inner cell (or cup).

All 2-volume cells are not alike and several different designs exist today. Minimizing the cup geometry presents a significant challenge in managing plume expansion as the ablated material can overshoot the cup height and, unless controlled, the aerosol will deposit on the outer cell window, inducing particle loss and elemental fractionation. The HelExTM cell is an active 2-volume cell, the first of its kind and well documented in scientific literature,1-5 that uses a vortex secondary cup gas flow that can be accurately tuned to contain and entrain the ablated aerosol efficiently to minimize deposition and maximize transmission through to the ICP-MS.

The data presented in this paper shows the effective spatial resolution achievable using such an active 2-volume cell by mapping a variety of samples such as geological thin sections, mollusk shell sections and biological thin sections. With the appropriate tuning parameters of the LA gas flows and the ICP-MS settings, we will demonstrate the data quality at a number of different resolutions between 4 µm and 10 µm to show what is possible.

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BIOIMAGING OF RICE TISSUE WITH THE USE OF A LASER ABLATION SYSTEM COUPLED TO THE AGILENT 7700X ICP-MS

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The combination of a laser ablation (LA) system with ICP-MS has been developed over the last years for the direct analysis of solid samples with almost no sample preparation. More recently, this technique has been deployed to study the metal distribution in biological samples. Indeed, the analysis of tissue section using LA-ICP-MS enables the generation of pictures showing the element pattern in the sample. Therefore, it is possible to identify the localization of the elements in the sample.

In the present works, the application of LA-ICP-MS has been deployed on a rice grain. After the section of the sample, its surface has been ablated with a 213 nm wavelength laser system. The abalation cell was directly connected to the Agilent 7700x ICP-MS for the elements analysis. Data were then converted into picture to create the element patterns present inside the rice sample.

EXAMINATION OF WRITING INKS BY LIBS TECHNIQUE FOR FORENSIC PURPOSE

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Standardized methodology for the ink analysis is based on the screening of ink sample dye composition. Sophisticated, but also destructive ones, separation techniques like thin layer chromatography (TLC) or capillary electrophoresis (CE) are most widely used for this purpose. There are very few methods offering analysis of the elemental composition of inks. Laser induced breakdown spectroscopy (LIBS) technique is not yet well established in forensic examination of the elemental composition of samples. However it fulfills the basic requirements of questioned document examinations, such as simultaneous multi-elemental characterization of a sample without any preparation, semi-destructive nature of analysis, short time of analysis, and simplicity.

The aim of the presented study was to evaluate the possibility of applying the LIBS technique to forensic analysis of writing ink layers deposited on a sheet of paper. The research was focused on the analysis of three colours of inks of different brands and types with the use of developed and optimized LIBS method. The discrimination capability of applied technique was evaluated. The ink samples were also examined with the use of CE technique as a reference method.

The elemental compositions of commonly available blue, black and red writing inks were established. For most of the studied inks it was possible to identify characteristic atomic emissions from one or more elements form group of Ba, Cr, Cu, Fe, Li, Mo, Mn and Ni. The detected elements indicated that the LIBS method is especially dedicated to the study of metallic or organometallic pigments with d-block elements and counter ions of anionic dyes. It was ascertained that the LIBS method is capable of revealing qualitative elemental differences between ink samples of different colours, types, producers and models.

The CE method allowed an efficient differentiation of blue and black inks but in contrast to the LIBS method it was insufficient in discrimination of inks of red colour.

The results revealed the great potential of LIBS as an effective, practical and robust technique dedicated to elemental characterization of writing inks, requiring a very small amount of sample. The combination of the great effectiveness of the proposed method and its advantages makes it a good alternative analytical tool to routinely used methodology for ink analysis. The applied CE technique provided additional information about dyes and additives used in analysed inks.

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KP-7

DEVELOPMENT OF A POLYMER BINDER AND A PELLET PRESSER FOR THE ANALYSIS OF POWDERED SOLID SAMPLES BY LA-ICP-MS

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Calibration strategies including preparation of homogeneous and matrix-matched calibration standards for quantitative analysis by laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) and/or laser-ablation inductively-coupled-plasma optical-emission-spectrometry LA-ICP-OES are more challenging than those in traditional solution introducing techniques [1,2]. Calibrations for LA-ICP-MS and/or LA-ICP-OES might be carried out using pressed powder with or without a binder, coprecipitate with addition of an elemental solution, glass fusion, metal complex with organic reagents, dried deposit with formic acid, and so on. However, taking into consideration the fact that there are various sample types for LA analysis, e.g. plant, soil, rock, metal, organic polymer, there is not a single method that could cover all of these sample types. Therefore, development of calibration standards and methods is still required for LA analysis.

In the present work, a fine powder of poly(methyl methacrylate) resin (PMMA) was obtained as the matching-matrix for the analysis of powdered solid samples by LA-ICP-MS. The PMMA powder was obtained by freezing pulverization of commercially available PMMA pillars and passing through nylon sieves with a pore-size of 250 µm. The PMMA powder was further mixed with an aqueous solution of CsCl to adsorb Cs, which was used as the internal standard in the measurement by LA-ICP-MS. The Cs-adsorbed PMMA powder was used as the binder and the matching-matrix to make sample disks for the measurement by LA-ICP-MS. The sample and the binder were simply mixed in a centrifuge tube and put into a laboratory-made disk presser, which was then put into an oven and heated at 110℃ for 2 h. At the optimized operating conditions, the linear correlation between the signal intensities of each elements (Al, P, Ca, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba) and the mass fractions of the sample was investigated with the certified reference material (CRM) of tea leaf powder issued by the National Metrology Institute of Japan (NMIJ), i.e. NMIJ CRM 7505-a. The square of the correlation factor was in the range from 0.78 for Fe to 0.92 for Zn. After the internal standard correction using Cs, the square of each correlation factor for all of the elements investigated was better than 0.99. A white rice flour CRM and a seaweed CRM were analyzed to confirm the usefulness of the present method.

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LASER ABLATION ICP-MS STUDY OF PROSPECTIVE GLASS INTERNAL REFERENCE MATERIALS

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The knowledge of concentration of uranium and thorium in rocks and minerals is of great importance for answering many geological questions. The same applies for the determination of U, Th concentrations in individual mineral phases of rocks. For such kind of analysis calibration standards are of great importance. There are several commercially available certified reference materials (CRM) made of glass that are commonly used in quantitative analysis of geological samples, for instance NIST Standard Reference Materials (NIST 610 – NIST 616). These CRMs are quite expensive and they do not sufficiently cover whole concentration range.

In our laboratory, we have two different batches of the glass standards with different average atomic number ($Z = 11.26$, and $Z = 24.80$). The concentrations of U and Th were determined in these glasses by instrumental neutron activation analysis (INAA), X-ray fluorescence (XRF) and spectrophotometry after complete digestion in the 1970s [1]. We analyzed these glass standards with up-to-date techniques ICP-MS and LA-ICP-MS. These techniques have lower limit of detection comparing to XRF, shorter time of measurement comparing to INAA, better linearity, and require less sample preparation comparing to spectrophotometry. All samples were analyzed after complete digestion by ICP-MS (Agilent 7700x, Agilent Technologies, Inc., Japan) with calibration prepared from certified reference materials of standard solutions (obtained from Analytika, Ltd., Czech Republic; certified by Czech Metrological Institute). Laser ablation (Analyte G2, Photon-Machines, Inc., USA) analysis was carried out with coupling to Agilent 7700x ICP-MS with quadrupole mass analyzer and Optimass 9500 (GBC Scientific Equipment Pty Ltd., Australia) with time-of-flight mass analyzer. In this case calibration was performed by NIST 610, NIST 612, and NIST 614 reference materials (NIST, USA).

All analyzed results were statistically evaluated and estimation of certified values of U and Th was performed. The uncertainty of measurement was evaluated and homogeneity of glasses was tested. All results will be presented in poster presentation. These glass standards will hopefully serve as internal reference materials for our future work.

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ANALYSIS OF HUMAN KIDNEY STONES: ELEMENTAL ASSOCIATION, IDENTIFICATION OF VARIOUS CONSTITUENTS AND QUANTITATIVE ANALYSIS BY LA-ICP-MS

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Urolithiasis is very painful disease and presents health trouble for approximately 1% of population of Czech Republic. Kidney stones originate from substances dissolved in urine and have systematically been divided according to chemical composition, namely: phosphate, oxalate, uric acid and cystine. There exist different causes of formation for particular urolith types relating to both acquired and inherited metabolic conditions. A comprehension of the mechanisms of urolith formation is of significant importance for prevention and medical treatment of this disease [1].

In this study, the examined samples of human kidney stones exhibit a wide range of variability in size, mineralogical structure and chemical composition due to different causations of patients´ disorders, their gender and age. Whewellite ($CaC_2O_4{\cdot}H_2O$), weddelite ($CaC_2O_4{\cdot}2H_2O$), apatite ($Ca_5(PO_4)_3OH$) and uric acid ($C_5H_4N_4O_3$) are the main mineralogical components of studied uroliths.

The aim of this study was focused on the development of a robust qualitative and quantitative analytical method for inter-elemental association through the growth zones of urolith samples using LA-ICP-MS. LA-ICP-MS method is commonly used for elemental mapping of one phase matrix, however, analysis of kidney stones requires solving problems concerning presence of various phases characterized by different physical and chemical properties. Moreover, these properties and lack of standard reference materials result in searching for special quantification approaches.

Consequently, the questions are devoted to: a) 2D imaging of elements of interest and revealing a composition, and identification of various constituents; b) study of elemental associations in various constituents; c) preparation of matrix-matched calibration standards and determination of elemental contents.

Acknowledgement

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OPTIMIZATION AND VALIDATION OF A LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY METHOD FOR DETERMINATION OF Cd, Cu, Pb AND Zn IN PLANTS

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A rapid and sensitive method was developed for the routine analysis of trace elements such as Cd, Cu, Pb and Zn in plants by LA-ICP-MS. The development and application of robust analytical methods for quantitative analysis of trace elements in these biological matrices may allow to acquire better understanding of the potential usefulness of these measurements in the analysis of plants suitable for phytoremediation.

Three different calibration strategies: matrix-matched external calibration, internal standardization and method of standard addition were tested. Matrix effects and different quantitation strategies were employed to demonstrate the utility of the analytical technique. The analytical performance of the method was checked by the analysis of two certified reference materials: SRM NIST 1547 Peach Leaves and INC-OBTL-5 Oriental Basma Tobacco Leaves using one-point calibration. Additionally SEM analyses were conducted to evaluate the efficiency of laser to sample interaction. Analytical results obtained by LA-ICP-MS were comparable to results obtained from analysis of digested plant samples by ICP-MS. An overall bias between 6 and 13% was found, depending on the sample while the overall precision was found to be better than 5% RSD for all samples. Statistical uncertainty in the analytical measurements was estimated in terms of precision (reproducibility and repeatability) and accuracy.

Quantification procedure was applied to study the distribution profiles for four elements (Cd, Cu, Pb, Zn) in the cross section of roots, stems and leaves of plants exposed to trace metals. The experiment was conducted in the laboratory under controlled conditions. This study enables better understanding on the fundaments of trace metals' transport from the roots to shoots in plants.

DEVELOPMENT AND APPLICATION OF METAL-TAGGED ANTIBODIES FOR IMMUNO-IMAGING BY USE OF LA-ICP-MS

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In immunohistochemistry disease-related proteins (biomarkers) are typically detected by antibodies. An absolute quantification of biomarkers by antibodies is presently not possible and usually only a single antigen can be detected in each assay.

Previously we have reported new methods for highly specific antibody-antigen conjugation by labeling of antibodies with different lanthanides in a multiplex approach for quantification by use of ICP-MS. For this purpose metal complex such as DOTA lanthanide markers (MeCAT) [1,2] were covalently bound to antibodies and quantified via laser ablation inductively coupled plasma mass spectrometry (ICP-MS). Our two-step strategy is based on a selective partial reduction of the antibody with Tris-(2 carboxyethyl) phosphine HCl (TCEP), and a subsequent partial metal label with MeCAT under physiological reaction conditions.

In our present work a multiplex approach for tissue samples is developed which is based on tagged antibodies which are incubated with the tissue sample. Laser ablation ICP-MS is used as imaging technique for the tissue slices.

In this context we have investigated different internal standards which can be applied in LA-ICP-MS and will report a procedure in which an internal standard was printed onto the tissue section to correct for variations and drift effects. In addition variations of the tissue thickness was corrected with iodine [3] as an internal standard.

We have applied these procedures for immune-imaging of cancer tissue with the MeCAT tagged antibodies. In summary, we improved signal to noise ratio, attained higher signal intensities and better lateral resolution. First results will be presented for a multiplex-immune-imaging of cancer tissues.

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ELEMENTAL ANALYSES OF SOILS AND SEDIMENTS FUSED WITH LITHIUM BORATE USING ISOTOPE DILUTION LASER ABLATION ICP-MS

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Metal contaminations in soils are a recurrent concern having implications in health, ecological and legislation issues. Traditional methods to determine metal concentration in soils and sediments involve an acid digestion step that is time consuming, prone to contamination and analyte loss. Particularly a complete dissolution of the sample can sometimes prove difficult when refractory phases are present. Several solid-state techniques can be used to determine metals concentration at the ppm level or below in soil and sediment samples but all of them have their pros and cons. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been widely investigated as a powerful analytical technique for the direct analysis of different types of materials. According to its unique features, LA-ICP-MS allows element and isotopic analyses of solids, including microanalysis and depth profiling, at trace concentration levels. However, its main limitations are related to quantification of the samples (due to the lack of reference materials) and elemental fractionation. In other words, a non-stoichiometric ablation process can take place, mainly with ns lasers which are the most widespread type of laser ablation systems. These issues will have an impact on the quantification of elements which is generally done by external calibration with matrix-matched reference materials and using an internal standard (generally the major element of the matrix).

One way to get around these limitations is to use isotope dilution mass spectrometry (IDMS) because the different isotopes of an element are expected to behave similarly (at least at the level of precision required for isotope dilution) and, therefore, can be considered as almost perfect internal standards. IDMS is internationally regarded as a reference measurement method directly traceable to the International System of Units. The application of isotope dilution in LA-ICP-MS can correct for some common fractionation and matrix effects arising during the laser ablation process that cannot be addressed using other calibration procedures. Until now different types of strategies have been applied for the quantification of powdered samples by LA-ICP-IDMS: solid-spiking and on-line IDMS. Promising results were found using such strategies although the requirement of preparing isotopically-enriched pellets and the inability to correct for errors derived from the ablation processes, respectively, limit the universal applicability of these quantification methodologies.

In this communication, we present the LA-ICP-IDMS analysis of Cr, Sr, Ba and Pb in soil and sediment samples fused with lithium borate. The advantages of using such sample preparation procedure include: homogeneous mixing of analytes, possible dilution for highly concentrated elements and stability over time. This practical study was focused on using standard instrumentation (ns-LA) for saving time for possible use as routine method as well as on the comparison of two ICP-MS instruments (quadrupole vs sector field ICP-MS). The homogeneity of the samples and limits of detection were carefully studied and the validity of the proposed quantification approach is demonstrated with the analysis of six certified reference materials.

EFFECTS OF HELIUM FLOW GEOMETRY ON ELEMENTAL FRACTIONATION IN LASER ABLATION ICP-MS

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The observation of elemental fractionation in LA-ICP-MS has been well documented, and is a major limiting factor for accurate quantification of direct solid analysis. Previous studies have highlighted the effects of laser wavelength, ablation atmosphere gas type (helium vs. argon), and plasma conditions on elemental fractionation. It is believed these parameters are controlling elemental fractionation by changing the particle size produced by the laser ablation system process and consequently how well these particles are digested in an argon plasma. It is well established that shorter wavelength and pulse width lasers produce a smaller proportion of large particles (>150 nm), as does ablation in helium vs. argon for shorter wavelengths. These smaller particles will be digested in the plasma more readily and therefore produce less elemental fractionation.

This study discusses an additional control of elemental fractionation: the geometry of helium flow over a sample during the ablation process. To test this effect, a Resonetics RESOlution laser ablation system with a Coherent 193 nm ArF excimer laser (~20 ns pulse width) connected to an Agilent 7500cs ICP-MS was utilized. The instrument was equipped with two constant geometry ablation cells of a different design, M50 and S155, both designed by Laurin Technic. In both cells, ablation takes place in an atmosphere of pure He. The ablation location is centred under a small funnel. In S155, Ar is mixed with He in the funnel above the sample, whereas in the case of M50 Ar is mixed with He outside the cell. In M50, He flows towards the sample from a side port and exits upward into the funnel directly above the sample. In S155, He flows as a "curtain" at the funnel's edge around the ablation spot and again exits upward into the funnel.

A series of analyses were conducted using the NIST612 as the calibration standard at a 80 micrometer spot size, and GSD-1g analysed as an unknown at various spot sizes. Results show GSD-1g measured at 32 micrometers in S155 have up to 20% deviation from expected GSD-1g values, especially for more volatile elements (B, As, Zn, Pb, Bi etc.). The same test with M50 generally had less (<10%) of an offset from the expected GSD-1g values. This suggests that the geometry of the helium flow has a strong influence on the particle size distribution of the ablation products for this laser wavelength and for this ICP-MS setup. A similar effect is seen for U-Pb down-hole fractionation trends in several zircon reference standards. The down-hole U-Pb trend for zircon reference standards 91500, Temora, GJ1 and Plesovice shows more U-Pb fractionation (10%) in S155 than in M50, thus highlighting the importance of constant helium flow geometry on geochronology by LA-ICP-MS.

The results of this study demonstrate the importance of ablation cell design, which controls helium flow geometries over the ablation site, which in turn controls elemental fractionation during laser ablation. Implications are that a laser cell that has uneven helium flow characteristics in different locations within the cell can potentially lead to inaccurate results, depending on the helium flow relationship over the calibration standard and the unknown samples.

A SINGLE SOFTWARE PLATFORM FOR LA-ICP-MS APPLICATIONS USING A NEW HIGH SENSITIVITY ICP-Q-MS

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The use of laser ablation micro sampling for imaging in geological, biological and clinical studies has meant that the small spot sizes required limit the absolute amounts of material ablated. In order to increase the elemental range available to analysts in such LA-ICP-MS applications, improvements in laser sampling and transport of the ablated material as well as ICP-MS instrumental sensitivity are required.

In this presentation a new high performance quadrupole ICP-MS system, the Thermo Scientific iCAP Q, will be described for laser ablation applications. New technologies introduced in the iCAP Q to improve sensitivity (e.g. skimmer cone inserts and QCell flatapole technology) will be demonstrated for a range of LA-ICP-MS applications.

Qtegra, a new software platform for a range of elemental instrumentation, will be described for LA-ICP-MS on the iCAP Q. With Qtegra's unique plug-in approach, a single software package can control a range of accessories coupled to ICP-MS. For LA-ICP-MS analyses the entire work through, from definition of laser sampling parameters to export into specialized laser ablation data reduction software packages (e.g. IOLITE) is achieved through a single user interface, significantly improving the ease of use and flexibility of LA-ICP-MS analyses.

Examples of performance from a high performance 193 nm excimer laser will be shown in both cell and non-cell ICP-MS analysis modes.

KP-15

ADVANCES IN DEVELOPMENT OF NON DENATURATING GEL ELECTROPHORESIS TECHNIQUE FOR URANIUM-PROTEIN COMPLEXES QUANTITATIVE ANALYSIS BY LA-ICP MS

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Understanding the role of a metallic pollutant in a living organism requires the knowledge of its trafficking in biological fluids and the identification of its molecular targets (proteins, metabolites, …) in contaminated cell or tissues. Then cellular process involved in metal uptake, transport, storage, and/or elimination can be established as well as the toxic species [1]. Uranium, naturally occuring or anthropically released in the environment, is a key element to study because of its radio and chemio-toxicity. It has a wide coordination chemistry and affinity for oxygen containing molecules such as nucleic acid, peptides and proteins [2].

However obtaining speciation information of uranium in living organism remains challenging due to the electrostatic nature of uranium complexes with biological molecules, and is dependent on the availability of adequate analytical techniques. During the last decade, new hyphenated analytical techniques have been increasingly applied for trace elements speciation analysis in complex samples. In particular, Inductively Coupled Plasma Mass Spectrometry (ICP MS), used as an atomic detector in chromatography and electrophoresis, and supported by Electrospray Ionization Mass Spectrometry (ESI MS/MS), has been revealed as a powerful [3].

This work, included in a wider project of ecotoxicology, emphasizes the analysis of proteins as molecular targets of uranium. For that purpose, classical proteomic approach (2D-SDS PAGE) has to be revisited and optimized for the analysis of uranium-protein complexes in the freshwater crayfish (*Procambarus clarkii*) after waterborne exposure. This communication will present the development of the first dimension protocol of gel electrophoresis, i.e. isoelectric focusing under non-denaturating conditions (ND-IEF). For that purpose in vitro uranium-protein complexes (U-Bovine Serum Albumin and U-Transferrin) were synthesized. Optimization of sampling and detection conditions by Laser Ablation - ICP MS contributed to the detection of uranium in standard protein bands. The mixing of different UO^{22+} amounts with BSA subsequently subjected to ND-IEF allowed establishing a linear calibration and assessment of U detection limit to 5 fmol. The methodology was applied to crayfish cytosol samples (hepatopancreas) after different uranium exposure conditions. Uranium amounts (in the dozen of pmol range) determined by ND-IEF LA-ICP MS were in good agreement with those determined in whole cytosol by ICP MS measurements. The first dimension of gel electrophoresis being validated allows us to consider the second non denaturating dimension for the separation of U-protein complexes in view of their future identification by molecular mass spectrometry

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UTILIZATION OF LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR ELEMENTAL MAPPING BIOLOGICAL TISSUES

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) offers possibilities of elemental mapping different types of materials including geological, biological and metallic samples. In this work we present utilization of LA-ICP-MS for semi-quantitative elemental mapping of different type of tumor and skin tissues. For this purpose we used LA-ICP-MS setup consists of laser ablation system UP213 (NewWave, USA) operating at wavelength of 213 nm and quadrupole ICP-MS Agilent 7500ce (Agilent, Japan) equipped with collision cell for suppressing possible isobaric interferences. Melanoma and healthy skin of miniature pigs were used in this study. The Zn, Cu and Fe were measured on all studied samples to findings their lateral distribution in melanoma with different progress.

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KP-17

ALIASING EFFECTS IN LASER ABLATION ICP MS: SEQUENTIAL DETECTION vs. LOW DISPERSION

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Ablation cells with short aerosol washout are gaining increasing attention because they principally would allow shorter total measurement times for imaging applications without compromising lateral or depth resolving power. Additionally, higher peak intensities can be achieved when the aerosol is introduced into the ICP as a short pulse. When using sequential detection with quadrupole or single collector mass spectrometers, however, such pronounced signal oscillations can severely affect the accuracy and precision of an analysis due to aliasing effects (often termed “spectral skew”) [1]. “Signal smoothing devices” [2,3] have been proposed to mitigate fluctuation in aerosol density but are potential sources for memory effects and carry over. In order to estimate the magnitude of aliasing effects on laser ablation signals, the influence of measurement parameters like scan duration of the mass spectrometer and laser pulse repetition rate on the precision and accuracy of the measurement were investigated experimentally and by numerical simulation. Two ablation cells with highly different aerosol washout times were used in the experiments with a 193 nm ArF excimer laser and helium as carrier gas. Scan duration of the MS was varied by changing the number of isotopes detected, integration and dwell times for different laser pulse repetition rates. Numerical simulations were carried out using an Excel spreadsheet, allowing all relevant parameters (pulse frequency, isotope count, dwell and settling times as well as shape of the individual aerosol pulse) to be modified and processed. Evaluation of ion signals and intensity ratios was based on within-run standard deviation of for a single ablation experiment and between-run standard deviation of three replicates as measures for precision and accuracy respectively.

It can be shown that simulation and experiments show the same trend, with the exception that the experiments also revealed a contribution of the 50 Hz power line. Generally short scan durations are of advantage, especially when using the low dispersion ablation cell as this increases temporal correlation of the ion signals. Low scan frequencies on the other hand can lead to a pronounced beat frequency of the ion signals and intensity ratios due to differences in their respective sampling phase. High scan frequencies for large isotope selections however can only be achieved with short integration and dwell times, which significantly affects the counting statistics related noise contribution.

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ADVANTAGES OF HIGH SENSITIVITY ICP-MS COUPLED TO LASER ABLATION

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Laser ablation coupled to ICP-MS is meanwhile matured to be an indispensable tool for solid analysis for already many applications and an increasing field of applications such as imaging to elucidate biomedical questions. Laser ablation devices have enormously developed during the last decades; and laser spot sizes are decreasing which allows for better and better spatial resolution. Consequently there is a need to increase sensitivity of ICP-MS instrumentation to meaningful detect signals which derive from smallest spot sizes. The presentation will describe the technical realization of a Quadrupol ICP-MS (Bruker Daltonics) which is designed to deliver highest sensitivity when coupled to laser ablation. Key elements are a 90 degree ion optic and an optimized interface and vacuum region. The presentation will present the figures of merit as well as challenging application examples.

SILVER NANOPARTICLES TOXICITY STUDIES BY PAGE-LA-ICP-MS

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In recent years, the fabrication of nanomaterials and exploration of their properties have attracted the attention of all branches of science, such as physics, chemistry, biology and engineering. Interest in nanoparticles (NPs) arises from the fact that the mechanical, chemical, electrical, optical, magnetic, electro-optical, and magneto-optical properties can be completely different from those of their bulk counterparts, and these differences are dependent on the particle size. From a biological and medical applications viewpoint, the primary interest in NPs stems from the fact that they are small enough to interact with cellular machinery and potentially to reach previously inaccessible targets, such as the brain [1].

Silver NPs are of interest because of the unique properties which can be incorporated into anti microbial applications, biosensor materials, composite fibers, cryogenic superconducting materials, cosmetic products and electronic components. The large use of nanomaterials has promoted the study of nanotoxicology and highlighted the need for safety assessment research to be performed in parallel to development of applications.

It is now well-recognized that the surfaces of biomaterials are immediately covered by biomolecules (e.g. proteins, natural organic materials, detergents, and enzymes) when they come in contact with a biological medium. The interaction between nanomaterials and environmental biomolecules results in the formation of a biological corona on the NP's surface. Formation of the corona is a dynamic, competitive process. The proteins present in a biofluid compete for the NP surface to form a bio-nano interface, the so-called "protein corona". Although there are several thousand proteins in human biological fluids competing to bind to the NP's surface, the protein corona is usually enriched with about 10-50 proteins that have the highest affinity for the surface.

In this work, first results of characterization of different chemical forms of Ag in a biological culture media by applying electrophoretic techniques (1D-PAGE) and detection of Ag species associated to proteins by Laser Ablation(LA)-ICP-MS will be shown. Collargol was used as Ag NPs, Dulbecco's Modified Eagle's Medium supplemented with Fetal Bovine Serum was used as biological culture media and Human hepatoma HepG2 was the cell line studied. Based on our previous research [2], different PAGE methods (denaturing and non-denaturing ones) have been applied for protein separation in the culture media after incubation with AgNPs and studies for successful detection of soluble Ag forms associated to proteins by LA-ICP-MS have been carried out.

Acknowledgement

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STUDY OF ELEMENTAL FRACTIONATION USING 1030 nm AND 257 nm HIGH REPETITION RATE FSLA/ICPMS

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Since the early days of this technique, LA-ICP-MS has been considered as promising technique for direct trace elemental analysis in solids. However, despite a wide range of applications, LA-ICP-MS is still not as popular as it should be mostly because of elemental fractionation occurring during the analysis. The reduction of the pulse duration from nanosecond to femtosecond in the past decade has widely improved the accuracy by reducing thermal effects, considered so far as one of the main sources of fractionation [1]. Claverie and al has shown that high repetition rate of an IR-femtosecond laser combine with the use of a galvanometric scanner set on high speed can reduce the particle size fractionation by the dilution of the large particle coming from the surface layer with finer particle coming to deeper level [2]. Further studies need however to be carried out to better understand the aerosol formation and some remaining fractionation effects that might occur when using femtosecond laser.

This study focuses on elemental fractionation occurring when ablating glass samples using high repetition rate femtosecond laser at 257 nm and 1080 nm. The effect of fluence, beam size and repetition rate (from 1Hz to 50 000 Hz) will be presented as regards with elemental fractionation and particle size distribution. Several elemental ratios characterized as indicator of fractionation (Cu/Zn; U/Th, U/Pb) were carefully studied.

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DEVELOPMENT OF FAST QUANTITATIVE ANALYSIS FOR BIOLOGICAL SAMPLES USING LA-ICP-MS TECHNIQUE

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Increasing of terrorism causes the more intensive illicit trafficking of radioactive and nuclear materials the last few decades. It also gives possibility for using of dirty bombs during the terror attacks. Other potential danger is in connection with radioactive and nuclear materials the possibility of nuclear accidents (e.g. Fukushima). During these events lots of people are affected in most of the cases and therefore detection of the contamination and selection of victims is necessary after the incident or accident as soon as possible for decision of further treatment. For fast selection and categorization of people taken biological samples can be more informative and using rapid measurement methods with small sample necessity for the analysis is essential.

In this work based on the requirements and idea described a rapid and relatively easy but sensitive method has been developed for quantitative analysis of 1 droplet blood or urine using LA-ICP-MS technique. Calibration technique has been developed for Cs and U analysis in biological samples using matrix-matched calibration. Applying the method estimation of inner contamination with radioactive materials of victims is relatively easily can be carried out.

KP-22

ELEMENTAL ANALYSIS BY A MINIATURE LASER ABLTION/IONISATION MASS SPECTROMETER, LMS

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The results of the studies of elemental composition of various solid materials using a miniature laser ablation/ionisation time of flight mass analyser (LMS) will be presented. The instrument is designed for in situ investigations of elemental (isotopic) composition of planetary surfaces [1]. In spite of a significant miniaturization of the mass analyser, high instrumental performance close to that of laboratory systems is achieved. The instrumental error of mass calibration is better than 10-4 and typical mass resolution ($m/\Delta m$) of 1000 is achieved at ^{208}Pb mass peak. With current dynamic range of 10^8 the studies of elements (isotopes) abundant at 10 ppb level can be conducted[1-3]. High reproducibility of the measurements conditions and precision of the results is achieved by implementation of a computer-based control (voltage settings on the ion optics, laser characteristics, sample position) and optimization procedure of ion transmission and mass resolution [4].

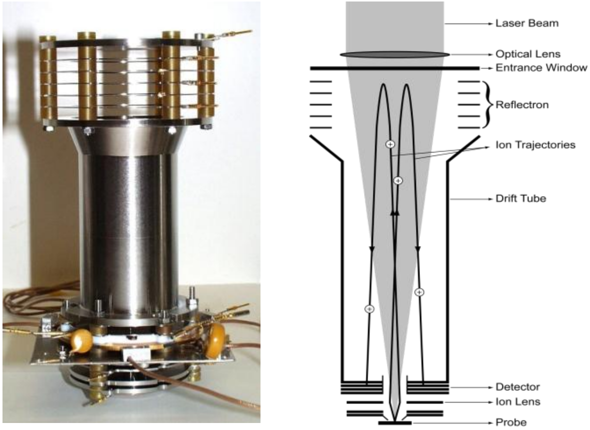

Fig.1. Left panel shows the prototype of LMS and on the right side the construction details and principles underlying operation of the instrument are displayed.

The instrumental performance for the quantitative elemental analysis of solid materials was investigated using both ns- and fs-laser radiation for ablation/atomisation/ionisation of NIST standards. The multi-parametric studies (laser fluence, wavelength, pulse duration) led to a range of instrumental settings that allow determination of best set of relative sensitivity coefficient's (RSCs) with low uncertainties allowing the quantitative elemental analysis with accuracy and precision in a pro cent range. Initial studies with fs-laser show also an increased detection efficiency of non-metallic elements and reduction of clusters.

The analysis of inhomogeneous samples including extraterrestrial materials will be presented with high spatial resolution (~Ø10-20 µm) comparable to the size of individual grains. Applying of both the chemical imaging of the surface and vertical chemical profiling is of considerable interest in number of applications including applications in space research. We demonstrate application of these methods in investigation of Allende meteorite and other inhomogeneous samples. High sensitivity of the instrument promises also detection of important from geological point of view trace elements (e.g., REE), radiogenic (Sr/Rd, Pb) and bio-relevant elements (H, C, N, O, S, P).

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EVALUATION OF ^{87}SR/^{86}SR ISOTOPIC RATIOS IN FISH SCALE HYDROXYAPATITE BY FEMTOSECOND LASER ABLATION COUPLED TO AN MC–ICPMS.

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Microchemistry of fish calcified structure presenting growing structures (scales and otoliths) is an essential source of information for studying migration patterns in large system like the Amazonian basin, where long term direct observations are difficult. Such information could be derived from analysis of trace elements occurring along these structures, requiring a high spatial resolution sampling techniques. Previous results showed that ^{87}Sr/^{86}Sr isotopic ratios appear to be a good marker to study fish migration along the Amazonian freshwater basin and that LA-MC-ICP-MS precision is sufficient to distinguish variations along life-history transects on both scale and otolith [1,2].

Up to now otolith chemistry stays the reference in the field of fish migration tough scales present some advantages on otolith: the removal is non lethal, sampling and scale preparation are time saving, easier and don't require specific skills. However, due to the high level of P into the scale hydroxyapatite, the ^{87}Sr/^{86}Sr isotopic ratio is biased as a result of the formation of ^{40}Ar^{16}O^{31}P^{+} species in the plasma. This potentially reduces the accuracy of the method compare to the otolith approach and careful optimisation of the MCICPMS detection fitted in a pseudo high resolution mode is required.

The poster will present the optimisation of the high repetition rate 257 nm Fs laser ablation MCICPMS coupling. A comparison of otolith and scale ^{87}Sr/^{86}Sr isotopic ratios derived from UVfsLA-MC-ICP-MS and TIMS analyses will be presented. As preliminary results, application to Amazonian fishes will also be presented.

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KP-24

LASER ABLATION ICP-MS ANALYSIS OF CELL LYSATES AFTER SILVER NANOPARTICLE TREATMENT: IS QUANTIFICATION POSSIBLE?

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Trace elements play not only an important role in physiological processes of the human body, they also have a prominent position in toxicology. Thus, the understanding of the interaction of mineral elements with biological tissues, individual cells or even cell compartments is of utmost interest to assess the potentially associated risk [1].

Traditionally, for inorganic bulk substances research on the impact of morphological aspects in risk assessment was rather limited. However, due to recent developments in material sciences, which contribute to an expanding utilization of inorganic materials with nanoscale dimensions or nanostructured surfaces, the identification, determination and quantification of the chemical composition of these “biomolecule-nanometal”-complexes is becoming more important [2].

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), as an analytical imaging tool for biological samples, has become a well established efficient technique analyzing metal containing biomolecules, especially proteins [3 - 4]. The advantages of employing LA-ICP-MS in this research area are its high dynamic range and low limits of detection for trace elements in solid samples as well as the potential to combine the imaging facility of the laser with the protein separating techniques [5 - 6].

Here, the following model system was developed: Two different cells lines (A549 and THP1) were examined after treatment with silver nanoparticles of different concentrations by LA-ICP-MS.

In order to establish an appropriate test protocol for the quantification of silver nanoparticles in the cells, well defined cell lysate droplets on solid surfaces were analyzed serving as proof of principle experiment. Calibration experiments were performed by using cell lysates treated with silver nanoparticle solutions of varying concentration. Monitoring the conditions throughout the whole experiment, compensating for experimental variability and so guarantying the comparability of individual experiments with each other lutetium was used as an internal standard. Parallel line scans were applied and signal intensity was integrated over the individual droplet area.

In summary, LA-ICP-MS has shown to be a promising tool for the imaging of nanoparticles in such biological samples and a technique suitable for the investigation of the uptake of inorganic nanomaterials by cells.

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KP-25

MULTIVARIATE OPTIMIZATION OF EXTRACTION PARAMETERS IN SINGLE-DROP MICROEXTRACTION FOLLOWED BY LASER-INDUCED BREAKDOWN SPECTROMETRY FOR TRACE ELEMENTAL ANALYSIS OF WATER SAMPLES

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Laser-Induced Breakdown Spectrometry (LIBS) is perhaps one of the most versatile techniques for elemental analysis, since it can be applied to a great variety of real-world analytical problems. However, in spite of its potential for the analysis of practically any kind of sample, most LIBS applications have been focused on solid samples analysis whereas its applicability to liquid samples has been, in comparison, poorly exploited.

The lower interest in LIBS analysis of liquids is mainly due to its inherent experimental drawbacks, which lead to low sensitivity and precision in comparison to solid analysis. Even if numerous studies have been performed to solve, or at least to reduce these drawbacks, LIBS technique still provides analytical results for liquids samples that are, in general, worst than those provided by other well established spectroscopic techniques.

In this work, an analytical procedure based on LIBS detection for the determination of heavy metals at trace levels in water samples is presented.

Heavy metals have become of particular interest in recent decades within the framework of environmental investigation. Water pollution is directly related to the degree of contamination of our environment, and this fact has lead to a growing interest in the contamination of water bodies and to more rigid environmental regulations on heavy metals pollution. Monitoring of heavy metals concentration in water samples is therefore needed in order to meet the rigid regulatory requirements and, for this purpose, most analytical procedures include a previous step for analyte enrichment in order to achieve the required limits of detection for trace level analysis.

Microextraction procedures are nowadays extensively used for analyte separation and concentration and, among them, Single-Drop Microextraction (SDME) methodology has been applied for trace elemental analysis with excellent results.

The proposed methodology is based on the application of SDME procedure to water samples, followed by LIBS analysis of the resulting analyte enriched microdrops. To this end, toluene was used as extracting solvent for SDME of heavy metals as ammonium pyrroldinedithiocarbamate (APDC) complexes. The main factors affecting SDME, such as microdrop volume, pH, APDC concentration, stirring speed and extraction time were optimized by a multivariate strategy based on an experimental design, using a Plackett-Burman design for screening and a central composite design for optimizing the significant variables. The enriched microdrops obtained under optimum SDME conditions were analyzed by LIBS, after drying the droplets on a solid substrate. The proposed methodology was finally tested for the determination of heavy metals in a certified reference material.

To our knowledge the combination SDME-LIBS has not been applied before, and due to the inherent advantages of both SDME and LIBS techniques, it appears to be a fast, simple and virtually solventless analytical methodology with great possibilities for automation and miniaturization, therefore presenting an emerging field of study.

Acknowledgement

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PARTICLES PRODUCED BY LASER ABLATION FOR PROFILING TITANIUM NITRIDE COATED SILICA

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Titanium nitride coated silica was profiled by laser ablation to investigate chemistry of the layered materials by depth. Titanium nitride coating shows high adhesive strength on substrate compared to other ceramic coatings. Adhesion strength is related to chemical interaction between coating material and substrate at the junction. To investigate the junction of coating and substrate, laser ablation was used as profiling tool.

As profiling proceeded, the particles generated by laser were collected on line and the particles observed according to depth by scanning electron microscope and particle size analyzer. Ablated surfaces were observed also by scanning electron microscope and atomic force microscopes with profiling process. Profiling process was divided into three stages, firstly on the coating surface, secondly on the junction of coating and substrate and thirdly in the substrate.

Helium and argon was used as carrier gas and particle collection was performed respectively. Particles and surface morphology was investigated according to profiling process and compared.

Profiling analysis of titanium nitride coated silicon was performed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). By Q-switched 213 nm laser sample ablated from titanium nitride coated surface and profiled at one point. Laser energy, beam diameter and pulse repetition rate were optimized to 1 mJ, 25 µm and 1 Hz. With these conditions ICP-MS signals were collected as profiling proceeded. Two carrier gases, He and Ar were used respectively and both results were compared.

Signal of titanium was increased during profiling coated layer and at the junction of coating and substrate titanium intensity was dramatically decreased otherwise silicon intensity was abruptly increased in both carrier gas. Profiling process was confirmed by scanning electron microscopy and correlated with ICP-MS.

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METHOD DEVELOPMENT FOR A MINIMAL INVASIVE INVESTIGATION OF ANCIENT COPPER ALLOYS AND FORMATED CORROSION LAYERS USING LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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For the investigations of cultural heritage objects non-destructive or minimal invasive, highly sensitive and multi-element analytical techniques are preferable. Therefore laser ablation inductively coupled plasma mass spectrometry LA-ICPMS procedure was developed for a fast and micro-destructive characterization of corrosion products as well as for the composition of the bulk metal. The LA-ICPMS method provides not only information on spatial elemental distribution of corrosion products at the surface but also information on the corrosion layer in the depth with good lateral and transversal resolution.

The influence of different corrosive environments on the corrosion progress for different copper alloys from an experimental archaeological study on ancient metal smelting processes and historical casting techniques has been investigated by LA-ICPMS. The LA-ICPMS results were compared to state of the art techniques – scanning electron microscopy with X-ray spectrometry SEM-EDX and X-ray diffraction XRD. The integrated data about the chemical and metallographic properties in combination with detailed knowledge of patina can be used for recognizing the archaeological characteristic of investigated objects. Moreover, it allows an evaluation of the actual condition status of the objects that is necessary for choosing specific conservation or restoration measures.

LA-ICP-MS AND PIXE-PIGE STUDIES OF GLASS BEADS – NEW INSIGHT INTO THE FINGERPRINTING OF MUSEUM OBJECTS

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The usefulness of application of LA-ICP-MS and PIXE-PIGE technique in the routine determination of a huge number of trace elements in glass material has been demonstrated in a large number of research studies [1-3]. The glass samples are characterized by these techniques for forensic purposes as well as to give some answers to archaeological projects [1]. One of the most crucial questions connected with the studies of glass beads are those addressing their provenance (where the glass came from) and the method of fabrication (which technology was involved in their production) [3]. The compositional analysis of archaeological glasses seems to be fundamental in the identification of: the probable source of glass material, type of raw material employed in the production stage and their processing as well as recipes for coloured glasses [2]. In order to answer these questions, comparative studies of various types of glass beads and their detailed chemical analyses are needed. The advancement of the sensitive, almost non-destructive and with a high spatial resolution for trace element studies techniques such as LA-ICP-MS or PIXE-PIGE has opened up new possibilities for the direct solid sample analysis of rare artefacts [1-3].

The aim of the present work is to demonstrate the potential of LA-ICP-MS and PIXE-PIGE techniques as tools applied to yet another domain of art and archaeology – art jewellery. The studied material consisted of early medieval glass jewellery originating from 11th to 14th century, found in the cemeteries located in the north-western part of the Chełmińska Land (around Chełmno) on Polish territory. The total number of analyzed glass beads, being only a small part of collection of glass jewellery, was 80. The source material originates from 104 graves and 25 single finds. The analyses were carried out using the inductively coupled plasma mass spectrometer with the time-of-flight analyzer, ICP-ToF-MS (OptiMass 8000, GBC) and with a 266 nm CETAC LSX-500 laser, for direct introduction of solid samples. Single point sampling by the laser ablation system was used. The ICP-MS parameters were optimized as recommended by [1]. Preablation time was set up in order to eliminate the transient part of the signal and to avoid surface contamination or corrosion influence, affecting the results of the study. Additionally, for comparison purposes as a complementary technique external-beam PIXE and PIGE (proton induced X-ray emission and proton induced gamma ray emission) spectroscopy was used to determine the elemental composition of glass jewellery. Measurements were performed at the 3 MeV Tandetron accelerator using the external collimated beamline dedicated to cultural heritage applications. In our research we employed mulitidimensional chemometric analyses such as PCA or CA to extract the valuable data, included in the rich structure of the studied glass jewellery. The obtained results turned out to be especially helpful in classifying the glass beads according to: the methods of forming, decorating type, colour agents used or type of glass applied.

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LA-ICP-TOF-MS INVESTIGATIONS OF PAPERS

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Papers as a writing and drawing support is generally made up of natural polymer - cellulose, which can be subjected to a very complex aging process. Acidic hydrolysis is thought to be the predominant degradation pathway for cellulose in paper. Oxidative processes are considered to occur when frequently used writing and painting media are applied [1]. The damage of paper material during the aging process starts with the irreversible breakage of mechanical, chemical, optical and physical properties. The process is dependent on the characteristics of paper like the kind and quality of fibres, sizing materials coatings, presence of acidic and/or metallic compounds [2]. Also, some external factors influence aging such as conditions of storage, temperature, humidity, light access, microbial and air pollutants, etc. Variability in paper manufacture enables the identification of a variety of subtle distinctions, which gives each batch of paper or even each sheet of paper a unique chemical fingerprint [1-3]. Thus, the identification and/or quantification of elemental components of paper can deliver some information of its origin, age or the technology of its production, which is crucial from the point of view of conservation and to forensic science in judicial problems encountered in forgery. Under normal conditions of paper storage the aging process is very slow and, in general, leads to well-known effects like yellowing. For this reason, many types of aging methods during which paper is subjected to extreme conditions are used to speed up the natural process. In the last decades the artificial aging tests (e.g. submitting the paper to intense UV, solar light, humidity, temperature or oxidization by NO4I) were used as a general research tool. The question which still needs to be answered is whether the elemental chemical composition is affected or not by artificial aging [3].

This work was dedicated to the elemental analysis of a few types of papers, including papers for photocopier (the comparison of elemental composition of single sheet of paper originating from one batch), colour papers and aged papers. Samples of white papers with weight of 80g/m2 and color ones with weight of 160g/m2 were analyzed. Studied samples were subjected to speed up ageing with the use of a climate and thermal chamber. Paper samples were submitted to color test using Spectrophotometer (CM-3600d, MINOLTA). The paper's surface was examined using scanning electron microscope SEM (S-4700, Hitachi). The differences in the paper composition were assessed using the laser ablation system (LSX-500, Cetac) with the inductively coupled plasma mass spectrometer with the time-of-flight analyzer (OptiMass 8000, GBC). The results confirmed that LA-ICP-MS technique can be successfully used to differentiate the paper substrate. Some considerable differences in the elemental composition were observed among various papers. The analysis carried out by LA-ICP-MS technique is relatively quick and does not require any special sample preparation. Another advantage is that it is almost non-destructive and the changes after the ablation are practically invisible to a human eye. The ablation pattern does not limit the readability of the document and the value of the proof, which is a very important aspect in forensic investigations. We can conclude that this technique can be applied in forensic studies directed at differentiation of papers.

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ANALYSIS OF PAPER AND GEL INKS BY LA-ICP-MS AND SEM TECHNIQUES USING CHEMOMETRIC APPROACH

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Still many of the methods used nowadays in the examination of documents are not able to discriminate between the source of paper and gel ink with a high degree of certainty [1]. The potential possibility of the ink-paper discrimination and the identification of the origin of ink can provide important forensic evidence, in cases like document fraud [2]. The analysis of questioned documents is becoming an increasingly important part of the forensic science examination considering the assessment of authenticity of a document, whether an individual pen or toner was used to make a signature or to create a document and if it is possible to identify the source of ink or toner. Thus, the differentiation of the ink or toner can provide crucial information for tracking their origins and offer scientific evidence for determining the questioned documents [2,3]. Therefore, it is of great importance to develop modern analytical methods for forensic examination of inks. Regardless of the fact that many chemical and/or physical analyses of paper and ink can be performed [1] the most important issue of forensic document examination is to choose the one with the largest discriminating power [2]. Recently, new techniques for ink analysis have been investigated such as: Raman spectroscopy, XRF, SEM, HPLC, MS or CE. Nowadays LA-ICP-MS technique is applied in various forensic ink investigations of documents as a quick and almost non-destructive analytical tool with a minimal sample consumption. This technique is thought to be an attractive from the point of view of forensic analysis due to the speed of analysis, multi-elemental and promising quantitative capabilities, good sensitivity and selectivity [1-3]. In order to improve the validity of the obtained data and to make the interpretation of the gathered results easier, many statistical treatments of the data and various chemometric approach have been additionally proposed.

The aim of this study was to assess the potential of LA-ICP-MS technique for the discrimination of paper and ink. The additional purpose of this work was to evaluate the difference among various inks used and the differences among the same ink. The paper with ink samples was cut into small squares. Each of the studied ink lines was a few cm long and cut into three pieces. Depending on the name of the brand of the pen spectra were collected from each of the three ink pieces. Additionally, for comparison purposes, the data were gathered also for the paper samples. The analysis was performed using the laser ablation system (LSX-500, Cetac) with the inductively coupled plasma mass spectrometer with time of flight analyzer (OptiMass 8000, GBC). The optimized ablation parameters for paper and ink were chosen based on the analysis of the specially prepared reference ink sample and the information gathered from the scanning electron microscopy SEM (Hitachi, Japan). The difference between variability of samples was examined against intra sample dispersion of LA-ICP-MS data. For this purpose statistical tests and chemometric tools were applied including Cluster Analysis and Principal Component Analysis.

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APPLICATION OF LA-ICP-TOF-MS TECHNIQUE IN FORENSIC INK STUDIES

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Nowadays, the most important problems which are still unsolved in forensic science are the document dating, and thus the evaluation of the time when a document and/or ink could have been once placed on a paper. This is partly a consequence of a huge variety of inks existing now on the market and, on the other hand, the complexity of the chemical processes which start when the ink is entered on the paper. As soon as the ink is introduced into a paper the aging process begins, being influenced by many external factors like light, humidity, temperature, storage conditions - in general [1]. It is thought that these days the majority of the examined documents in forensic laboratory contains pen inks, among them ballpoint pens (containing oil-based inks and dyes as colorants) which are considered the most commonly used, especially for personal signatures. The second, less often used group of modern writing instruments, is the so called non ball point pens which have water-based inks and dyes and/or pigments as colorants [1, 2]. The ink characteristics such as color or viscosity are dependent upon the composition and concentration of all ink components. Standard procedure of forensic examination of ballpoints pen inks involves establishing whether or not entries on a document were made with a single pen or at a single point in time. Thus, the differentiation and dating of pen ink (determination how long the ink was deposited on the paper which would enable the assessment of the date of the document) seems to be crucial in nowadays forensic ink studies and can provide important information enabling tracing back their origins and provide evidence in the analysis of questioned documents. Therefore, it is fundamental to develop and establish new methods for forensic examination, differentiation and dating of inks [2]. Lately, quick and nondestructive techniques have commonly been applied in the ink forensic examination of documents as: Fourier transform infrared spectrometry, Raman spectroscopy, visible and near infrared reflectance and microscope. Recently, there has been a considerable interest in the discrimination of the pen inks by elemental analysis using the laser ablation ICP-MS spectrometry, which has bigger discriminating power and higher sensitivity [3].

The aim of this work was to discriminate the studied inks entries on paper and identify their characteristic components using almost a non-destructive approach to forensic examination. Additionally, the effects of various aging methods on the surface properties and the composition of ink and paper were investigated. The studied samples include e.g. red-gel pen Pentel K106, blue-gel pen Uniball Signo Dx, blue pen paste Stobilo Alpha, black pen paste Pelikan Stick. Ink and paper samples were subjected to speed up ageing action with intensive power of individual destructive factors like the temperature or luminous intensity. Ink and paper samples were submitted to color test using Spectrophotometer (CM-3600d, MINOLTA). The surface of the samples was examined using scanning electron microscope SEM (S-4700, Hitachi) and optical microscope (Motic). The differences in the composition of samples were assessed using the laser ablation unit (LSX-500, Cetac) with the inductively coupled plasma mass spectrometer with the time-of-flight analyzer (OptiMass 8000, GBC).

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CHARACTERIZATION AND QUANTIFICATION OF TIO_2 NANOPARTICLES IN SUNSCREEN LOTION USING LASER DIFFRACTION AND ICP- OES SPECTROMETRY

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The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) was established by the European Commission in 2004 [1], in order to provide scientific advice on the safety of issues requiring comprehensive assessment of risks related to new technologies such as nanotechnology.

Nowadays nanotechnology is present in our daily life and the use of nano particles is common practice in many application fields such as nanotubes for textile applications, nanotechnology for sun screens, and nanoparticles in bodycare products. The influence of silver nanoparticles on the human body is evaluated in recent studies [2].

The distribution of nanoparticles in bodycare products such as sunscreens, shower gels and body lotions is evaluated using a nano particle size analyzer. The IG-1000 is using the induced grating method, which allows the determination of particles in the sub nano range. Thereby no cross-contaminations of foreign particles or agglomerates is influencing the measurements. No refractive index or special pH-value is required.

Furthermore a method has been developed and optimized for the determination of titanium in sunscreen lotions with different sun protection factors using ICP-OES.

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DIODE LASER THERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR ANALYSIS OF BIOLOGICAL MICROSAMPLES

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A new sample introduction technique to inductively coupled plasma, diode laser thermal vaporization (DLTV) [1] is presented. In contrast to existing sample introduction systems based on laser ablation, the technique employs low-cost components, such as a diode laser, a simple laboratory-built chamber and common filter paper as a sample carrier. Well-defined submicroliter sample volumes are deposited on a preprinted filter paper and dried samples are vaporized in the prototype laser ablation chamber equipped with the diode laser. The diode laser power is sufficient to induce pyrolysis of the preprinted paper with deposited samples and the generated aerosol is carried out into the ICP MS.

The prototype chamber design is kept as simple as possible: it is made of glass tube and equipped with a near infrared continuous-wave diode laser attached to a common syringe pump serving as a translational stage for fast line scan along the paper strip. The minimal dead volume reduces turbulent flow and provides very fast wash-out. The prototype can hold up to 24 samples; analysis time per sample ~ 8 s has been achieved. Selection of optimal conditions, experimental arrangement, linear scan speed and other parameters is discussed.

The limits of detection of Co, Ni, Zn, Mo, Cd, Sn and Pb deposited on the pre-printed paper were found to be in a low pg range. The technique was applied to determination of lead in whole blood without any sample treatment. Using a multielemental calibration set prearranged on the carrier, LDTV ICP MS provided rapid and reproducible quantitative analysis and it presents an alternative to conventional nebulizer-based analysis of metals in liquid samples. Advantages are also easy preparation, archiving and transportation of samples on the paper strip and high throughput due to minimization of memory effects.

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KP-34

EXTRACTING OIL INCLUSIONS BY FEMTOSECOND LASER ABLATION FOR GC-MS ANALYSIS

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Fluid inclusions are micron-scale fluid-filled cavities in rock which were formed during diagenesis where mineral cement is added to pores or micro fractures. They record movement of past to present-day fluids (oil, gas, and water) through the rocks. Detailed molecular and isotopic data of petroleum inclusions, used in organic geochemistry to give information on source, maturity, and alteration of hydrocarbons, have been obtained so far by mechanical crushing followed by solvent or thermal extraction - gas chromatography–mass spectrometetry (GC-MS). Unfortunately, this crushing process does not allow the discrimination of geochemical signatures for different fluid inclusion generations. More recently, a laser ablation technique coupled with a GC–MS has been used to analyze individual petroleum inclusions [1]. In this study, straight chained, branched and cyclic alkanes and aromatic hydrocarbons with carbon numbers ranging from 4 (iso-butane) to 19 (pristane) have been identified with success. However, hydrocarbons with higher carbon numbers including biomarkers were not present on the GC-MS chromatograms.

The goal of our study is to investigate the potential of high repetition rate femtosecond laser pulses as sampling tools for the analysis of biomarkers in petroleum fluid inclusions. Well characterized oil was sampled using different laser ablation parameters and collected on glass fiber filters placed at the outlet of the ablation chamber. Filter extracts were then analyzed by GC-MS-MS and GC-GC-MS to reveal the conditions in which biomarker compounds remained unaltered after ablation. The second phase of this project will apply the developed techniques and protocols to the ablation and analysis of biomarkers in fluid inclusion assemblages.

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KP-35

SHORT-RANGE REMOTE LIBS THROUGH A SHIELDING WINDOW FOR MONITORING NUCLEAR WASTE MATERIALS

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One of the merits of laser-induced breakdown spectroscopy (LIBS) is the capability of remote detection.[1] We have developed a short-range remote (LIBS) system for the purpose of on-site monitoring nuclear waste materials. The LIBS measurement is required to be performed for remote nuclear waste materials located ~1.5 m apart from a shielding window. A second harmonic of Q-switched Nd:YAG laser beam was focused by a beam expander consisting of plano-concave (f = –50 mm) plano-convex (f = 300 mm) lenses. Plasma emission from the remote sample was collected through a Schmidt-Cassegrain telescope (aperture = 280 mm). The collected emission was focused by a plano-convex lens (f = 70 mm) on the core of a optical fiber (450 μm dia.) connected to a spectrometer. In the 50-cm Czeny-Turner spectrometer, the plasma emission was dispersed by a grating with 1200 grooves/mm and detected by an intensified charge-coupled device (ICCD) detector. The analytical performances of our remote LIBS system were evaluated for the lead-glass (70 mm thickness) and plastic (polycarbonate, 14 mm thickness) shielding windows. Also, the optical transmission spectra of the lead-glass and plastic windows were investigated using several optical sources such as a multi-line He-Ne laser, a UV lamp, a Nd:YAG laser. From these results, performances of the remote LIBS system were found to be significantly influenced by the optical transmittance of the shielding window in the wavelength region where the plasma emission spectra were recorded. Particularly, near 400 nm, a cut-off wavelength of the optical transmittance of both lead-glass and plastic windows, the remote LIBS measurement through the plastic window showed better performances due to the higher optical transmittance of the plastic window in this wavelength region. Using this remote LIBS system, we detected many Ce II lines in the wavelength region between 400 nm and 440 nm through the plastic window from 3% $CeCl_3$ in LiCl-KCl eutectic molten salt. This sample simulates salt wastes from pyrochemical process in nuclear industry.[2] The feasibility of our short-range remote LIBS system through a shielding window for on-site monitoring in nuclear industry will be discussed.

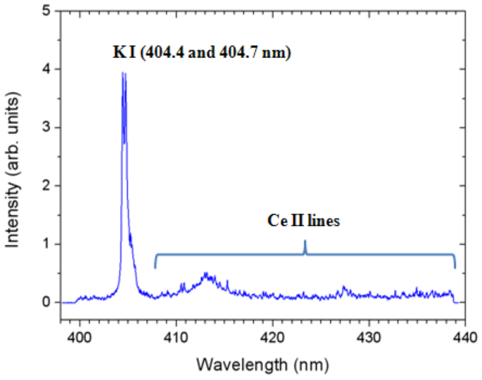

Fig. 1. Remote LIBS spectra of the LiCl-KCl molten salt with 3% $CeCl_3$.

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KP-36

UTILIZATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR FAST ONLINE DETERMINATION OF ELEMENTS OF INTEREST IN MINERALS

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We report on the utilization of Laser-Induced Breakdown Spectroscopy (LIBS) for determination of elements of interest in minerals.

LIBS is a simple atomic emission spectroscopy technique capable of real-time, essentially non-destructive determination of the elemental composition of any substance (solid, liquid, or gas). This technique is presently undergoing rapid research and development among others as the method for geochemical analysis. LIBS has attractive potential as the field tool for rapid man-portable and/or stand-off chemical analysis.

In this work we focused on the determination of the spatial distribution of precious metals (Pt, Ni, etc.) in the ore cross-section. As reference techniques for LIBS, Energy dispersive X-ray spectroscopy (EDS) and TESCAN Integrated Mineral Analyzer (TIMA) were utilized. For localization of metal structures inside the mineral sample μCT system was used. The advantages and disadvantages of combining LIBS with μCT will be detailed.

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HIGH SPATIAL RESOLUTION ELEMENTAL MAPPING USING FS-LA-ICP-MS AND FS-LIBS

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Without a doubt, femtosecond (fs) lasers offer compelling advantages in direct solid sampling laser ablation chemical analysis with mass or optical detection. From the chemical analysis point of view femtosecond lasers reduce matrix effects due to a nominalthermal effects (no fractionation) and provides nanometer-scale particle aerosol that is ideal for transport, vaporization and ionization in the ICP. From the laser-material interaction point of view fs-lasers are the primary choice for improving spatial resolution during ablation due tonominal heat affected zone and non-linear absorption. Femtosecond laser pulses in conjunction with high-numerical aperture objectives which offer tight focusing conditions, or near field effects which offer sub-diffraction limited surface modification, are basic strategies for increasing spatial resolution in laser ablation. Even though ablation sampling down to sub-30 nm has been achieved in this group for fs near-field apertured laser ablation, the limited ablated mass makes detection of traces elements by LIBS spectral emission very challenging.

In this study we assess spatial resolution limits for fs-LA and-LIBS as well as we report on the simultaneous used of high spatial resolution fs-LA and -LIBS for elemental mapping of major, minor and trace constituents in a wide range of samples.

DEVELOPMENT OF THE MOBILE STAND-OFF LASER-INDUCED BREAKDOWN SPECTROSCOPY SETUP

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Here we present the development of the Laser Induced Breakdown Spectroscopy (LIBS) setup in the Stand-Off mobile configuration. The setup with potential applications mainly in the field of archeology, geology and metal industry enables to move the LIBS technique and its advantages out of the laboratory. The stand-Off configuration (Fig.1.) utilizes refracting telescope to focus high energy laser pulse onto the sample surface in the given distance (~ 6 m) and reflecting telescope to remotely collect the radiation of the induced plasma.

The process of the development is described from the first table-top testing setup to the present fully mobile setup, together with the design intentions for the near future. Some of the spectra obtained from analysis of different materials in the distance of 6.2 m will be shown to demonstrate the performance of the current setup.

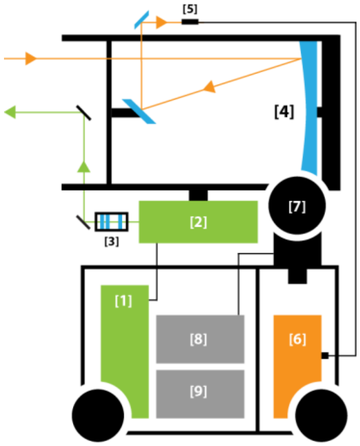

Fig.1. 1) Laser PSU, 2) Laser head, 3) Focusing optics, 4) Collection optics, 5) Optical fibre, 6) Spectrometer+ICCD detector, 7) Electromotors, 8) Controll unit, 9) PC

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KP-39

ANALYTICAL BENEFITS OF A ROTATING XY SHUTTER AND AN INFINITELY VARIABLE APERTURE FOR LASER ABLATION SAMPLING

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LA-ICP-MS is now a common technique for elemental imaging and elemental analysis of growth bands – applications where improved spatial resolution is desired. Both growth band analysis and elemental imaging can benefit, with respect to analytical data quality, from utilization of a rotating XY shutter beam shaping device (XYR configuration) to generate square and rectangular ablations.

In the case of growth band analysis, such as in the characterization of otoliths, speleothems and tree-rings, a NWR laser ablation unit equipped with a rotating XY shutter has been demonstrated to provide improved spatial resolution, and higher sensitivity. The XY shutter dimensions can be adjusted using ActiveView software in one micron increments such that a slit can be generated to yield high spatial resolution in once axis, and generate higher signal response in the other. In essence, high spatial resolution analysis can be achieved without compromising signal intensity, as is the case when a simple circular ablation is utilized.

Additionally, the angular rotation of the XY shutter enables continuous ablation perpendicular to the growth band, eliminating the possibility of sampling multiple growth bands simultaneously when the growth bands are curved. A non-rotational slit compromises spatial resolution by simultaneous sampling of multiple growth bands during its linear traverse. The same is true during ablation in the axis of the curved growth band, in that rotation enables the slit to traverse along the band without simultaneous ablation of its neighbor.

The advantages of the rotating XY shutter (XYR configuration) are demonstrated on Indian Creek flowstone (Holocene, Edwards Aquifer karst system, Central Texas) demonstrating significant curvilinear growth banding.

For elemental imaging applications the use of a square ablation is desired such that consistent dosage of laser energy is supplied to the sampling site as the laser is scanned across the sample.

The analytical benefits of an Infinitely Variable Aperture (IVA configuration) are also demonstrated. These include higher signal response for ablation of micro-features, via 1 micron adjustement of the crater size to exactly match the micro-feature size.

ANALYSIS OF HIGH-PURITY CU USING HIGH-SENSITIVITY LA-ICP-MS

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Copper has become a ubiquitous component of the modern world as a result of its extensive use in electronic devices and wiring thanks to its high electrical conductivity. Consequently, copper is in high demand globally, and increasingly in its purest commercial form at 99.999999% purity for ultra-high specification components. The requirement to certify trace elements at these low levels is beyond the capabilities of techniques such as XRF and Arc/Spark OES, hence more sensitive instrumentation is required to analyse contaminants at ppb levels, preferably without the need for extensive sample preparation/digestion.

Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS) meets these requirements, while new advances in system and sample chamber technologies on the NWR-series laser ablation systems from ESI enable the user to operate in a hands-off, autosampler-like mode. The availability of high-quality, certified reference materials has increased recently, making LA-ICP-MS a viable technique for the industrial determination of contaminants in copper.

This work demonstrates fully quantitative analysis of solid Cu by laser ablation ICP-MS using commercially available calibration standards and standard reference materials. Low ppm levels of contaminants in solid Cu are made possible.

KP-41

HIGH THROUGHPUT ANALYSIS OF INDUSTRIAL GRADE NIMONIC ALLOYS USING LA-ICP-OES

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Small changes in the elemental composition of metals can have a strong impact on the physical properties of the resulting alloy, such as changes in malleability or resistance to sheer stress. Unpredictable metal behavior can have devastating effects when employed in nautical, aeronautical and automotive industries. Buyers of metal parts for such industries therefore require increasingly accurate compositional information from their suppliers.

LA-ICP-OES offers a precise, high throughput, minimally-destructive solution. Because the LA-ICP-OES solution is a direct sampling technique, the use of acid for dissolution is eliminated, and therefore the sample preparation time, hazard, and risk of contamination are lowered.

For this study, an ESI NWR266$^{\text{Macro}}$ laser was coupled to a Thermo ICap ICP-OES. The NWR266$^{\text{Macro}}$ has up to a 780um diameter spot size, which makes it uniquely suited to bulk analysis. The large cell (100mm x 100mm) can accommodate many samples at a time, and bi-directional triggering between the ICP and laser can be used to automate the process. Analysis took 115 seconds per sample and involved three repetitions of each measurement. We used six nickel alloy standards[1][2][3] to successfully create calibration curves with coefficients of determination (R^2) greater than 0.997 for several of the certified elements with . This work demonstrates the achievable accuracy and precision for nimonic alloys with LA-ICP-OES.

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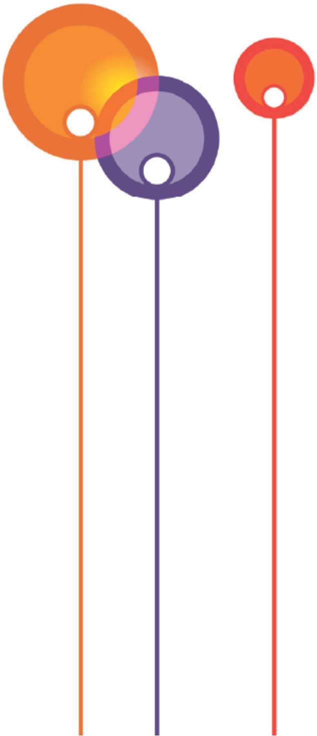
L section

Isotopic analysis



LEAD ISOTOPE ANALYSIS: REMOVAL OF ^{204}Hg ISOBARIC INTERFERENCE FROM ^{204}Pb USING A QUADRUPOLE ICP-MS EQUIPPED WITH MS/MS TECHNOLOGY

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Lead is an element whose isotopic pattern naturally varies more than any other element in the periodic table. The various stable isotopes are derived from uranium and thorium decay (^{238}U – ^{206}Pb, ^{235}U – ^{207}Pb; ^{232}Th – ^{208}Pb) with the only non-radiogenic isotope being the ^{204}Pb isotope. Lead is an important element for providence testing (e.g. tracing the origin of an artefact, food product, pollution event etc.) and its isotope analysis has been used in applications as far afield as pollution tracer studies for TEL (tetraethyl lead fuel additive), ore, olive oil & wine origin testing and forensic analysis of bullets.

One of the most important and difficult analyses for lead isotopes is for the archaeological dating of ore and Pb containing artefacts. For successful dating, all of the stable isotopes of Pb are required however there is an isobaric overlap from ^{204}Hg on the ^{204}Pb isotope. If any Hg is present in the sample, reagents or as a contaminant in the Ar gas, this would significantly bias the data.

Removal of the Hg-based isobaric overlap can be achieved by addition of ammonia to a collision-reaction cell (CRC) equipped instrument. Mercury ions undergo rapid charge-transfer reaction in the presence of ammonia (the Hg^+ ion is neutralised to Hg^0 and the charge is passed to the ammonia molecule) and fortunately lead does not react to any appreciable level.

This could lead to the successful removal of Hg isobaric interference from Pb – however the potential issue of new molecular interferences created within the cell remain unless the reaction can be sufficiently controlled by ion pre-selection. This poster demonstrates the benefit of a MS/MS capable ICP-MS for the effective interference-free analysis of lead isotopes.

APPLICATION OF Sr ISOTOPE RATIOS FOR THE DETERMINATION OF ORIGIN OF PREHISTORIC WOOD

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Wood artifacts from prehistoric times have been preserved in a salt mine environment in Hallstatt, Austria, for more than 3000 years. These artifacts present a unique archive of information on past mining industry. $^{87}Sr/^{86}Sr$ isotopic ratios are a recognised geochemical tool for the determination of origin in various fields as natural variations of the isotopic composition between regions are directly reflected in living organisms.

In this case, however, the storage conditions present a challenge with respect to inorganic contamination by the repository material. The extent of penetration of salt into the wood tissue was screened using LA-ICPMS. A decontamination strategy based on acid leaching was developed and successful separation of contamination and natural strontium could be achieved. This was shown by measurement of $^{87}Sr/^{86}Sr$ in leaching solutions and digests of wood using multiple collector ICPMS. The assumption of non-exhaustive removal of secondary salts was included into the evaluation by adoption of a mixing curve, which allows the mathematical extraction of biogenic Sr isotope ratios of the wood samples.

As a basis for the determination of possible origins of the wooden prehistoric artifacts (which are assumed having been traded), modern trees from several selected regions in Austria were analysed for their Sr isotopic ratios. The regions were chosen based on archaeological knowledge of settlements in the time period of interest and due to geological and silvicultural considerations. Four tree species, which are also represented in the archaeological finds, were sampled. Thus, we can present the first steps towards a map of Sr isotopic signatures bioavailable to different trees in Austria.

MEASURING ^{26}Mg/^{24}Mg AND ^{44}Ca/^{40}Ca ISOTOPE RATIONS IN ENVIRONMENTAL SAMPLES BY Q-ICP-MS

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An *in situ* multi-isotopic (^{26}Mg and ^{44}Ca) tracing experiment was carried out in April 2010 in a beech plot (Breuil-Chenue SOERE site, 58, France). Many samples of different kinds were collected during the tracing experiment (soil solution, soil cationic exchange capacity (CEC) extractions and vegetation samples). Although ICP-MS is less precise than TIMS or MC-ICP-MS, ICP-MS analysis times are shorter (typically 5min/sample) and often samples do not necessitate chemical purification prior to analysis which also reduces sample contamination risks.

Isotope ratio measurements with ICP-MS may be biases by spectral interferences (isobaric, polyatomic or doubly charged) and non-spectral interferences (matrix effect, mass bias drift).

The objective of the current study was to assess the precision and accuracy of ^{26}Mg/^{24}Mg and ^{44}Ca/^{40}Ca isotope ratio measurements with ICP-MS (Bruker 820MS) and define the different factors that need to be taken into account when developing methods for isotope ratio analysis on ICP-MS.

STRONTIUM ISOTOPIC ANALYSIS OF HUMAN SKELETAL TISSUE IN A PRESENT-DAY FORENSIC CONTEXT

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Strontium isotopic analysis of bone and tooth tissue of archaeological relevance is often relied on to obtain information on the geographical origin of humans, obviously confounded to a diet consisting of local agricultural products. There is less information as to the applicability of this approach in present-day forensic cases as a result of consumption of foodstuffs from various geographical origin.

This poster reports on the successful application of Sr isotopic analysis in such present-day forensic investigations. Although the technique is neither detailed nor exclusive in determining the residence of a person during life, it can provide essential clues in reconstructing the origin or provenance of human remains and, in this way, help in the identification of unidentified individuals in a forensic context.

The skeletal remains of four unidentified individuals were investigated for their Sr isotopic composition with the aim of helping in the identification of the origin and identity of the unknown individual.

Dissolution of the bone and/or dental (enamel) tissues was accomplished by means of a hotplate digestion using a HNO_3/HCl mixture (2/1). After isolation of the Sr fraction from the tooth or bone matrix via an extraction chromatographic separation, the $^{87}Sr/^{86}Sr$ isotopic ratio was measured using multi-collector ICP-MS (ThermoScientific Neptune) at Ghent University. Mass discrimination was corrected for by Russell’s law on the basis of a $^{86}Sr/^{88}Sr$ ratio of 0.1194. Repeated analyses of NIST SRM 987 $SrCO_3$ yielded an average $^{87}Sr/^{86}Sr$ ratio with a corresponding 2s uncertainty interval of 0.71026 ± 0.00007, in excellent agreement with the accepted $^{87}Sr/^{86}Sr$ ratio of 0.710248 ± 0.000023for this material [1].

On the basis of the measured $^{87}Sr/^{86}Sr$ ratio of the tissues, (a limited number of) potential areas of residence could be identified, while certain other regions could be excluded. Although the methodology does not allow pinpointing the exact location of residence, it provides data that are complementary to information obtained via independent evidence (DNA analysis). It, therefore, provides an additional argument concerning the assessment of an individual`s identity.

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LP-5

ISOTOPE DILUTION ANALYSIS FOR FORAMINIFERAL Mg/Ca PALEOTHERMOMETRY

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The magnesium/calcium ratio in foraminiferal calcite accumulated in deep sea sediments is a well established proxy of ocean paleotemperatures [1]. As the relationship between Mg/Ca and temperature is exponential, the accuracy of calculated temperature depends dramatically on the maintenance of the relative measurement precision across a wide range of ratios. Such an issue constitutes still an analytical challenge despite in the last two decades several alternative approaches have been developed. The lack of analytical standardization results in poor interlaboratory reproducibility which hampers data comparison and the actual reliability as climatic proxies [2].

Thus, even though inductively coupled plasma-mass spectrometry (ICP-MS) is a powerful tool to increase the accuracy and precision of Mg/Ca determinations, some analytical criticisms remain unresolved. A number of approaches have been proposed but poorly optimized and never directly compared. Those mainly used nowadays [3] are based on the simultaneous determination of Mg and Ca, but since the ratio ranges between 0.4 and 3 (mg g^{-}), high levels of Ca have to be introduced (up to 200 µg g^{-1}) giving potential problems of matrix and memory effects, poor precision for Ca (as the less abundant isotope has to be monitored, ^{46}Ca, 0.004%), contamination problems for Mg and questionable comparability of the analytical performances for the two elements. Isotope dilution analysis (IDA) offers a possible solution for some of such problems, but it has only been tested under not-fully optimized conditions, remains uncompared with other quantification strategies and not been fully implemented in practice [4].

In this study two improved methods based on IDA-ICP-quadrupole-MS for the determination of the Mg/Ca ratio in foraminifera are presented. Classical IDA with individual sample spiking and on-line IDA were implemented to fully explore the capability of such techniques in terms of analytical performances as well as practicality in real samples. The methods were developed and validated by using standard solutions and three materials certified for Mg/Ca ratios (BAM-RS3, ECRM-752 and CMSI-1767) distributed in the range of realistic values [2]. Double dilution was performed in order to determine Ca and Mg independently of the specific instrumental conditions required such as H_2 flow in the reaction cell (for Ca), Ar flows, lenses voltage and integration times. Optimization allowed the acquisition all isotopes of both elements, in particular the resolution of the most problematic interferences ($^{48}Ca^{2+}$ for $^{24}Mg^{+}$ e $^{40}Ar^{+}$ for $^{40}Ca^{+}$). Such optimization guaranteed higher robustness of IDA procedures (i.e. mass bias correction and estimation of isotopic abundances) as well as the use of ^{40}Ca (the most abundant isotope, 96.941%) as the reference isotope resulting in further improvements for data reliability.

The two IDA methods were also systematically compared with external calibration (with and without on-line internal standardization) in order to provide a first solid reference for the choice within the most updated methods for Mg/Ca determination in foraminifera, facilitating interlaboratory comparisons.

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LP-6

DETERMINATION OF $^{129}I/^{127}I$ IN FUKUSHIMA SOIL SAMPLES BY ICP-MS

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The accident at the Fukushima Daiichi nuclear power plant (FDNPP) resulted in a substantial release of radionuclides into the environment, including atmospheric of radioiodine and radioceium. The distribution of radiocesium has been studied, and the map of radiocesium contamination was made. On the other hand, the measurements of ^{131}I were limited, because of short half life of this isotope (8 days). In the event of a nuclear plant accident, an effective dose estimation of released ^{131}I is important. To reconstruct the early distribution of ^{131}I in the environment, ^{129}I has been used as a follow-up tracer due to its much longer half-life (15.6 Myr). The determination of ^{129}I in soils in Fukushima is of importance to investigate distribution of radioiodine released from the FDNPP. Recent advances in ICP-MS using a reaction cell have enabled us to determine the long-lived radionuclide ^{129}I in a number of environmental matrices. In order to improve the precision and accuracy of the $^{129}I/^{127}I$ isotopic ratio measurements, interfering signals such as ^{129}Xe have been reduced by using O_2 as a reaction gas [1,2]. We developed a method for the determination of ^{129}I in soil samples which uses an ICP-MS equipped with an octopole reaction system, permitting the investigation of radioiodine released by the Fukushima Daiichi Nuclear power plant (FDNPP) accident. The determination of ^{129}I by ICP-MS is capable of providing a high sample throughput compared to other methods. Nonetheless, the high background caused by ^{129}Xe impurities in argon plasma gas and polyatomic ions such as $^{127}IH_2^+$ have made ICP-MS determinations of this isotope difficult to carry out. In this study, oxygen was used as a reaction gas for reducing the background intensity of m/z 129, principally by ^{129}Xe. The contribution of polyatomic ion such as $^{127}IH_2^+$ could be effectively corrected for by assuming a production ratio. The detection limit for ^{129}I was successfully improved (0.1 pg). The measured $^{129}I/^{127}I$ ratios in NIST standard solution are consistent with the certified value of 0.981×10^{-6} within the analytical error. In order to confirm the applicability of the method to the measurement of soil samples, several samples collected in Fukushima were analyzed. The measured $^{129}I/^{127}I$ ratios in the samples are consistent with values determined by AMS within the analytical error. This method provides a powerful tool for the investigation of radioiodine contamination in Fukushima and elsewhere.

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LP-7

DETERMINATION OF ISOTOPIC RATIOS OF URANIUM ($^{235}U/^{238}U$) FOR THE DIFFERENT ORIGINS IN BARCELONA'S TAP WATER DISTRIBUTION SYSTEM IN ORDER TO DETERMINE THE SOURCE OF A WATER LEAK.

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The Tap Water Distribution System of Barcelona and their Metropolitan Area have more than 1000 km of pipelines, being one of the longer and important Drinking water network from South Europe, with a constant distribution of up to 300.000 m^3 of tap water per day. Rarely is the week that one or more samples arrives to our Laboratory, to identify the origin of a water sample, suspicious of being a water leak from tap water distribution system. The major causes of this located flooding are coming from the natural groundwater leaching from rain or other natural causes, such as sea water intrusion. Indeed, a precise methodology is required to identify the most likely origin of flooded water.

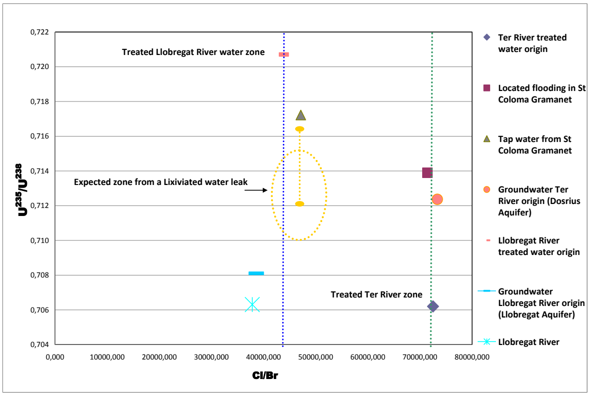
The isotopic studies using different isotopic ratios, such as $^{87}Sr/^{86}Sr$, $^{235}U/^{238}U$, etc., showed good results in a similar environmental problems, but in the most of published studies the technology applied, high resolutions ICP-MS equipments, is forbidden for most of environmental laboratories.

Therefore, following the methodology previously published by F. Vanhaecke *et al* [1] with minor modifications, we have applied a methodology to evaluate the isotopic ratio of $^{235}U/^{238}U$ from the different water origin in Barcelona´s tap water system, with a very high precision (RSD $\leq$ 0.2 %) necessary in these studies and working with more classical technique based on quadrupole ICP-MS (7500 cICP-MS Agilent).

The developed methodology has been applied, together to classical determination of conservative elements such as chlorine and bromine ratios, to determine the origin of the most important water leak occurred during last year 2012.

The most probable origin deduced by the results showed in the figure 1. was a leak of a treated Ter River water origin, located at few kilometres near of water flood-out, that has been percolated around the ground.

The diagram here presented demonstrates that the aquatic flood was not coming from the system of nearby drinking water, which mostly was fed by water treated about the Rio Llobregat.



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ALTERNATIVE METHOD FOR FAST AND PRECISE Pb ISOTOPE RATIO DETERMINATION IN CRUDE OIL, ASPHALTENES KEROGEN AND SEDIMENTARY ROCKS BY GC-MC-ICPMS

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A method for Pb isotope ratio determination in crude oil, asphalthene, kerogen and rock source is proposed. The method consists in two-separation steps: first Pb is ethylated and extracted in isooctane. Then, the isooctane extract is injected in a gas chromatograph for a second separation of Pb from the matrix.

By this method the total time of the procedure was reduced 15 times compared to the classical ion-exchange separation of Pb and the conventional-continuous sample introduction in the MC-ICPMS. Seven isotopes (^{202}Hg, ^{203}Tl, ^{204}Pb, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb) were monitored simultaneously with peak duration of 23 s. Data treatment was done using the method based on the slope of the linear regression of transient intensities of different isotopes. Precision (2RSD$_{EXT}$, n=21) obtained for the $^{208/206}$Pb and $^{207/206}$Pb ratios were 49 and 69 ppm, and the accuracy was 0.0033 and 0.0007 ‰ for the $^{208/206}$Pb and $^{207/206}$Pb ratios respectively (expressed as the relative deviation to the certified value).

LP-9

CHALLENGES FOR MASS FRACTION MEASUREMENTS OF ^{166m}Ho USING ION-COUNTING MULTI-COLLECTOR ICP-MS AND ISOTOPE DILUTION

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The operation of nuclear facilities and their eventual decommissioning must be done in a way to minimize environmental impacts. The radioactivity in the nuclear waste must be assessed properly and standardised methods are needed. Metastable holmium 166 (^{166m}Ho) is a long-lived radionuclide present in nuclear fuel after irradiation as a fission product. Part of the aim of the project ENV09 Metrology for Radioactive Waste Management of the European Metrology Research Programme (ERMP) is the determination of the half life of 166mHo with a combined expanded uncertainty of less than 3%.

The determination of the half life of ^{166m}Ho entails measuring the activity concentration and the mass fraction of ^{166m}Ho with sufficiently small uncertainties. A priori it should be possible to determine the ^{166m}Ho mass fraction at the required uncertainty level from the combination of an isotope dilution (ID) approach using natural ^{165}Ho as a spike and measurements by multi-collector ICP-MS.

The determination of n(^{166m}Ho)/n(^{165}Ho) in the project material as well as in the ID samples was a crucial step. This isotope ratio in the project sample was around 1:2000, since the ^{166m}Ho is produced by neutron activation of ^{165}Ho. Therefore, a combination of Faraday cups and ion counters was employed which requires corrections for detector background, deadtime and gain. Moreover, spectral interferences exist at m/z+ 166 due to the tailing of the signal from ^{165}Ho^{+}, the formation of HoH^{+} and the presence of ^{166}Er^{+}, even after chemical separation by ionic High Performance Liquid Chromatography, originating from natural Er impurities as well as from the decay of ^{166}Ho to ^{166}Er. This also required corrections. Finally, only few micrograms of ^{166m}Ho were available and a setup for running these measurements at a sample flow rate of 15 µL min^{-1} had to be implemented.

This poster presentation will describe the analytical protocol developed for these measurements, and will discuss in particular the way the different corrections required contribute to the final uncertainty associated to the n(^{166m}Ho)/n(^{165}Ho) measurements.

LP-10

ISOTOPE DILUTION MASS SPECTROMETRY AS A NEW STRATEGY FOR QUANTITATIVE ELEMENTAL ANALYSIS OF SOILS AND SEDIMENTS BY PULSED GLOW DISCHARGE TIME OF FLIGHT MASS SPECTROMETRY

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Metal contaminations in soils are a recurrent concern having implications in health, ecological and legislation issues. Traditional methods to determine metal concentration in soils and sediments involve an acid digestion step that is time consuming, prone to contamination and analyte loss. Particularly a complete dissolution of the sample can sometimes prove difficult when refractory phases are present. Several solid-state techniques can be used to determine metals concentration at the ppm level or below in soils and sediments but all of them have their pros and cons.

Glow discharges (GDs) have been widely investigated as powerful atomization, excitation and ionization tools for the direct analysis of a great variety of materials, both for bulk and for depth profile characterization. Advantages of GD sources coupled to mass spectrometry (MS) include fast sputtering rate, high depth resolution, multielement and isotopic capability, high sample throughput, minimal matrix effects, good detection, and experimental simplicity. Additionally, pulsed GDs (PGDs) have been recently proposed as attractive analytical alternatives to the more common GD operation mode using continuous powering. Among the different mass analyzers, GD-time-of-flight (ToF) MS systems are increasingly used here due to their high sampling rate and ability to collect complete mass spectra with the same precision, sensitivity and resolution regardless of the total number of isotopes being measured. PGD-ToFMS permits the quasi-simultaneous detection of ions along the GD pulse period and, thus, the observation of the different time domains with different ionization mechanisms in the formed plasma (denoted as prepeak, plateau and afterpeak regions). This allows the selection of the integration time detection window that provides the highest analyte signal with minimum spectral interferences. However, the main limitation of GD sources is related to quantification of the samples due to the lack of certified reference materials (CRMs).

Isotope dilution mass spectrometry (IDMS) is internationally regarded as a reference measurement method directly traceable to the International System of Units. In contrast to other calibration strategies, if the isotope equilibration is achieved the analytical result is not affected by signal drifts, matrix effects or analyte losses. To our knowledge, the application of isotope dilution in GD-ToFMS has not been investigated so far.

In this communication, the analytical potential of radiofrequency PGD-ToFMS is investigated for the first time in combination with IDMS for fast quantitative analysis of soil and sediment samples fused with lithium borate. The advantages of using such sample preparation procedure include: homogeneous mixing of analytes, possible dilution for highly concentrated elements and stability over time. The study was focused on the optimization of GD experimental parameters and the selection of the pulse region for each isotope of interest for the accurate measurement of isotope ratios. Limits of detection were carefully studied and the validity of the proposed quantification approach is demonstrated by the analysis of certified reference materials.

ACCURATE QUANTIFICATION OF MERCURY IN MARINE SAMPLES BY USING ISOTOPE DILUTION HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Determination of mercury content in the low ng·kg^{-1} range remains a fundamental analytical challenge and a great source of complexity for the realisation of reliable profiles of dissolved mercury.

Although the detection sensitivity of ICP-MS allows the direct measurement of mercury at sub-ng g^{-1} levels the physical deposition of salts on interface cones and polyatomic interference from the major ions in environmental matrices does not allow a simple analysis. Therefore, sample pre-treatment or matrix elimination prior to sample introduction into the plasma is often inevitable.

To achieve SI-traceable values with small combined uncertainties of mercury amount contents in marine samples, measurement procedures, according to sound metrological principles, were developed. The measurement method in all cases were based on isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) applied as a primary method of measurement. The correct assessment of the analytical procedural blank was of the crucial importance for obtaining reliable results. In order to achieve the lowest possible procedural blank, all sample-processing steps were accomplished in a class-100 clean chemical laboratory.

The estimation of the total uncertainty associated to each measurement result was fundamental tool for sorting the main sources of measurement biases. Preliminary forecast of the uncertainty budgets was used as a strategy to ensure that determination in mercury in seawater could be achieved with demonstrated traceability to a stated system of reference within less than 2% expanded uncertainty ($k=2$).

By looking at the distribution of uncertainty contributors in these studies, it could be seen that corrections for procedural blank and isotopic ratio precision are important issues due to the complexity of marine samples.

ELIMINATION OF ISOBARIC INTERFERENCES IN LEAD ISOTOPIC RATIO DETERMINATION OF ANCIENT GOLD SAMPLES USING REACTION CELL MODE FOR ICPMS

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The identification of provenance of ancient gold findings often basis on analysis of elemental pattern and lead isotopic ratios. The lead isotopic ratios in gold from different regions vary and the difference between older known gold regions of Europe and South America show different isotopic ratios than more recent gold sources e.g. in Africa or Alaska. Therefore, lead isotopic ratio pattern has a great potential to identify gold sources or to prove authenticity. Mainly used in provenance studies are the isotope ratios ^{204}Pb/^{206}Pb, ^{207}Pb/^{206}Pb and ^{208}Pb/^{206}Pb, but ^{204}Pb is isobaric interfered by ^{204}Hg and mercury is often present in ancient gold due to historical mining processes, where mercury was used to form amalgam alloys. Also historical fire gilding processes e.g. for silver objects involve mercury, whereas modern galvanic processes.

The removal of isobaric interferences such as ^{204}Hg on ^{204}Pb would require a resolution larger than 1000, so it is even not possible in high resolution magnetic sector field plasma mass spectrometry (HR-ICPMS) or multi collector (MC-ICPMS) to remove these interferences.

Therefore, we here propose a strategy to use an ion-molecule reaction with ammonia for QQQ-ICPMS to selectively remove isobaric Hg interference (termed chemical resolution) on ^{204}Pb and thus improve accuracy, precision and quantitative detection limits of lead isotopic ratio analysis of ancient gold objects. The efficiency of the removal of isobaric interferences by chemical reaction will be compared to conventional strategies like inter-element corrections and prospects and limitations for the analysis of cultural heritage will be evaluated.

LP-13

DETERMINATION OF Pu ATOM RATIO IN SETTLING PARTICLES USING ISOTOPE DILUTION HR-ICP-MS

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Anthropogenic radionuclides such as ^{239}Pu (half-life: 24,100 yr), ^{240}Pu (half-life: 6,560 yr) and ^{241}Pu (half-life: 14.325 yr) have been released into the environment as the result of atmospheric nuclear weapons testing, disposal of nuclear wastes and nuclear fuel-cycle reprocessing operations, etc. Most radionuclides globally dispersed in atmospheric nuclear weapons testing were released into the environment during the 1950's and 1960's. In the North Pacific Ocean, two distinct sources of Pu isotopes can be identified; i.e., the global stratospheric fallout and close-in tropospheric fallout from nuclear weapons testing at the Pacific Proving Grounds (PPG) in the Marshall Islands [1]. The Pu input from the close-in tropospheric fallout from the Pacific Proving Grounds mainly took place in the early 1950s whereas the maximum deposition of the global stratospheric fallout occurred in 1963. The mean atom ratio of ^{240}Pu/^{239}Pu from the global stratospheric fallout is 0.180 based on soil sample data [2], whereas that from close-in tropospheric fallout from the Pacific Proving Grounds is 0.33–0.36 [3,4]. The atom ratio of ^{240}Pu/^{239}Pu is a powerful fingerprint to identify the sources of Pu in the ocean. The objectives of this study were to measure the $^{239+240}$Pu concentrations and ^{240}Pu/^{239}Pu atom ratios in settling particles from the East China Sea continental shelf and to discuss the transport and scavenging processes of plutonium.

The $^{239+240}$Pu activities were measured with α-spectrometers equipped with passivated ion implanted silicon detectors and a multichannel analyzer. After determining $^{239+240}$Pu activities by α-spectrometry, Pu on the stainless steel disc was extracted with HNO_3. Pu isotopes were measured with a sector field inductively coupled plasma mass spectrometer (SF-ICP-MS; Element 2, Thermo Scientific) that was equipped with a guard electrode to eliminate secondary discharge in the plasma and to enhance overall sensitivity. A high-efficiency sample introduction system with a membrane desolvation unit (APEX-Q, Elemental Scientific) was used for sample introduction. Additionally, the normal skimmer cone was replaced by a high-efficiency cone. Details about operation condition optimization have been described elsewhere [5]. Activities and fluxes of $^{239+240}$Pu showed large seasonal variation. ^{240}Pu/^{239}Pu atom ratios in settling particles ranged from 0.21 to 0.25 and they were significantly higher than the global fallout ratio of 0.18. High atom ratio may prove the existence of close-in fallout Pu originating from the Pacific Proving Ground. The North Equatorial Current and Kuroshio Current were proposed as pathways for transporting PPG Pu to the western North Pacific and its adjacent seas.

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LP-14

A COMPARATIVE STUDY OF IRON ISOTOPIC RATIOS IN TRANSGENIC AND NON TRANSGENIC SOYBEAN BY ICP-MS

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Some comparative studies concerning alterations in proteins, metalloproteins, metals and enzymes have demonstrated significant differences among transgenic and non-transgenic soybean seeds [1,2]. Fe, for example, is present at higher concentration in transgenic than in non transgenic soybean seeds [1]. These differences suggest that the genetic modifications are providing not only tolerance to herbicide but also cause many changes in the whole metabolism of the transgenic plants. Taking into account that Fe is an essential plant micronutrient, required for life-sustaining processes, from respiration to photosynthesis, some questions raised with this information are: Have the other transgenic plant parts higher amounts of Fe? Are the processes related to intake, transport and storage suffering some changes due to genetic modification? A potential tool for obtaining a better insight in these processes is to use tracer experiments employing stable isotopes [3], in which stable isotopic tracers with an isotopic composition different from the corresponding natural one is added to the studied system and changes in the selected isotope ratio monitored. As ICP-MS can provide this isotopic information, it is an excellent choice for carrying out Fe metabolism studies. Fe isotope ratio determination is difficult by quadrupole-based ICP-MS due to severe isobaric and polyatomic interferences. Thus, this work aims to evaluate Fe distribution (total Fe) and Fe isotopic ratios in different plant parts (roots, stems and leaves) of transgenic and non transgenic soybean employing ICP-MS with dynamic reaction cell (DRC). The strategy combining correction equations and H2 as reaction gas for eliminating interferences was evaluated and it did not eliminate completely the Ca-based interferences disturbing the Fe isotopes and the ^{52}Cr and ^{60}Ni signals used for isobaric corrections. For total Fe determination the isotopes ^{54}Fe and ^{56}Fe were the best option and the use of Ca-matrix matched blanks depended of Ca concentration present. Two certified reference materials - NIST-SRM 1643e (Water) and 1573a (Tomato leaves) - were analyzed for total Fe and the concentrations found were in agreement with the certified values. The Fe concentrations found for roots, stems and leaves of grown 21-day-old soybean plants and for the original seeds were 401.4 ± 20.4; 65.1± 2.7; 133.2 ± 2.1 and 52.1 ± 0.7 mg kg $^{-1}$, respectively, for transgenic; and 441.1 ± 20.8; 46.8 ± 1.6; 135.6 ± 1.2 and 50.7 ± 1.6 mg kg $^{-1}$ for non transgenic soybean. It is possible to observe that transgenic stems and seeds presented higher values than non transgenic ones, but, roots and leaves presented lower values. According these results, it is clear that only the total concentrations cannot prove that one or another soybean plant is up taking more Fe from the soil. The isotope ratios (^{54}Fe/^{56}Fe, ^{57}Fe/^{56}Fe and ^{58}Fe/^{56}Fe) obtained for a 50 μg L^{-1} Fe standard solution were 0.0597 ± 0.0002, 0.0237 ± 0.0004 and 0.0033 ± 0.0001 in comparison to natural ones (0.0637, 0.0231 and 0.0031). These isotope ratios are disturbed when the Ca concentration increases in the solution and then, the Fe-Ca separation must be performed. As factors related with signal acquisition procedures can affect isotopic precision data, optimization of these parameters was done. Besides, experiments to improve accuracy are in progress.

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BROMINE ISOTOPE ANALYSIS – A TOOL FOR INVESTIGATING BIOGEOCHEMICAL CYCLE OF BROMINE-CONTAINING ORGANIC AND INORGANIC COMPOUNDS IN THE ENVIRONMENT

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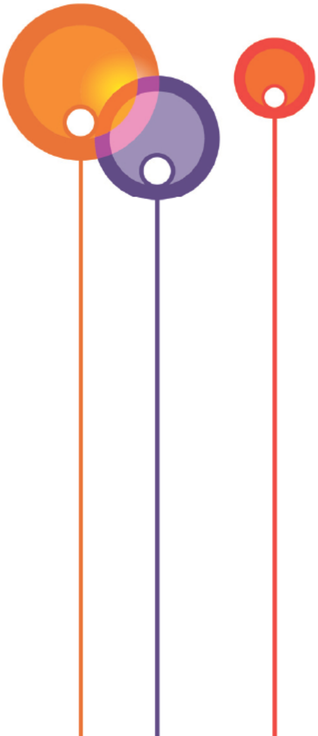
Brominated organic compounds are found widely in the environment. Nowadays, more than 1600 organobromine compounds produced naturally by marine organisms are known. Synthetic brominated organic compounds are often applied as flame retardants, pesticides and water treatment agents. Due to a possible toxic effect of these compounds on human health, investigation of their biogeochemical cycle in the environment is of the utmost importance. In this sense, the examination of isotopic composition of bromine in the individual organic compounds may serve as a powerful tool for understanding their origin and fate in the environment.

Based on the fact that mass difference between isotopes ^{81}Br and ^{79}Br is small, it could be assumed that isotope fractionation of bromine in organic compounds as a result of different biotic and abiotic processes will be relatively small. Therefore, highly sensitive and highly precise techniques must be used for the bromine isotope ratio analysis of the individual compounds.

The work presents a new methodology for the precise determination of bromine isotope ratio in individual organic compounds based on the simultaneous introduction of brominated organic compounds and strontium as an external standard into MCICPMS. Attained external precision (2σ) up to 0.1‰ allows applying the new technique for the determination of bromine isotope fractionation occurring during different chemical and biological transformations of the specific brominated organic compounds. In the present study, bromine isotope enrichment factors were determined for the debromination processes undergoing by different mechanistic pathways.

M section

Speciation analysis, metallomics and nanoparticle analysis



METALLOTHIOLOMICS – INVESTIGATION OF THIOL PEPTIDE REGULATED METAL HOMEOSTASIS IN ALGAE BY LC-ESI MS, LC-ICP MS AND ELEMENT IMAGING TECHNIQUES

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Intracellular thiol peptides are highly important for biological processes, containing the major active form of sulfur (thiol or sulfhydryl group: –SH). The tripeptide glutathione (GSH, γ-Glu-Cys-Gly) serves as intracellular metal binding thiol ligand in algae, fungi and seed plants. In the same way phytochelatins (PC) of the general structure $(\gamma\text{-Glu-Cys})_n\text{Gly}$ ($n = 2$–6) form metal complexes. They are synthesized in plants under metal stress by phytochelatin synthase from GSH. Thiol peptides play the most important role in the plant and fungi metal homeostasis. Recently, for entirety of thiol peptides and their metal complexes the term metallothiolome was coined and the concept of metallothiolomics summarizes all analytical approaches for the investigation of the thiol peptide regulated metal homeostasis [1]. The approaches for the characterization of the metallothiolome are basing primarily on LC-MS coupling systems. Within this concept, LC-ESI MS is employed for identification of metal-thiol peptide complexes as well as for identification, structural characterization and quantification of the metal-free apo forms. LC-ICP MS is used for detection and quantification of metal-thiol complexes. In addition, techniques for imaging of metals and other concomitant elements (e.g. S and P) approach the local distribution of the metallothiolome in a biological cell. Synchrotron generated high flux X-ray beams focused down to a size of about 0.5 µm allow elemental imaging by micro X-Ray Fluorescence (µXRF) at single cell level. EXAFS and XANES provide additional information about the chemical environment of metals and thus their coordination by thiol groups. Elemental imaging by mass spectrometry can be achieved with nanoSIMS, a technology providing for metals a spatial resolution of 0.2 µm and for light elements even 0.05 µm, thus it is suitable for localization of metals and sulfur at subcellular level.

This presentation introduces the concept of metallothiolomics in a general way and illustrates it for the investigation of metal stress in the two different green algae *Chlamydomonas reinhardtii* and *Micrasterias denticulata*. Identification and quantification of thiol peptides (phytochalatins) revealed that both algae responded mainly to Cd stress, however, *M. denticulata* showed also low phytochelatin production after Cr exposure [2,3]. The physiological characterization of metal stress in algae was completed by relative quantification of mRNA transcripts and modeling of thiol peptide - enzyme interactions [4]. The possibilities of metal localization and speciation by synchrotron based X-ray techniques are demonstrated in individual cells of the Cd-stressed aquatic fungus *Heliscus lugdunensis*. Moreover, the potential of nanoSIMS for imaging of metal stress in cells will be discussed.

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MP -2

ANALYSIS OF LANTHANIDE LABELLED PROTEIN DIGESTS VIA RP-IP-nanoHPLC COUPLED TO ICP-MS AND MALDI-MS

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Knowledge about the identity and abundance of proteins is the key to understanding biological pathways. Peptide analysis after protein digestion is one of the main foci in the field of proteomics. ICP-MS and its capability for absolute quantification recently found their way into this research field. In order to detect peptides sensitively by ICP-MS, they have to be labeled, most commonly with a metal. Several different approaches were already published for this purpose comprising e.g. direct covalent tagging with mercury [1] or a far less toxic labeling with triple charged metal ions using bi-functional chelating agents [2,3]. One of these chelating agents is DOTA (1,4,7,10-tetraazacyclododecane-1,4,7-tris-acetic acid), which is a very strong chelator for lanthanide ions. Those rare earth metals are easily ionized and sensitively detected in ICP-MS, show a low background during analysis and are not present in biological samples. Peptides of interest can be labeled using DOTA-compounds targeting different functional groups in amino acids.

In this study two different DOTA compounds were utilized, selectively targeting either amino or sulfhydryl groups. Those reagents were used for derivatization of model peptides as well as applied for the first time to complex mixtures of tryptic peptides in several protein digests. Model peptides in the first step allowed the development of a pre-cleaning step for lowering the metal background caused by the derivatization. The protein digests were labeled separately with different lanthanides and analyzed together as a multiplex using IP-RP-nanoHPLC with UV detection coupled to ICP-MS or complementary to matrix assisted laser desorption ionization (MALDI) MS. MALDI-MS enabled the identification of the peptides detected in ICP-MS after labeling and gives a hint regarding labeling efficiencies of the different DOTA-compounds. A previous study even showed that peptide detection with MALDI-MS is enhanced by DOTA [4].

A universal strategy for the alignment of the chromatograms obtained after ICP-MS and MALDI-MS analysis was tested. In this context, the UV detection was found to be a useful supplement to the detection with both MS systems. Also the differences between the two different DOTA labelings were investigated and show further possibilities for a more selective peptide quantification as well as possible limitations of the method.

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MP -3

SILVER NANOPARTICLE CHARACTERIZATION AND STABILITY ASSESSMENT THEREOF IN CELL CULTURE MEDIA BY ICP-MS IN SINGLE PARTICLE MODE

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Engineered nanomaterials are used increasingly around the world. In recent years, environmental concerns are being raised that call for risk assessment, toxicity studies, and safety policies. It is therefore important to provide analytical tools that are able to characterize various types of nanomaterials in a sensitive and fast fashion. In this study, the analytical performance of three sample introduction systems, a PFA micronebulizer with Peltier-cooled cyclonic spray chamber (PC^3), a PFA micronebulizer with heated cyclonic spray chamber and three-stage Peltier-cooled desolvation system (APEX Q), and a monodisperse droplet generator (Microdrop) with in-house built spray chamber, were compared for the characterization of silver nanoparticles (AgNP) with different sizes (20 – 100 nm) using single particle inductively coupled plasma mass spectrometry (SP-ICP-MS). With continuous polydisperse and pulsed monodisperse droplet sample introduction 20 nm NP were successfully detected. Detection efficiencies (20 – 100 nm AgNP) were in the range of $5.8 \cdot 10^{-5}$ – $8.2 \cdot 10^{-5}$ counts per atom, cpa (PC^3), $7 \cdot 10^{-5}$ – $9.5 \cdot 10^{-5}$ cpa (APEX Q), and $8.1 \cdot 10^{-5}$ – $1.2 \cdot 10^{-4}$ cpa (Microdrop). Size measurements performed by SP-ICP-MS were validated by transmission electron microscopy measurements. Because silver toxicity depends on the silver species in the sample, simultaneous detection of AgNP and free Ag(I) ions was studied with droplet sample introduction.[1] Consequently, the long-term stability of AgNP with different stabilizing agents was investigated in cell culture media that are often used in toxicological studies.

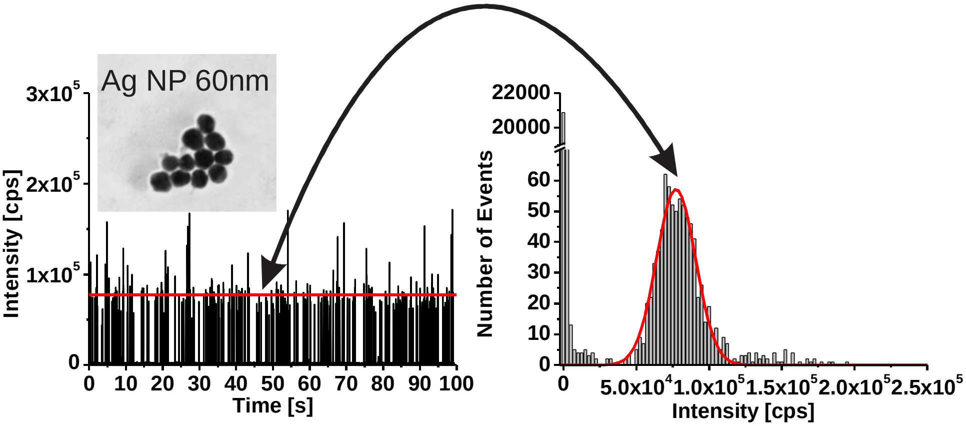

Fig.1 Typically obtained ICP-MS signal distribution of transient NP signals (^{107}Ag, 60nm AgNP; on the left) and corresponding histogram (on the right) [1].

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MP-4

STUDY OF ARSENIC SPECIES OCCURRENCE IN SPANISH DAILY FOOD CONSUMPTION

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Arsenic is a toxic element when it is in inorganic forms (As(III) and As(V), especially the first). The intake of this element in human (by water and food) has been estimated to be in the range 12 to 20 μg As per day [1], contributing in a greater extent a diet rich in seafood with typical levels ranging from 5 to 50 $\mu g \cdot kg^{-1}$. However, these levels in seafood are not considered as a health hazard because arsenic is mainly present as non-toxic organoarsenicals (arsenobetaine and arsenosugars, this later predominantly in algae). Other foods such as milk, meat, cereals and vegetables also contribute to arsenic intake in the diet although in a lower magnitude [2]. More recently, however, rice and rice-based products have been identified as significant dietary sources of inorganic arsenic [3], increasing the concern about potential exposure of specific groups of population to these toxic species. Therefore, the main issue about arsenic toxicity from diet is nowadays related to inorganic arsenic, what is driving the need for selective, sensitive and robust method for determining the iAs content in foods, covering a wide range of matrices.

The present work consider the application of a speciation analytical approach based on acid extraction of arsenic species from daily food consumption, and latter speciation by HPLC-ICP-MS. The approach has been applied to rice and rice-based food, as well as wheat flour, bread, and products containing bran, barley and other cereals from different areas of Spain. In addition, rice-based and cereals infant foods were also considered. Finally, changes in arsenic speciation of some of these foods after cooking were considered.

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COMBINED TECHNIQUES: LC – ICP MS AND LC – ESI-LTQ ORBITRAP MS AS A POWERFUL TOOL TO INVESTIGATE ELEMENTS SPECIATION IN PLANTS

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Investigation of elements speciation in plants requires special approach that allows us to deal with different obstacles emerging during the work with plant samples. To date, analytical information on molecular forms of metabolites involved in accumulation of elements such as iron, zinc, copper, aluminum or selenium are very limited because of the lack of methodology that would work when applied to complex biological matrix. The major problems that can appear and impede the analysis are low concentrations, various labilities, unstability and high diversity of complexes present in plants. Part of theses issues can be solved by using diverse techniques such as HPLC to purify, separate and preconcentrate compounds, ICP MS for detection and quantification or ESI MS/MS for identification of elements complexes and determination of their structure. However, results obtained using just one of the analytical techniques may be incomplete and require further investigation therefore the best solution is using the combination of hyphenated techniques based on high-resolution separation by chromatography or electrophoresis with sensitive detection by elemental and molecular MS [1,2].

The online coupling of size exclusion column (SEC) and hydrophilic interaction column (HILIC) to either a collision cell ICP MS (for elemental mass spectrometry) or an ESI-LTQ Orbitrap MS (for high resolution molecular mass spectrometry) instruments has been chosen for elements speciation analysis in plant saps and extracts. The optimization of chromatographic conditions and using different kinds of columns allowed separation of varied compounds and additionally a collision cell ICP-MS and an ESI-LTQ Orbitrap MS instruments gave us the great potential as the detection system. The advantages of using both instruments were their high sensitivity and spectral selectivity for element isotopes and for isotopic profile of molecules containing the elements of interest, respectively. The comparison and combination of data obtained by coupling LC in parallel with ICP MS and ESI MS/MS allowed us to develop a strategy to detect and to quantify systematically species present in plants.

This approach has been successfully used to achieve information about speciation of various elements present in plants like *Pisum Sativum, Arabidopsis halleri, Brassica nigra* or *Plantago Algarbiensis.*

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PHYTOCHELATINS PRODUCTION IN MICROALGAE *CHLORELLA SOROKINIANA* IN RESPONSE TO METALS

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Phytochelatins (PCs) are small peptides with the general structure (γGluCys)nGly (n= 2-11), with Gly potentially replaced by Ala, Ser, Glu, or missing. PCs heavy metal-binding peptides play important roles in the detoxification of toxic heavy metals and the regulation of intracellular concentrations of essential metals in eukaryotes, including higher plants, fungi and microalgae.

Chlorella sorokiniana is an alga that is known for its ability to accumulate metals and this work explores the ability of *Chlorella* to bioconcentrate and to detoxify different species of selenium and mercury. When *Chlorella* is exposed to Se in the form selenate, the element is rapidly absorbed within first minutes at the cell surface where it is irreversibly fixed. After 24-48 hours, about 40% of the total fixed Se is located inside the cells in organic forms, being important the presence of selenomethionine [1]. *Chlorella* also produces the potential detoxification of phytochelatins compounds, when exposed to selenate.

Numerous studies have shown that Hg is highly toxic and concentrations at or lower than 0.005 $mg \cdot L^{-1}$ cause reduction in both the survival and reproduction of various species of microalgae.

In this work, the microalgae *Chlorella sorokiniana* has been exposed to selenium and mercury. This technique, applied earlier for the determination of mercury PCs in plants [2], was adapted for the separation and identification of Hg/Se biothiols synthesised from sodium selenate and mercuric chloride with reduced glutathione (GSH) and cysteine (Cys). The presence of phytochelatin complexes were characterized with a metallomics approach that involves mercury and selenium RP-HPLC-ICP-MS profiling and achieved by mass spectrometry analysis (QqQ-TOF).

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MP-7

CHARACTERIZATION OF METALS BOUND TO MARINE DISSOLVED ORGANIC MATTER BY SIZE EXCLUSION AND ANION EXCHANGE HPLC HYPHENATED WITH ICP-MS

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A speciation procedure based on the use of size exclusion chromatography (SEC) followed by anion exchange chromatography (AEC) hyphenated with inductively coupled plasma – mass spectrometry (ICP-MS) was developed for assessing metals bound to marine dissolved organic matter (DOM). Surface seawater samples (100 L) were subjected to tangential flow ultrafiltration (10000 Da cut off) for isolating and pre-concentrating dissolved large molecules. The isolated fraction (retentate) consisted of 1 L, which was further freeze-dried and re-dissolved to 250 mL with ultrapure water. After HI Trap desalting of the re-dissolved retentate, SEC with UV detection showed marine DOM ranging from 6.5 kDa (lower than the permeable volume of the SEC column) to 17 kDa. A further characterization of this fraction by AEC with UV detection revealed the existence of four groups of macromolecules exhibiting retention times of 2.3, 2.8, 4.5 and 14.0 min. AEC hyphenated with ICP-MS showed the presence of strontium and zinc in the first AE fraction isolated from the SEC fraction; while manganese was found to be bound to the second AE fraction. Cobalt was found to be bound to molecules comprising the third AE fraction. After off-line ICP-MS determinations, percentages of metals bound to the isolated marine DOM were 0.24, 1.5, and 0.011% for Co, Mn, and Sr, respectively. However, percentages lower than 0.01% were found for Zn binding isolated marine DOM ($2.7 \cdot 10^{-3}$%).

MP-8

WATER SOLUBLE HALIDES SPECIATION IN ATMOSPHERIC PARTICULATE MATTER BY ANION EXCHANGE HPLC-ICP-MS AFTER PRESSURIZED HOT WATER EXTRACTION

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Water soluble bromine (bromide and bromate) and iodine (iodide and iodate) species in atmospheric particulate matter (PM$_{10}$ and PM$_{2.5}$) were measured by inductively coupled plasma-mass spectrometry (ICP-MS) after anion exchange high performance liquid chromatography (HPLC). The leaching of the water soluble iodine and bromine fractions was performed by pressurized hot water extraction (PHWE). Optimum extractive conditions showed that the pressurized leaching procedure can be performed in 9 min (5 min as a pre-heating time, 2 min as a static time, 1 min as a purge time, and 1 min as an end relief time). The use of diluted acetic acid as a modifier did not improve the target recoveries, and efficient recoveries could be assessed by using water as a solvent. Because the particulate matter are homogeneously dispersed onto the filters, dispersing agent (diatomaceous earth) was not needed. This fact reduces the time for filling the extraction cells. Leaching of water soluble halides were reached at 100°C and 1500 psi, after only one extraction cycle for 2 min (static time).

Total bromine and iodine were determined by ICP–MS after applying a microwave assisted alkaline (TMAH) extraction procedure. Similarly, total water soluble bromine and iodine were also assessed by ICP-MS. Optimized HPLC conditions consisted of an isocratic elution with 175 mM ammonium nitrate plus 15% (v/v) methanol as mobile phase (optimum flow rate of at 1.5 $\mathrm{mL \cdot min^{-1}}$). Analytical performances, such as limits of detection and quantification, repeatability and analytical recoveries of the over–all procedure have been established. Results obtained show that water soluble halides accounted for approximately 20.9 ± 1.3 and 11.8 ± 0.6% of the total bromine and total iodine, respectively. Percentages of 79% of bromine and 89% of iodine were found as non water soluble fractions, which may be organic non water soluble species in addition to molecular iodine (I_2). Bromide (Br^-) and iodate (IO_3^-) were the major species, and they accounted for 100% of the total water soluble bromine and iodine, respectively.

SPECIATION ANALYSIS OF CHROMIUM IN DRINKING WATER SAMPLES BASED ON ION-PAIR RESERVED-PHASE HPLC-ICP-MS: FULL VALIDATION OF THE ANALYTICAL METHOD

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Interest in the trace determination of Cr is growing because of its significant differences in chemical behavior, bioavailability and toxicity. Chromium exists in environment in several species of which Cr(III) is considered to be essential nutrient for the proper function of human body (at the trace level), unlike Cr(VI), which is thought to be strongly toxic owing to high oxidation potential, and ability to penetrate biological membranes - main reason of its cancerogenic and mutagenic properties [1].

A rapid, as well as sensitive method for separation and quantitative determination of chromium compounds in drinking water by HPLC-ICP-MS was submitted. Considering that the presentation of an analytical result must be accompanied by some indication of the data quality, a detailed validation of the method (according to the international guidelines ISO/IEC 17025:2005) was performed [2]. In the validation process a number of parameters for both the analytical procedure (among others selectivity, linearity, limit of the detection and quantification, precision) and the measurement result (the uncertainty budget of measurement) were estimated [3,4].

As a consequence of method validation experiment, the obtained LOQ, repeatability as well as intermediate precision were satisfying for the quantification Cr(III) and Cr(VI) in water matrices. Trueness of the presented method was verified by standard addition method. The recovery rate of both determined analytes resulted between 93% and 113%. Considering that the validation of the method and the evaluation of measurement uncertainty are crucial for quantitative analysis, the assessment of uncertainty budget mentioned above was carried out in two different ways: modelling approach and single-laboratory validation approach. The measurement uncertainties of the results were found to be 4.4% and 7.8% for Cr(III), 4.2% and 7.9% for Cr(VI) using the classical concept and method validation data, respectively. In conclusion, the obtained results demonstrate that the method can be applied effectively for the destined purpose.

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SPECIES STABILITY - SPECIATION ANALYSIS OF CHROMIUM: A CASE STUDY OF WATER SAMPLES FROM SURROUNDINGS OF RADOM

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Elemental speciation has become an essential part of the environmental researches considering the fact that toxicity of many elements depends on their oxidation states. In the literature, the opposite properties of two most important species of chromium: Cr(III) and Cr(VI) were widely described. In most cases, environmental contamination by chromium comes from industrial activities, such as galvanization, production of steel, pigments and tanneries. As a consequence of many industrial processes a significant amount of this element is presented in waste waters.

There is only few recent studies on chromium species stability, sample storage and preservation, however, it is important stage of analytical process. The aim of this work was to perform stability tests of the species of this element in water matrices. The research materials were collected from Radomka basin, area of Radom, south-eastern part of Poland. This place is an excellent example of anthropogenic pollution of environment by chromium, which is a result of tanneries industry location and activities of numerous factories. As a consequence there is a need of chromium species monitoring (especially Cr(VI)) in industrial surroundings [1,2].

Stability tests were carried out on water samples spiked with the standard solutions of single and both Cr forms at 10 $\mu g \cdot L^{-1}$ diluted with mobile phase. In order to investigate the influence of container material on species stability, the samples were kept in glass and plastic. The examined water was frozen and thawed directly before analysis, then it was carried to the freezer back until further use. The tests were performed within a short period of time, the solutions were analysed at 0, 1, 3 and 16 day. A HPLC-ICP-MS method for quantitative determination of chromium species, Cr(III) and Cr(VI), was used.

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MP-11

SPECIATION ANALYSIS OF SUGAR PHOSPHATES VIA ANION EXCHANGE CHROMATOGRAPHY COMBINED WITH ICP-DRCMS

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Sugar phosphates are central compounds of the cellular metabolism and important intermediates of the pentose phosphate pathway. In general, the analysis of sugar phosphates is aggravated by their high polarity, low concentration levels in real samples, their instability and rapid metabolic turnover as well as their poor UV absorbance. Accordingly, a sensitive and selective method is necessary for accurate quantification of sugar phosphates. Several methods for analysis of sugar phosphates such as HPLC-UV [1], HPLC-PAD [2], CE-MS [3], LC-MS [4], GC-MS [5] have been reported indicating the urgent need for enhancement of both separation efficiency and sensitivity. In this work, we developed an anion exchange chromatography (AEC) combined with inductively coupled plasma quadrupole mass spectrometry with dynamic reaction cell (ICP-DRCMS) as a new approach for analysis of sugar phosphates.

Chromatographic separation of sugar phosphates was carried out employing gradient elution with NaOH and Na_2CO_3. The high concentration of sodium hydroxide and sodium carbonate in the mobile phase leads to ion suppression in the ICP. For removing the sodium ions present in the mobile phase, a self regenerating anion suppressor was placed between anion exchange column and sample introduction device in ICP-MS. The phosphorus monoxide ion (m/z=47) was detected by ICP-MS with dynamic reaction cell (DRC) mode in order to eliminate polyatomic interferences. The limits of detection and limits of quantification were improved via analyte pre-concentration with a newly developed solid phase extraction based sample preparation procedure.

In this study, the novel method has been applied for purity control of comercially available sugar phosphate standards and for cross validation of GC-MS and LC-MS based methods, which are currently developed in our lab, aiming at the accurate quantification of sugar phosphates in cellular samples. Analytical figures of merit will be presented and discussed.

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MP-12

PHOSPHORUS-TAGGED METABOLOMICS FOR ANALYSIS OF PHOSPHOLIPIDS IN ALZHEIMER'S DISEASE

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Phospholipids play a central role in the biochemistry of all living organisms, since they are responsible of biological compartmentalization, forming part of lipid bilayer that serves as structural barrier to protect cells and subcellular components from external conditions. In addition to their structural role, some phospholipids participate in other biological activities, such as cellular signaling or storage of arachidonic acid and other polyunsaturated fatty acids that can be metabolized to biologically active eicosanoids.

In Alzheimer's disease and other neurodegenerative disorders, abnormalities in membrane phospholipids are well known occurring processes, principally related to overactivation of phospholipase A2 but there are also evidences of the role of phospholipases C and D, although they have been much less studied [1]. The postulated mechanism of this pathological phospholipid breakdown supposes a complex sequence of cellular events in hypoxic neurons, involving release of glutamate and influx of large amounts of calcium into neurons, which finally induce overactivation of catabolic enzymes including phospholipases [2].

Metabolomics presents a high potential in health survey, since metabolites may be considered as the final product of interactions between gene and protein expression at the cellular environment, therefore, it is very valuable for understanding biochemical and biological mechanisms associated to these complex systems [3]. In this study, a metabolomics approach based on direct infusion mass spectrometry was performed in blood serum samples of Alzheimer's disease patients, allowing to study metabolites involved in dysregulated biochemical pathways. In this way, imbalances in phospholipids levels in AD respect healthy control samples were found, attending to the type of fatty acid contained in the structure.

Finally, a target analytical approach focused on phospholipids was optimized, based on separation of different species by reverse phase UPLC and complementary detection by molecular and atomic mass spectrometry. The presence of phosphorus in the structures of phospholipids enables its quantification by phosphorous-tagging with inductively coupled plasma mass spectrometry (ICP-MS), without the use of structurally matched standards, with a high sensitivity. Alternatively, identification of corresponding phospholipids can be achieved by mass spectrometry analysis (QqQ-TOF). Thus, the tendency observed in metabolomic profiles could be assessed.

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MP-13

COMBINATION OF METABOLOMICS AND METALLOMICS IN *P. CLARKII* TISSUES TO ASSESS THE POLLUTION IN DOÑANA NATIONAL PARK

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The study of environmental issues is generally performed by the use of bioindicators that reflect the biological response to the presence of contaminants. Invertebrates have been frequently proposed for this aim [1]. The red swamp crayfish Procambarus clarkii lives in a wide range of environmental conditions, even in highly polluted waters and it was introduced into the marshes of the lower Guadalquivir River (SW, Spain) in 1974, colonizing quickly all the aquatic systems around in the absence of natural predators, reaching the Doñana National Park. Therefore, the crab can be used as bioindicator to measure the effects of pollutants in this important ecological reserve. In this context, omics sciences are suitable tools to evaluate the global biological response to contamination.

Metabolomics studies the complete set of low molecular weight compounds in living organisms, which may be considered as the final product of interactions between gene and protein expression and the cellular environment. Thus, metabolomics aims to determining a sample’s profile at a specified time under specific environmental conditions for a better compression of biological systems [2]. Metallomics is focused on the study of metal-species related to cells, organs and tissues, using multidimensional analytical approaches in which inductively coupled plasma mass spectrometry plays a fundamental role. Due to the importance of metals in biological systems, metallomics provides complementary information about the biochemical changes associated with pollution [3].

In this study, crab specimens were sampled in different areas of Doñana National Park, for the dissection of digestive glands, gills and abdominal muscles, extraction and analysis. To assess heavy metal contamination, total metal content was performed, since it is one of the most important pollutants in marine origin organisms in this area. In addition, to evaluate the effects of these pollutants in the metabolism of the crab a supplementary analysis of metabolites was performed. Metabolomic analysis was carried out by direct infusion into a high resolution mass spectrometer with electrospray source. Finally, metabolomic profiles of different sampling points were compared using partial least squares discriminant analysis (PLS-DA), in order to obtain a relationship between pollution levels and the metabolic response of the organism.

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MP-14

CHARACTERIZATION OF METALOTHIONEINS IN MOUSE LIVER UNDER CADMIUM EXPOSURE

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Characterization of cadmium-binding proteins is of great importance in environmental research, due to the high toxicity of this metal. For this purpose, model organisms are usually employed in exposure experiences to toxic metals, in order to elucidate the mechanisms of uptake, transport, metabolism and detoxification of metals. In this way, laboratory mice Mus musculus has been extensively proposed to deep insight into the knowledge of metal toxicology in relation to organisms exposed to environmental metal pollution [1]. Cellular metal overload have a great impact in organisms, causing deregulation in numerous metabolic processes, as well as altered distribution of metal-containing biomolecules. Metallothioneins (MTs) are low molecular weight proteins (around 7 kDa) responsible of detoxification processes of heavy metals, which are especially up-regulated in situations of metal contamination. These proteins are enriched in cysteine groups that easily complex metals, whose apparent element specificity results from a disproportional oversupply due to particular physiological conditions, metal excess in environmental or laboratory exposure. For this reason they have been used as conventional biomarkers in environmental studies.

In this work has been performed a metallomic approach for the characterization of metal complexes with MT isoforms in liver of Mus musculus exposed to cadmium. Exposure experiment was carried out by subcutaneous injection of $CdCl_2$ aqueous solution containing a growing dose of toxic element ranging 0.1 to 1.0 mg of Cd per kg of body weight per day during a total of 10 days. Several subgroups were sacrificed at different days of exposure experiment and the liver extracted for the study. In a first step, extracts were submitted to size-exclusion chromatography coupled to ICP-MS for the screening of metal-binding proteins in the different exposure groups [2]. Further, the protein fraction corresponding to MT was collected and subjected to reverse phase chromatography (RP-HPLC) in order to separate isoforms, which were finally identified by nanoelectrospray mass spectrometry (nESI-QqQ-TOF). Results obtained by SEC-ICP-MS showed the up-regulation of Cd,Cu,Zn-MT in liver under cadmium exposure. Moreover, identification by RP-HPLC-nESI-MS allowed establishing differences in MT isoforms among exposure groups. Thus, was observed that isoform MT1 presented higher affinity for Cd than MT2. Moreover, increasing cadmium exposure also inducted a change in the ratio of acetylated and de-acetylated MTs.

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SPECIATION ANALYSIS OF MERCURY, TIN AND LEAD BASED ON A NOVEL MICROWAVE-INDUCED PLASMA EXCITATION SOURCE AS DETECTOR IN GAS CHROMATOGRAPHY

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In 2009, the Federal Ministry of Economics and Technology in Germany has launched the R&T project *"Plasma Emission Detector for Heavy Metals and their Chemical Species"*. The national consortium consists of the *University of Münster* as project coordinator, the *Leibniz Institute for Plasma Science and Technology, INP Greifswald*, and the *Federal Institute for Material Research and Testing, BAM* in Berlin. Main objective of this project was the development of a new plasma-based speciation analysis system for mercury, tin and lead species at trace and ultra trace concentration level.

A gas chromatograph was equipped with a novel miniaturized microwave-induced plasma excitation source developed by INP Greifswald. It allowed the sensitive and element selective detection of the target elements after GC separation of the different chemical species. Detection and data evaluation was performed applying a compact spectrometer (15 cm) and specially developed system control and data evaluation software.

The project development and results from analytical performance investigation and real world applications will be presented.

MP-16

MASS SPECTROMETRY TECHNIQUES (CE-ICP-MS, ESI-MS) IN PROBING OF RUTHENIUM ANTICANCER DRUG MECHANISM OF ACTION UNDER CONDITIONS SIMULATING HUMAN BLOOD AND CANCER CYTOSOL ENVIRONMENTS

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Discovering novel anticancer drugs is a real challenge for improvement of survival rates of patients. So far, cisplatin is the best known and frequently used anticancer metallodrug. The main drawback of applying cisplatin is its severe side effects and a limited range of treated cancers. Novel anticancer drug ought to be free of such side effects, or at least create less danger, and to possess a wider spectrum of action. Indazolium *trans*-[tetrachlorobis(1*H*-indazole)ruthenate(III)] – KP1019 is one of the most promising non-platinum anticancer metallodrug candidates which successfully passed the first stage of clinical tests.

The development of analytical methods capable of providing a better understanding of how metal-based drug is transported to cancerous targets remains a challenging task. In our previous studies, a hyphenated technique that combines electrophoretic separation with sensitive and element-specific detection using inductively coupled plasma mass spectrometry (ICP-MS) has been effectively demonstrated to direct monitoring of metallodrug-protein interactions [1,2]. This permitted us to improve our knowledge on the mechanism of drug transport into cancer cells and complete information about the KP1019 action pathway in human body.

The influence of cytosol complexing (citric acid) and reducing (glutathione, ascorbic acid) agents on the stability of metallodrug and its adducts with main serum transport proteins, albumin, apo-transferrin and holo-transferrin, was investigated by CE-ICP-MS and electrospray ionization mass spectrometry (ESI-MS) under abnormal conditions of cancer cell cytosol. The experimental evidence that cytosol components with reducing/complexing properties affect the integrity of ruthenium-based drug–protein adducts was obtained. From holo-transferrin adduct with KP1019 under action of glutathione and/or ascorbic acid ruthenium and iron species are released, what was clearly seen on CE-ICP-MS electropherograms. To confirm activation-by-reduction mechanism, in which Ru(III) species liberated under cancer cytosol conditions are transformed to reactive Ru(II) forms, ESI-MS experiments were carried out.

Acknowledgement

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MP-17

SIZE EXCLUSION CHROMATOGRAPHY AND SIZE MIGRATION CAPILLARY ELECTROPHORESIS COUPLED WITH ICP MS FOR SEPARATION OF PHYTOCHELATINS COMPLEXES

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Phytochelatins (PCs) are thiopeptides having the general formula of $(\gamma\text{-GluCys})_n\text{Gly}$, where n is usually ranged from 2 to 11. Glutathione (GSH, n = 1) and these thiol reactive oligopeptides are capable of binding metal ions through the thiolate groups [1]. PCs play a key role in detoxification and homeostasis of metal and metaloid ions in plants, especially for Cd^{2+}, Hg^{2+}, Ag^{+}, Sb^{3+} and species of arsenic and selenium [2] Recent findings confirm postulation that complex of heavy metal with glutathione or PC can be suitable co-substrate to create metal-enzyme complex through ligand exchange [2-4]. In consequence, PCs are expected to play two contradicting roles: (1) as ligands creating reversible complexes for activation of PC synthase and (2) as ligands creating stable complexes responsible for deactivation of heavy metals and termination of their synthesis [2-4]. As stability of metal complexes is increasing with the length of phytochelatins, the synthesis of long phytochelatins should be suitable. However, PC_5 is usually the longest due to high and hazardous consumption of glutathione [1]. On the other hand, Mutoh and Hayashi [5] reported that metal complexes with PCs can rearrange into agglomerates (to high molecular complexes (HMC) through medium molecular complexes (MMC)) with higher efficiency of cadmium binding. They summed up that the ability of plants to create high molecular complexes from low molecular ones is more productive for detoxification of toxic metals than synthesis of longer PCs.

Size exclusion chromatography (SEC) and capillary zone electrophoresis (CZE) coupled to ICP MS were applied to characterize low, medium and high molecular cadmium complexes (LMC, MMC and HMC) with glutathione (GSH) and phytochelatins (PCs). The dominant stoichiometry of the complexes formed *in vitro* was established as 1:1 using Electrospray MS. Calculated molecular masses of Cd_1L_1 complexes were used for calibration of size exclusion and capillary electrophoresis method. It was found that exclusion limit of SEC column is much lower (2 kDa) for cadmium complexes than for free peptides (10 kDa) and the majority of high molecular cadmium species was eluted in void volume of the column. On the other hand, CZE method based on semi-empirical Offord's model elucidating peptide migration allowed to show high propensity of Cd-PCs complexes to polymorphism upon complexation. All this information is of great importance for studies of the mechanism of metal deactivation in plants.

Both SEC and CE ICP MS methods confirmed the ability of thio-peptides to create complex adducts with cadmium ions and that the presence of disulfide bridges is one of the factors responsible for their creation. Although, the selectivity of CE method is much better in comparison to SEC the resolution is insufficient to establish the stoichiometry of the complexes. This shortcoming can be compensated by new generation ICP MS, which allows observing sulphur and cadmium simultaneously. CE coupling to ICP MS toward analysis of cadmium complexes with phytochelatins can be attractive alternative to ion pair chromatography.

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SPECIATION ANALYSIS OF COBALT AND MANGANESE IN VARIOUS DIET SUPPLEMENTS

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The project was focused on diet supplements – especially fruits, exported to EU from many different countries. The diet supplements are very sustenance part of human health and help to compensate the deficiency of some elements in daily human diet. Additionally the speciation analysis of the diet supplement and next in vitro simulation of gastrointestinal digestion helps us to understand the bioavailability of elements in the human body. The knowledge about element species bioavailability for human, determines better understanding about intake the diet supplements. The investigations can help us to understand what kinds of element form – cobalt and manganese- are available for human and which from them are absorbed by human tissues.

The identification of various cobalt and manganese species in diet supplements was carried out, followed by a careful investigations of their metabolism. That aim was usually obtained by *in vitro* enzymatic digestion of food products. The preliminary characterization of metal species extracted from food stuffs and products of their digestion were performed using size exclusion chromatography (SEC) coupled to ICP MS. In the case of existing the unknown species not identified by comparison of their retention times with standards, the assessment of species structure by ESI MS (e.g., by RPLC or SEC/HIC) was carried out.

In vitro bioavailability investigation was used for the information about the bioavailability of elements. Two step digestion model simulating gastric (pepsin digestion) and intestinal (pancreatin digestion) juices were used.

The fractionation of cobalt and manganese species in berries showed that different bioligands acted as complexing agents for the metals: polysaccharides, proteins, flavonoids and organic acids. Sugars and organic acids are important primary metabolites that contribute to grapevine growth and berry development [1]. Additionally, manganese, in Noni juice, is complexed by bioflavonoid – rutin, anthraquinone - alizarin and glycosides - asperulosidic acid (ESI MS identification).

Spirulina is microscopic and filamentous blue - green algae that have a long history of use as food [2]. It is a rich source of vitamins, especially vitamin B12 and provitamin A (β-carotene), minerals, carotenoids, and phycocyanins [3]. SEC–ICP MS studies confirmed that vitamin B12 exists in Spirulina platensis. The digestion leads to conclusion that in algae, vitamin B12 exists only in one, the most stable form and also as its degradation products e.g. cobalamine. The gastrointestinal digestion showed that cobalt has good stability after digestion and very high bioaccessibility for human body.

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METALLOMIC AND METABOLOMIC STUDY OF LABORATORY MOUSE *MUS MUSCULUS* UNDER EXPERIMENT EXPOSURE TO EVALUATE ARSENIC/CADMIUM INTERACTIONS

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Arsenic (As) and Cadmium (Cd) are important inorganic toxicants in the environment, which are the origin of numerous environmental issues. Arsenic toxicity is due to its reaction with sulfhydryl groups in cells [1], although recent studies suggest the generation of reactive oxygen species (ROS), such as superoxide, hydroxyl radicals and hydrogen peroxide during arsenic compounds metabolism [2]. Arsenic exposure has shown to depress the functions of antioxidant defense system leading to oxidative damage of cellular macromolecules including DNA, proteins and lipids. Interactions between As and Cd in acute liver injury have been reported [3], but little is known about their potential interaction in nephrotoxicity and neurotoxicity, especially during chronic exposure.

In order to get information about the toxicological effects of the couple As/Cd, we have designed experimental exposure experiments using the mouse *Mus musculus* to assess its biological response against metal pollutants and evaluate the antagonistic or synergist interaction when As and Cd are simultaneously administered. For this purpose, a metallomic approach based on size characterization of metal biomolecules by SEC-ICP-MS and identification of altered biomolecules with organic mass spectrometry, followed by metabolomic study based on direct infusion to a mass spectrometer (DI-ESI-QTOF-MS) followed by discriminant analysis (PLS-DA), has been used to compare the biological response of *Mus musculus* under exposure conditions. In the exposure experiment 64 male mice *Mus musculus* were exposed to arsenic as sodium arsenite (3 $mg \cdot kg^{-1}$, orally through gastric intubation) either alone or in combination with cadmium (0.2 $mg \cdot kg^{-1}$, subcutaneously injected) during 10 days. The most relevant results will be presented.

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MP-20

SPECIATION AND METABOLISM OF ORGANOTIN COMPOUNDS IN ZEBRAFISH LARVAE

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Organotin compounds are extensively known as endocrine disruptors and their extensive use as biocides in antifouling paints for many years has led to serious environmental and health problems. The fate of tributyltin (TBT) in aquatic ecosystems and its ecotoxocological consequences are directly dependent on its persistence and thus on the occurrence of biotic and abiotic degradation mechanism. Bioaccumluation tests have been performed in several marine organisms but a unification in the protocol followed is needed.

Previous experiments, performed according to the OECD guideline 305, on bioconcentration of TBT using zebrafish larvae showed both a high bioaccumulation (within the range 840-1280) and a partial capability of depuration. To evaluate if a metabolic process is involved in the depuration process, a speciation study of zebrafish larvae in both uptake and depuration phase has been carried out.

The analytical method used was based on the use of an ultrasonic probe assisted extraction for accelerating the sample treatment and derivatization by ethylation followed by detection using Gas Chromatography-Flame Photometric Detector (GC-FPD). An ICP-MS has been also employed for methodology validation.

The results obtained have shown the capability of larvae to metabolize TBT directly and quickly in MBT, as DBT was not found in any of the analyzed samples. However, a high percentage of TBT, in the reduced scale of time studied, still remained in the samples.

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MP-21

USE OF METALLOMICS, METABOLOMICS AND REDOX PROTEOMICS IN ENVIRONMENTAL METAL POLLUTION ASSESSMENT USING *MUS SPRETUS* MICE FROM DOÑANA NATIONAL PARK AS BIOINDICATOR

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Anthropogenic and natural activities have increased contaminants levels in the terrestrial and aquatic ecosystems. The importance of monitoring the exposure and studying the effects of heavy metals on living organisms has increased in the last decades. Studies of small mammals, mainly free-living mice (*Mus spretus*), have been used as bioindicators in numerous environmental studies because they can provide useful information for assessment of risk of metals to humans1-3. In the present work, we consider the use of mouse *Mus spretus* to assess its biological response against contaminants in the relevant ecological area of Doñana National Park and surroundings (southwest Spain) in which many migrating birds land for breeding and feeding.

For this purpose, total metals determination in kidney tissue from mice by ICP-ORS-MS, a metallomics approach based on size characterization of metal biomolecules by SEC-ICP-ORS-MS and metabolomics approach based on direct infusion to a mass spectrometer (DI-ESI-QTOF-MS) followed to discriminant analysis (PLS-DA) has been used to compare the biological response of Mus spretus living in three different areas of Doñana National Park and surroundings, complemented by measure of up/down-regulation of enzymes related with oxidative stress, such as Mn-superoxide dismutase (Mn-SOD), Cu/Zn-superoxide dismutase (Cu/Zn-SOD), catalase (CAT), peroxidases and glutathione reductase (GR) in connection with environmental contamination issues.

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TRACE-LEVEL SPECIATED ANALYSIS OF CHROMIUM(III) AND CHROMIUM(VI) USING LC-ICP-MS

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Due to it widespread use in industrial applications such as chromium plating, dye manufacturing and preservation of wood and leather materials, chromium concentrations in environmental samples are monitored on a routine basis. With the European Union CEN/TC 52/WG 5 N 788 have specified maximum admissible chromium concentrations in safety of toy part 3: Migration of certain elements. As with many other trace elements, chromium (Cr) is typically found in more than one chemical form, each of which with different chemical properties and behavior, such as bioavailability and toxicity. For chromium, Cr(III) is essential to human beings and involved in different processes in the body while Cr(VI) is highly toxic. In order to provide this critical information a supporting speciation analysis is required to determine the amounts of the different Cr species in the sample. The speciation analysis of Cr however is a challenging task, since the stability of different Cr species is easily affected by conditions during sample collection and treatment. For example, low pH values may lead to the degradation of Cr(VI) to Cr(III) due to the increased redox potential, while high pH values may lead to the precipitation of Cr(III) as $Cr(OH)_3$. An additional difficulty in the accurate speciation analysis of Cr by ICP-MS is the numerous spectral interferences (e.g. 35Cl16O1H+ or 40Ar12C+) on the most abundant chromium isotope, ^{52}Cr.

To directly measure Cr(VI), it must be separated from Cr(III), typically by anion exchange liquid chromatography (LC), prior to the ICP-MS measurement. This study has shown that the LC-ICP-MS is suitable for the separation and analysis of the carcinogenic Cr(VI) Cr(III) species at low 5 ppt levels S/N>4.2 and 4.6. The chromatographic separation is rapid and ICP-MS detection has the sensitivity to ensure that this method is suitable for monitoring Cr(III) and Cr(IV) in toys in accordance with the EU directive.

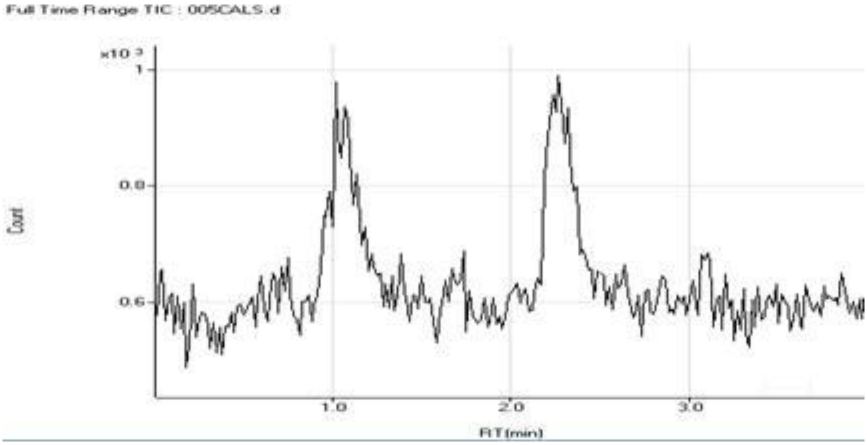

Fig.1 Cr(VI), Cr(III) 5 ppt chromatographic separation.

AUTOMATED MULTIPLE EXTRACTION PROCEDURE COUPLED ON-LINE TO ICP-OES FOR ASSESSMENT OF BIO-ACCESSIBLE TRACE METAL FRACTIONS IN AIRBORNE PARTICULATE MATTER

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Airborne particulate matter (APM) came into focus of scientific research over the last years due to medical tests showing its detrimental effects on human health [1]. Metal contents have been classified as a presumably harmful component of APM [2] due to their possible absorbance into human lung tissues. This holds true primarily for particles with an aerodynamic diameter less than 10 microns (PM10). To enhance risk assessment the evaluation of pools of bio-accessible fractions becomes necessary rather than a determination of total metal concentration. An in-vitro physiologically based extraction test using synthetic gastric juice (SGJ) which mimics the conditions of the human digestive tract is suggested in order to appraise the bio-accessibility of inhaled and subsequently ingested metals [3].

In present study a dynamic sequential injection procedure as a front end to ICP-OES is proposed for on-line determination of bio-accessible trace metals in airborne particulate matter samples. The method is based on a preliminary extraction of samples with SGJ under dynamic conditions and the subsequent on-line ICP-OES measurement of the dissolved fraction of trace metals. The assembly permits an automated successive measurement of three sample replicates in less than 15 minutes. The developed on-line extraction procedure offers increased sample throughput, reduced risk of sample contamination and overcomes readsorption processes as compared to traditional batch-wise systems. Furthermore, it provides information about the leaching process. The developed procedure was applied to the determination of bio-accessible trace metal fractions under worst-case scenarios in PM10 samples from Palma de Mallorca (Spain) and Vienna (Austria).

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NATURAL REACTIONS TO NATURALLY HIGH SELENIUM AVAILABILITY: COMPLEXITY OF Se-METABOLITES IN *LECYTHIDACEAE* NUTS

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Lecythidaceae nuts are in the spotlight of various selenium researches because of their relatively high selenium (Se) content [1]. It is well-known that the main selenium species found in both Brazil nut (*Bertholletia excelsa*) and monkeypot nut (*Lecythis minor*) is selenomethionine (SeMet), contributing to 80% of total selenium [2]. Due to the taxonomical proximity it would be expected to discover similarities in the remaining fraction of Se-metabolites.

The characterization of water soluble, small molecular weight Se-metabolites of the two *Lecythidaceae* nuts was attempted in our study. In order to clean-up unknown Se-species, the aqueous extracts of the defatted nuts were subjected to a multidimensional orthogonal purification process that was carried out by subsequent SEC, SCX and IP-RP-HPLC steps monitored with ICP-MS detection. This process was inevitable in order to attain sufficiently pure and concentrated fractions for further ESI-MS analyses. HPLC-qToF-MS was chosen as a suitable technique to identify the recovered Se-compounds. The identification was based on accurate mass measurements and fragmentation data obtained in MS-MS mode.

The mapping of Se-compounds in the two nuts showed significant differences that can be the results of concentration-dependent alterations of metabolic pathways, as monkeypot nut accumulates selenium in 10-fold higher concentration than Brazil nut. Besides identifying known Se species, such as selenocystathionine (m/z 271) [3], γ-glutamyl-Se-methylselenocysteine (m/z 313) and γ-glutamyl-SeMet (m/z 327), dozens of highly abundant Se-species were also assigned. The new compounds can be grouped in the classes of multiselenides (up to 6 Se atoms in one molecule), Se-homocysteine related molecules, and SeMet derivatives.

As a conclusion we can state that the two different nuts do not only differ in total Se-concentration, but also their metabolism and hence their Se-speciation patterns are also remarkably different. Concerning the biological aspects of selenium speciation, the newly identified multiple Se-containing compounds can help to explain the toxicity of high Se *Lecythidaceae* nuts.

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CHROMIUM SPECIATION IN FEED SAMPLES

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Chromium is an element that exists under two oxidation states, Cr(III) and Cr(VI). Whereas Cr(III) is essential to life, Cr(VI) is considered carcinogenic. Cr(VI) speciation is now performed in routine for environmental samples (water, soils…) by HPLC – ICP MS. However it is much more difficult to achieve in feed samples due to extraction problems, carbon interferences and the lack of knowledge on the behavior of the chromium linked with the matrix. This is why at this moment, no reliable data are available to assess Cr species uptake for humans. The objective of our work was therefore to develop (an) analytical method(s) for chromium speciation in different kind of feed samples (milk, cereals, meat…). Because Cr(III) is not stable at alkaline pH, and as Cr(VI) is transformed into Cr(III) at acidic pH and finally as neutral extraction media generally don't allow full extraction of both species, the method(s) developed focused on the determination of Cr(VI), the most toxic form.

For milk, a multi-dimensional approach, based on purification of the raw milk by SE HPLC and followed by Cr(VI) specific determination by ion-exchange HPLC – ICP MS was developed. For solid samples (cereals, meat…) the recovery of Cr(VI) by alkaline extraction has first been investigated. In each case, the interactions between Cr(VI) and the matrix were particularly studied. Protocols of purification, pre-concentration (when necessary) and improvement of chromatographic conditions will be presented.

In the absence of Certified Reference Materials, the methods were in-house validated. Validation parameters, including specificity, linearity, reproducibility, repeatability, accuracy, LOD and LOQ will also be presented.

SEC (DAD) ICP-MS FOR THE METAL-PROTEINS INTERACTION STUDIES

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SEC (Size Exclusion Chromatography) is a widely used as a technique for the separation of protein mixtures. Several research groups have coupled it with an ICP-MS instrument to study metal-proteins interactions [1,2]. Even though this combination is highly sensitive, the identification of the proteic moiety just on the basis of the observed MW is not possible and additional techniques should be used. Often, protein alterations during sample manipulation occur with the possible consequence of misinterpretation of the results.

In this work we have investigated protein alteration on the results of metal-protein interaction studies. Fillets of Perch fish muscle containing Hg and As have been extracted by liquid phase homogenisation using a low ionic strength buffer to recover soluble peptides and proteins. Once the filtered (0.45 µm filter) extracts have been injected on the SEC column, the DAD chromatogram obtained revealed a well distributed mass range of eluting bio-molecules (from 50 to 1 kDa). The co-elution of arsenic and mercury has been monitored by ICP-MS, demonstrating the presence of these elements in several proteic targets. Both elements have been subsequently investigated by anion exchange or reversed phase LC ICP-MS to carry out further elemental speciation analysis.

The whole extract has been analyzed by MALDI-TOF and the major peaks found corresponded to parvalbumin (PV, 11.4 kDa) and myoglobin (MYO, 16.9 kDa). Other minor peaks detected revealed the formation of oligomeric forms (from 2 to 4 subunits) of these proteins. Since these forms seem to be the only proteic species present at high molecular weights that interact with As and Hg, their presence in the metals-containing fractions eluted from the SEC column has been investigated.

MALDI-TOF and MALDI-TOF/TOF analysis after SEC elution has revealed that all the collected peaks had an actual mass of < 20 kDa, suggesting that the oligomers were formed during the extraction procedure and dissociate after elution. Both PV and MYO are metal binding proteins (they bind Ca^{2+} and $Fe^{2+/3+}$ respectively) but at this time no interaction with As or Hg species has been reported in the literature. Moreover, these results suggest that protein alterations (such as the oligomerisation process) can render SEC data unreliable, since the apparent molecular weight (MWa) measured is very different from the actual one.

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MP-27

ANION EXCHANGE HPLC – ICP-MS FOR THE SPECIATION OF BIOAVAILABLE SELENIUM FROM SEAFOOD

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In-vitro bioavailability of total selenium and selenium species (selenite, Se(IV); selenate, Se(VI); selenocystine, SeCys$_2$; selenomethylcysteine, SeMeCys; selenomethionine, SeMet; and selenomethionine oxide, SeOMet) has been assessed in different raw seafood (white fish, cold water fish and mollusk) samples by using a simulated gastric and intestinal digestion/dialysis method. Pepsin (6.0% (m/v)) at pH 2 was used for simulating the gastric digestion stage; whereas, a mixture of pancreatin (4.0% (m/v)) and bile salts (2.5% (m/v)) dissolved in 0.1 M sodium hydrogen-carbonate was then used for the intestinal digestion. During the latter step, 10 kDa molecular weight cut off (MWCO) dialysis membranes containing 20 mL of PIPES buffer solution (pH of 7.5) were used to simulate intestinal absorption (dialysability based *in vitr*o method). Inductively coupled plasma – mass spectrometry (ICP–MS) was used to assess total selenium contents after a microwave assisted acid digestion sample pre-treatment, and also to quantify total selenium in the dialyzable and non-dialyzable fractions. Selenium speciation in the dialyzates (bio-available selenium species fraction) was assessed by anion exchange high performance liquid chromatography (HPLC) coupled with ICP-MS detection. Major Se species (SeMet and SOMet) from dialyzate were identified and characterized by liquid chromatography coupled to mass spectrometry (HPLC-MS). Accuracy of the procedure (total selenium determination) has been assessed by analyzing DORM–2 certified reference material. Accuracy of the in vitro procedure has been established through a mass-balance study which led, after statistical evaluation (95% confidence interval), good accuracy of the whole *in vitro* process for total selenium and for selenium speciation. Low dialyzability percentages of total selenium have been found from fish and mollusk samples (6.69 ± 3.39 and 5.45 ± 2.44%, respectively). Similarly, low dialyzability percentages for total selenium, as a sum of selenium species concentrations, have also been obtained.

MULTIELEMENTAL DETERMINATION OF ARSENIC(III), ARSENIC(V) AND CHROMIUM(VI) IN WATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Determination of elements species in environmental samples is current issue because of toxicity, bioavailability and mobility in the environment depends on the oxidation state of elements in the sample. Total concentration of elements informs insufficiently about negative influence of human body and other living organisms. Speciation analysis in water is necessary for several elements, for example arsenic and chromium because of toxicity of their species. The differences in health effects of arsenic and chromium species are well known. Arsenite is more toxic than arsenate, while organic arsenic (arsenocholine and arsenobetaine) are regarded as non-toxic. Cr(III) and Cr(VI) have opposite toxicities: trivalent Cr is an essential nutrient, Cr(VI) is a recognized carcinogen and respiratory irritant [1-3].

Multielemental speciation has recently gained a lot of attention. This is due the fact that it can be applied when sample volume is minor. However, saving time and reagents are the main reasons that multielemental speciation is applied.

It was maked an attempt to determine selected arsenic and chromium species in water using combination of high performance liquid chromatography (HPLC) with inductively coupled plasma mass spectrometry (ICP-MS). The aim of these work was to examine anion exchange column coupled with ICP-MS to quantitative analysis of As(III), As(V) and Cr(VI). Optimization of chromatographic and ICP-MS operating conditions was accomplished to achieve successful separation and reproducibility. The influence of composition, concentration, pH and flow rate of the mobile phase and column temperature on retention times and signal intensity was studied.

Acknowledgement

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MP-29

STUDY OF ARSENIC SPECIATION IN RAW WAKAME, COOKED WAKAME AND URINE EXCRETED AFTER WAKAME SEAWEED INGESTION

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Seafood, including seaweeds, is one of the most important contributors to arsenic intake by humans. Arsenic is mainly present in seaweed as carbohydrate compounds, commonly called arsenosugars [1]. Humans are able to metabolize the ingested inorganic arsenic into DMA(V), a less toxic compound [2]. However there are other arsenic species, such as arsenobetaine, which are directly excreted into the urine without being metabolized [3]. In this work, the arsenic species distribution in Wakame seaweed will be compared with the arsenical distribution in cooked Wakame, and the arsenic species excreted into urine by several volunteers who previously were fed on Wakame seaweed.

Total arsenic content was determined in raw and cooked Wakame seaweed, as well as in the urine samples of four volunteers by inductively coupled plasma-mass spectrometry (ICP-MS). Seaweed samples (raw and cooked) were subjected to an acid digestion treatment (8 mL HNO_3 69% (m/v), 2 mL H_2O_2 33% m/v) before their introduction into the ICP-MS system. Urine samples were donated by four volunteers who consumed 150 g of Wakame in one meal. Volunteers rejected to eat arsenic-rich seafood for four days before and four days after ingestion of Wakame. Urine samples were diluted ten times with 2% HNO_3 (v/v) before arsenic quantification by ICP-MS. Total arsenic results in urine suggested that the retention of arsenic into the human body was 30-40 hours.

Arsenic speciation studies in seaweed and urine samples were carried out by HPLC-ICP-MS. Arsenical extraction from raw and cooked Wakame was performed by solvent extraction (0.1 g of seaweed, 10 mL of 20 mM ammonium acetate buffer (pH 7.4), 1 h sonication bath, 30 min centrifugation at 3000 rpm). Urine samples were filtered (0.22 µm) after being directly analyzed. Arsenic species separation was performed on an anion-exchange PRP-X100 chromatographic column by using 20 mM NH_4HCO_3 (pH 9.0) and 1% MeOH (v/v) as mobile phase.

Results suggested that the heat treatment did not affect the arsenic species distribution in Wakame seaweed, being glycerol-ribose, phosphate-ribose and sulfonate-ribose the main arsenic species found in both, raw and cooked Wakame. However, arsenosugars were not observed in the urine of the four volunteers under study, being DMA(V) the predominant arsenic specie found. It is worth mentioning that arsenobetaine was not detected in raw and cooked Wakame seaweed, however it was identified in the urine.

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METROLOGICAL APPROACH IN SPECIES ANALYSIS

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In the last decades the comprehension increased that not only the presence of an element but also its chemical form is relevant for assessing its toxicity in the environment. Nevertheless, on the legislative level speciation of relevant elements is rarely found. Only the most important toxic compounds like methylmercury and organotin were regulated in food and water. One reason might be that the elemental species are often instable and tend to be converted into each other or are easily degraded e.g. by light or during the analytical process. However, the Water Framework Directive (2000/60/EC) lists maximal allowable concentrations for tributyltin (TBT) of 0.0015 $\mu g \cdot L^{-1}$ and for polybrominated diphenylether (PBDE) an allowable annual average of 0.0005 $\mu g \cdot L^{-1}$. As the limits of quantification must exceed 50% of the so called environmental quality standard (EQS) named aboved sophisticated methods for extraction, preconcentration and detection are necessary. In this presentation a possible way for the determination of PBDE at very low concentration leading to traceable measurement results will be presented, which is currently developed within the European Metrology Research Program (EMRP) project ENV08.

Another important field in species analysis are biomolecules containing metals. For many metalloproteins, however, the situation is a bit different from the elemental species in the environment. As many of them are found to be markers for several diseases they are routinely analysed in clinical laboratories either for the diagnosis of these diseases or in the process of developing an efficient treatment. Thus, the same directives that ensure the quality of the results for other clinical relevant parameters apply for metalloproteins as well. Different approaches for the metrologically validated determination of metalloproteins will be presented. Using Se-Met, which can serves as a marker for the selenium status of an individuum, species-specific and post-column online isotope dilution mass spectrometry (SS-ICP-IDMS) will be compared. Iron containing proteins are usually a challenge in IDMS as the background is high, except when working in a clean room, and spike material is only available with low enrichment in ^{57}Fe. Under such conditions conventional IDMS meets its limits. J. Vogl described a triple IDMS method to solve such problems for elemental analysis, which serves also well in species analysis. Using the iron transport protein transferrin as an example the potential of triple IDMS in species analysis is demonstrated.

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MP-31

INDIRECT Se-METABOLOMICS: COMPLEXITY OF INFLUENCED NON-Se PATHWAYS

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Usual seleno-metabolomics is achieved through multidimensional chromatographic clean-up procedure monitored by ICP-MS and ESI-MS based identification after a demanding search for selenium patterns in molecular mass spectra [1]. This approach is labor demanding and indicates nothing about any other metabolites influenced by the Se enrichment. Therefore, detection of other than Se species should give a hint on the influence of the enrichment process on the metabolome of the given organism.

In the recent work the Se-metabolism related compounds were searched and detected in moderately Se enriched hedgehog mushrooms (Hericium erinaceus). The hypothesis was that the Se uptake also changes non Se-related metabolic pathways and we focused on Se-free compounds. The goal was to detect and identify the most related compounds by LC-MS after a metabolomic software assisted differentiation process between treated and untreated mushroom samples. In the case of moderate enrichment Se does not induces stress but must start or enhance new way of metabolic pathways which results in decreased/increased abundance of the unknown target analytes. In our study we present that different levels of Se enrichment are required to be able to assign molecules that can be related to theoretically independent biochemical pathways.

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QUANTIFICATION OF IRON CONTAINING BLOOD PROTEINS BY MEANS OF LC/ICP-MS

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Iron is an essential metal for human life even though in its free form it is toxic to cells and might damage tissues. Therefore, a strict controlled iron metabolism is needed in the human body which is achieved by different proteins. The following investigation focuses on two iron containing proteins: hemoglobin and transferrin. Transferrin is one of the major proteins that control the iron metabolism and is responsible for the iron transport where as hemoglobin is responsible for the oxygen transport and storage. Together with the iron storage protein those two proteins contain almost all iron present in the body. The blood concentrations of these two proteins are important indicators in clinical diagnostics. Transferrin is a biomarker for congenital disorders of glycosylation, cerebrospinal fluid leakage as well as for certain cancers. In case of hemoglobin higher and lower level might induce diseases like heart attacks, strokes or fatigue. Due to this fact, accuracy and reliability in the quantification of transferrin and hemoglobin is essential. Up to now, most metalloproteins are determined using immunoassays, immunoturbidimetry or fluorometry, however no primary reference method that is traceable to the SI is in use.

One aim of the EMRP project HLT05 is to develop primary reference methods for quantification of the chosen proteins transferrin and hemoglobin. Liquid chromatography (LC) coupled to inductively coupled plasma mass spectrometry (ICP-MS) was chosen for the quantification as ICP-MS offers low detection limits and the selective detection of iron. As all molecular information is lost in the plasma source of the ICP-MS a LC separation was developed to obtain species information and remove most of the matrix. In case of transferrin and hemoglobin ion exchange chromatography turned out to be the most powerful separation technique. In case of coupling to ICP-MS for detection a further advantage of ion exchange chromatography is the organic free mobile phase as the plasma tolerates only limited amounts of organic solvents.

To achieve a traceable and matrix independent quantification a species-specific isotope dilution mass spectrometry method is developed using ^{57}Fe labeled proteins as spike.

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Cr(VI) DETERMINATION IN SOIL SOLUTION BY SPECIATED ISOTOPE DILUTION ICP-MS

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Disposal of tannery waste onto land has been a common practice worldwide, causing contamination of terrestrial and aquatic ecosystems with Cr. After long term disposal, Cr(III), that is used for leather tanning, can be oxidized to Cr(VI) by the soil components, mainly by manganese(IV) oxides. The so formed Cr(VI) compounds in soil are very soluble and mobile, consequently they can be easily leached from the top soil and accumulated into subsurface soil, surface and ground water.

In order to assess the environmental hazard of Cr(VI) accurate and reliable analytical procedures for its determination are needed. So far, different extraction procedures were reported for the determination of exchangeable Cr(VI) in soils [1-4]. The most common extracting reagents were water and phosphate buffers at different pH (4.5, 7.2 or 8) and reagent strengths. In any of them the possible species interconversions due to the extracting reagent, extraction time and temperature or co-extracted matter were not studied.

The main aim of our study was to evaluate the degree of species interconversion that may occur during the extraction of exchangeable Cr(VI) from soil with phosphate buffer in order to set up an extraction method that will be effective, accurate and with minimal or no species interconversions. For this purpose speciated isotope dilution mass spectrometry (SIDMS) was applied.

The study was performed on soil samples from the field treated with the tannery waste for seventeen years. Samples were analyzed in the twenty second year after the last waste application. Soil samples were spiked by enriched stable isotopic solutions of ^{50}Cr(VI) and ^{53}Cr(III) that were added to phosphate buffers (0.1 M KH_2PO_4-K_2HPO_4 (pH 7.2) and/or 0.1 M K_2HPO_4 (pH 8)) before and/or after extractions. For the extraction mechanical shaking and/or ultrasound assisted extraction were compared. The separation and detection of Cr species were performed by high performance liquid chromatography – inductively coupled plasma mass spectrometry (HPLC-ICP-MS).

It was observed that 0.1 M KH_2PO_4-K_2HPO_4 induced 90% reduction of Cr(VI) during the extraction with mechanical shaking, while with 0.1 M K_2HPO_4 the extent of reduction was around 40%. For complete extraction long extraction times were needed (48 to 72 h). Due to high reduction rate by 0.1 M KH_2PO_4-K_2HPO_4 further analyses were performed only by 0.1 M K_2HPO_4 and ultrasound assisted extraction. For total extraction of exchangeable Cr(VI) with maximum 10% reduction of Cr(VI) sequential ultrasound assisted extractions were needed.

The optimized analytical procedure with limit of detection (LOD) 0.1 ng g^{-1} of Cr(VI) was sensitive enough for the determination of exchangeable Cr(VI) in soils. In the field soil samples analyzed the concentrations of exchangeable Cr(VI) were found to be about 100 ng g^{-1}.

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USE OF STABLE ISOTOPE-ENRICHED SELENITE TRACER TO DIFFERENTIATE AND DETERMINE NATIVE AND SPIKED SELENIUM BEHAVIOR IN SOILS

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Selenium is an essential trace element for living organisms of great environmental concern because its concentration range between deficiency and toxicity is very narrow. Among the different radionucleides of interest, selenium is considered because of the presence in high level long-lived nuclear waste of ^{79}Se coming from fission.

In the context of the future French underground repository for nuclear wastes located in Meuse/ Haute Marne, it is mandatory to determine the radiological consequences following potential biosphere contamination on a very long time scale. For safety assessment purposes selenium transformations and distribution among the different components of soil have to be clearly understood.

Soil solid/liquid partition coefficients (Kd) reported in literature for Se spiked soils in short-term experiments differ from those reported for native Se leading to an overestimation of both Se mobility and bio-availability on long time span.

In this study, an analytical method based on the use of stable enriched tracers in conjunction with inductively coupled plasma mass spectrometry (ICP-MS) was performed to investigate dynamic environmental processes that occur in soil. The application of the stable isotope in the environmental studies is not limited to the classical isotope dilution analysis, actually this method allowed to monitor not only the behavior of the added tracer but at the same time the endogenous element present at trace level.

As isotopically enriched tracers are not dangerous for ecosystems and human beings (no radioactivity) they have been used in the field experiment allowing a kinetic monitoring of distribution/speciation changes of native and added Se under real environmental conditions.

Three soils types (culture; forest; grassland) were spiked with isotopically enriched selenite (^{77}Se(IV)) at concentration close to natural occurring levels (μg kg^{-1}).

Time courses of respective Kd and distributions of native and freshly added Se in specific soil extracts were evaluated. By hyphenating chromatographic separation with ICP-MS (HPLC-ICP-MS), Se speciation was determined.

The results obtained after three months of *in situ* experiments showed, as expected, that native Se was stable in terms of distribution and speciation. For grassland and forest soils, freshly added ^{77}Se(IV) reached Kd values close to the native one. However for the three types of soils, ^{77}Se(IV) phosphate buffer and NaOH extractabilities, indicative of exchangeable Se and Se associated to soil organic matter, didn't change significantly after three months of incubation suggesting slow soil Se retention processes.

THE USE OF HPLC-ICP-MS AND STABLE ISOTOPES IN THE INVESTIGATION OF Cr SPECIATION IN TEA INFUSIONS AND BREAD SAMPLES

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Recently the presence of Cr(VI) in tea infusions [1] and bread samples [2] was reported in the literature. These statements were made on the basis of determination of total Cr concentrations in alkaline and aqueous sample extracts by ETAAS, without applying any speciation analysis. If Cr(VI) really exists in bread samples and tea infusions, consumption of bread and tea would represent a health threat for the majority of the human population. It is well accepted that due to the presence of organic matter foodstuffs of plant and animal origin cannot contain Cr(VI).

To confirm that the reported data on the presence of Cr(VI) in foodstuffs are an artefact of inappropiately applied analytical methodology, Cr speciation was investigated in tea infusions and bread samples by the use high performance liquid chromatography – inductively coupled plasma mass spectrometry (HPLC-ICP-MS) [3]. ^{50}Cr(VI) and ^{53}Cr(III) stable isotopes were applied to follow species interconversions during the extraction procedures. Separated Cr species eluted from the column were followed at m/z 50, 52 and 53 [4].

The high sensitivity of the HPLC-ICP-MS method (LOD for m/z 52 0.033 ng Cr(VI) mL^{-1}) enabled reliable determination of Cr(VI) at concentration levels that were much lower than the total Cr content present in sample extracts. The speciation analysis data demonstrated that in samples investigated Cr(VI) concentrations were below the LOD. In tea infusions ^{50}Cr(VI) was almost completely reduced due to the presence of antioxidants, while the high content of organic matter in bread appreciably reduced ^{50}Cr(VI) even in highly alkaline (pH 12) bread extracts.

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QUANTIFICATION OF PROTEINS WITH NON-COVALENTLY BOUND METALLOENZYMES

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Metalloproteins play an important role in vital functions. Nearly two thirds of all enzymes contain metal ions forming often the active centre of the enzyme. As many of them are important markers for diseases like superoxide dismutase for Down's syndrome in prenatal diagnostic, hemoglobin for anaemia or e.g. transferrin and caeruloplasmin for deficiency diseases they are particularly relevant in medical diagnosis. Therefore, it is necessary to develop primary reference methods for the quantification of these metalloproteins, which are traceable to the SI system.

The investigations focus on two copper containing proteins: superoxide dismutase (SOD) and caeruloplasmin (Cp). SOD1 is a dimer which contains two copper and two zinc ions per molecule. It helps to prevent oxidative stress by catalyzing the disproportionation of the superoxide radical to hydrogen peroxide and oxygen. Furthermore it is an important marker for inflammatory processes and is involved in anticancer and antiaging mechanisms. Cp contains six to seven copper ions and is the major copper carrying protein in blood. Among others it is a marker for copper deficiency and dysfunction in the copper metabolism (Menke's disease, Wilson's disease) and an acute-phase protein.

Because of the low concentration range in which SOD and Cp occur in biological samples low detection limits are needed. For this purpose inductively coupled plasma mass spectrometry (ICP-MS) is sufficiently sensitive. To separate the proteins of interest from other proteins appearing in blood serum before analyzing, a HPLC is coupled to the ICP-MS. Different columns like reversed-phase columns and ion exchange columns and different eluents are tested to optimize the separation. To quantify metalloproteins like SOD and Cp isotope dilution mass spectrometry (IDMS) is a suitable method because it is able to ensure the traceability of the results. To perform species specific ID-ICP-MS adequate spike material is needed. This spike material is prepared from commercially available SOD by replacing the natural copper and zinc by copper and zinc ions enriched in one isotope. For preparation of apo-SOD as well as remetallation different methods are tested. To test if the developed method can be transferred to similar proteins, the developed method for SOD will be transferred to Cp.

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ARSENIC SPECIATION IN URINE USING MICRO LIQUID CHROMATOGRAPHY-ICP-MS FOR ROUTINE BIOLOGICAL MONITORING

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There are many species of arsenic that are found in the environment, wildlife and humans. These species have differing bioavailability and toxicology. Inorganic arsenic species are carcinogenic, but to assess exposure most laboratories report a ‘total’ arsenic result. Separate quantitation of individual arsenic species allows differentiation of dietary arsenic from inorganic arsenic (and its metabolites) and would improve exposure assessment and risk management.

Separation of five arsenic species (arsenobetaine (AB), arsenite (As^{3+}), arsenate (As^{5+}), dimethylarsinate (DMA), and monomethylarsonate (MMA)) in urine was achieved using a hyphenated µLC (micro liquid chromatography) system, coupled to an inductively coupled plasma – mass spectrometer (ICP-MS).

In this study 444 urine samples from a total of 81 workers in the semi-conductor industry were analysed for arsenic. Each worker provided pre and post working week urine samples in spring and autumn. To interpret the levels of arsenic found in the semi-conductor workers, urine control samples were collected and analysed from 50 volunteers who were not exposed to arsenic in their work place.

The limits of detection for the analytes were all less than 0.03 $\mu g \cdot L^{-1}$. Overall, the arsenic exposure in semi-conductor workers was low. Both arsenite and arsenate were present at very low levels, with a 90th percentile value of $<0.3\ \mu g \cdot L^{-1}$.

Statistical analysis showed there was no significant difference between the pre and post working week samples for any of the five species. However, there were significant differences observed for AB and DMA (gender) and for As^{3+} (smoking status).

A routine method to measure five species of arsenic in urine by µLC-ICP-MS has been established. More data is required to aid the interpretation of the results.

RELATIONSHIP BETWEEN DIET AND URINARY ARSENIC SPECIES IN TWO ETHNIC GROUPS FROM LEICESTER, UK

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There is increasing concern regarding exposure to arsenic through the diet and its impact on human health. For example, a recent study reported higher inorganic arsenic (iAs) in one ethnic group due to their high intake of rice [1]. The aim of the current study was to determine the relationship between diet and urinary arsenic species in two ethnic groups (Libyan and Somali). This is the first study to determine arsenic species in the Libyan ethnic group.

Ethical approval for this study was obtained from De Montfort University Research Ethics Committee. Each volunteer provided urine samples, completed a questionnaire and signed an informed consent form. The group consisted of 16 Libyan (mean age: 36, SD: 6) and 25 Somali (mean age: 38, SD: 10) living in the city of Leicester. With the exception of four females in the Libyan group, all the volunteers were males. Micro liquid chromatography-ICP-MS was used to determine arsenic species in urine samples. Mann-Whitney U test was used to assess if statistically significant differences exist in urinary arsenic species between the two ethnic groups.

The percent and median levels of five As species detected in the urine of the two groups are as follows: 3% Arsenobetaine (AB) (0.09 $\mu mol \cdot mol^{-1}$ creatinine), 74% Dimethylarsenic acid (DMA) (2.47 $\mu mol \cdot mol^{-1}$ creatinine), 5% As(III) (0.15 $\mu mol \cdot mol^{-1}$ creatinine), 12% Monomethylarsenic acid (MMA) (0.39 $\mu mol \cdot mol^{-1}$ creatinine) and 2% As(V) (0.22 $\mu mol \cdot mol^{-1}$ creatinine) in the Libyan group compared with 4% AB (0.16 $\mu mol \cdot mol^{-1}$ creatinine), 77% DMA (2.93 $\mu mol \cdot mol^{-1}$ creatinine), 4% As(III) (0.15 $\mu mol \cdot mol^{-1}$ creatinine), 14% MMA (0.52 $\mu mol \cdot mol^{-1}$ creatinine) and 1% As(V) (0.05 $\mu mol \cdot mol^{-1}$ creatinine) in the Somali group. No significant difference between the two ethnic groups was detected: AB ($p = 0.78$), MMA ($p = 0.96$), As(III) ($p = 0.64$), MMA ($p = 0.98$), As(V) ($p = 0.17$).

The similarity in urinary arsenic species profile between Libyans and Somalis may not be surprising since the analysis of the questionnaires reveals that they have similar diets with a relatively high consumption of meat products. Both of these ethnic groups have lower concentration and percentage of DMA and AB in urine compared to what was reported previously for Bangladeshis and Caucasians from Leicester [1]. This can be attributed to lower fish and rice intake by Somalis and Libyans. Urinary arsenic species present in Somalis from Leicester was previously reported [2] but As(III) or As(V) was not detected. The precise reason for this is not clear but the detection of As(III) and As(V) in the current study could be due to the higher sensitivity of the techniques used.

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MP-39

DEVELOPMENT OF ANALYTICAL STRATEGY TO STUDY SELENOPROTEIN EXPRESSION IN HUMAN CELL LINES

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Selenoprotein family is one of the most important bioactive forms of selenium in human health. Selenium, which is an essential trace element, is incorporated as a rare aminoacid, selenocysteine, in twenty five selenoproteins. Initially demonstrated in Kashin Beck and Keshan diseases, selenium deficiency is associated with several pathological conditions, including cancer, neurodegenerative diseases, immune and muscular disorders [1]. Chronic selenium deficiency is hypothesized to decrease antioxidant defenses and redox regulatory pathways through a dysregulation of selenoprotein expression.

Our laboratories are interested in understanding the synthesis and regulation of human selenoproteins, which is critically dependent on the availability of adequate analytical methodology. In mammals, these proteins are predominantly present in the kidney, liver, muscle and brain, where they are involved in fundamental processes of antioxidant defense, redox homeostasis and redox signaling pathways. The instrumental developments were carried out on selenoproteomes expressed in well-defined human cell lines in culture known to express detectable selenoproteins levels. They include: Hek293 (embryonic kidney), HepG2 (hepatoma), HaCat (keratinocyte), and LNCap (prostate cancer) cell lines. The design of cell culture conditions and Se depletion/supplementation allowed the validation of the approach to study the regulation of selenoproteins synthesis in mammalian cells [2].

The analytical strategy developed in the present work involved separation of extracted proteins by isoelectric focusing gel electrophoresis using immobilized pH gradient (range 3-10 not linear) strips. Selenoproteins were detected in the gel by Laser Ablation - ICP MS that we have previously optimized [3]. The gel pieces of interest were excised, digested with trypsin and analyzed by capillary RP HPLC with parallel ICP MS and ESI MS/MS. The high resolution of the ESI LTQ Orbitrap mass spectrometer allowed identification of selenoproteins in a complex high abundant protein matrix. The identified selenoproteins included glutathione peroxidases (GPx1, GPx4), thioredoxin reductases (TR1 and TR2), selenoprotein P (SelP) and selenoprotein 15 (Sel15). A strategy was also set up to validate the developed procedure.

Our results validate this methodology to analyze and quantify the relative abundance of selenoproteins in complex samples such as raw cell extracts, and allow us to compare the selenoproteome from different cell lines.

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SELENIUM METABOLOMICS IN YEAST USING BIMODAL (REVERSED-PHASE/HYDROPHILIC ION INTERACTION) LIQUID CHROMATOGRAPHY – ICP MS AND ELECTROSPRAY HYBRID QUADRUPOLE TRAP/ORBITAL MASS SPECTROMETRY

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Selenium-rich yeast produced by growing *Saccharomyces cerevisiae* in the presence of selenite is the principal component of many feed and food supplements used to cope with the selenium deficiency in animals and man. The ultimate formation of selenomethionine and selenocysteine is accompanied by the synthesis of a plethora of organoselenium metabolites. Their large scale analysis is indispensable for the understanding of the mechanisms of the Se incorporation to enable a better control of the biotechnological process, for the characterization of the commercial products in terms of speciation of selenium and for the control of the provenance of the supplements available on the market.

In this context, we developed a new method, based on bimodal (reversed-phase/hydrophilic ion interaction) liquid chromatography on a porous graphitic carbon stationary phase (PGC) for the high resolution large scale separation of selenium metabolites. The identification was carried out by electrospray hybrid quadrupole trap/Orbital mass spectrometry (Orbitrap MSn) and quantification by ICP MS fitted with a frequency-matching generator allowing a quasi-uniform response over the large (20-90%) acetonitrile mobile phase concentration range. Both modes of detection are complementary and the morphology of HPLC - ICP-MS chromatograms was remarkably similar to that of HPLC multi-ion extracted ESI-MS ones, allowing an easy quantification of selenocompounds identified by ESI-MS. The reversed-phase (RP) separation mode offered distinctly higher separation efficiency than the hydrophilic ion interaction (HILIC) mode, but the latter was nevertheless complementary and useful to validate the detection of several compounds.

The method allowed the detection of 64 metabolites including 30 Se-Se or Se-S conjugates (3 triple S/Se/S ones) and 14 selenoethers. 21 previously unreported metabolites were detected on the basis of the selenium isotopic pattern usually matched with the sub-ppm mass accuracy. 9 of these metabolites were subsequently identified using the multi-stage high mass accuracy (<5 ppm) mass spectrometry.

MP-41

RNA ANALYSIS UTILIZING SIZE-EXCLUSION CHROMATOGRAPHY HYPHENATED WITH ICP-MS

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RNA analysis is widely performing in genetic testing, microbial identification, and some other biological studies. In general, capillary gel electrophoresis using modified capillary filled with agalose or poly-acrylamide is applied to those analyses. However, the reproducibility of the electrophoresis method is low and the maintenance of the modified capillary is troublesome. Determination of the phosphorus content in the nucleic acid molecule using ICP-MS or ICP-OES is one of the accurate methods in these analytical fields. We have reported the interface device equipped with the high performance concentric nebulizer [1] for connecting LC or CE with ICP-MS [2,3]. In this study, we have coupled the size-exclusion chromatography (SEC) with ICP-MS using the interface device to quantity phosphorus content in the RNA fragments. The diol column was employed as a SEC column, which was derivatised with 1,2-dihydroxypropane on the silica particles, for the RNA separation. Then the concentration of each RNA fragment was obtained from the measured concentration value of phosphorus.

The low range RNA ladder consisted single-strand RNA fragments between 50 to 1000 nucleotides RNA molecules (NEW ENGLAND BioLabs, Inc.), some of specific RNA sequences synthesized by in vitro enzymatic transcription and nucleotide monomers were analyzed. The LC-10ADvp system (Shimadzu) with YMC-Pack Diol-200 column (4.6×300 mm, 5 µm, 20 nm, YMC) as a HPLC system and Agilent 7700 ICP-MS system (Agilent technologies international) were used. 0.1 M Tris-HCl (pH 8.1) was used as the elution buffer, and the flow rate was set at 0.2 mL·min^{-1}. LC was connected with ICP-MS using the interface device (AIF-03, S.T. Japan Inc. and AIST) and programmable temperature spray chamber (Iso Mist, Glass expansion). ^{31}P and ^{78}Se as an internal standard were measured in this experiment. RNA solutions as well as phosphorus calibration solution diluted from the P standard solution (Kanto chemical) were analyzed using SEC-ICP-MS.

The calibration curve was made by the analysis of P standard solution. The calibration curve of phosphorus shows linearity increasing in intensity from 0.1 to 10 ng·g^{-1}. The RNA ladder, specific RNA fragments and nucleotides monomer molecule were well separated by SEC, and the concentration of phosphorus (^{31}P^{+}) in each RNA sequence was determined by ICP-MS. The concentration of RNA was obtained basically from the analytical values of P and theoretical average molecular weight of nucleotides in this study. The RSD of the reproducibility of retention time and peak area using the SEC were 0.05 and 1.1% (n=5), respectively.

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MP-42

IN VITRO NANOTOXICITY OF SILVER NANOPARTICLES: CHARACTERIZATION OF SILVER FORMS BY AsFlFFF–UV-Vis–ICPMS

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The study of the hazards of engineered nanoparticles is mainly done by applying standard toxicology tests used for bulk forms of the same materials. However, engineered nanoparticles may possess new properties, mainly linked to their size, but also to other physical and chemical parameters of the nanoparticles. Furthermore, these properties can be altered by the medium used to suspend or disperse the nanoparticles. Special attention must be given to the characterization of the nanoparticles in order to facilitate a correct interpretation of the toxicological results. The recommended minimum physical and chemical parameters for characterizing nanomaterials in toxicological studies should include: Particle size/size distribution, agglomeration state/aggregation, shape, overall composition, surface composition, purity, surface area, surface chemistry and surface charge. In addition, some overarching considerations should be taken into account, such as its stability, including the material release through dissolution and the context/media—how do nanomaterial properties change in different media?

In vitro cell-based assays are important tools in the field of nanotoxicology. The considerations mentioned above with respect to knowing how the nanomaterial behaves in the test system are especially important because nanoparticles can exhibit strong interactions with culture media. As speciation strongly affects the bioavailability of nanoparticles, it is very important to develop proper methods to characterize the transformation of these nanoparticles.

In this work, a nano silver product (with a total silver content of around 70% that contains metallic silver nanoparticles below 20 nm) has been characterized and its toxicity studied in a human hepatocellular carcinoma cell line (HepG2). Cell viability was evaluated by the Neutral Red Uptake Cytotoxicity assay. Asymmetric Flow Field Flow Fractionation (AsFlFFF) coupled to UV-Visible and ICP-MS detection was used for characterization of silver nanoparticles and Ag(I) species present in the culture medium after the toxicity assays. The stability and behavior of silver nanoparticles were also studied in the culture medium alone (DMEM, Dulbecco Modified Eagle's medium, supplemented with fetal bovine serum).

Three different situations were studied, corresponding to three different levels of cell viability observed (100%, 50% and 10%). Nanoparticle aggregation as well as dissolution and complexation of Ag(I) with serum proteins were observed. These results were compared to those obtained in toxicity assays made with $AgNO_3$ at the same cell viability levels.

The presence of silver nanoparticles in cells was also studied by their solubilization in tetramethylammonium hydroxide (TMAH) and subsequent analysis by AsFlFFF-ICP-MS. Analytical methodology as well as detailed results and main conclusions will be presented.

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NANOPARTICLE CHARACTERISATION USING FFF-ICP-Q-MS AND FFF-SP-ICP-Q-MS

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Nanoparticle (NP) use in several different industries has generated a need for their accurate and precise characterization. Of the methods developed with this goal in mind, Field Flow Fractionation (FFF) coupled to ICP-MS has proved to be one of the most promising. FFF has a separation principle based on the differing mobilities of different particle sizes in a laminar liquid flow contained in a channel between two plates. Smaller particles flow faster through the channel, enabling a separation based on the size of the particles travelling through the channel. FFF is compatible for particle sizes in the low nm to low µm range and is thus perfectly suited to NP separation. ICP-MS offers a sensitive detection technique able to detect the element contained in the NP, either as an original constituent of the NP or as a tag.

This paper presents the coupling of the Wyatt Technology Eclipse FFF system to the new Thermo Scientific iCAP Q. The new Qtegra software platform enabled control and seamless integration of all the instruments into one workflow. Samples containing varying NP sizes were used to demonstrate the potential of the technique for NP characterization. Additionally, different flow and data evaluation approaches, including single particle analysis (sp-ICP-MS) were evaluated.

COMPARISON OF GC-MS AND GC-ICP-MS FOR THE DETERMINATION OF PBDES IN MARINE SAMPLES FROM A FOOD SAFETY MONITORING PROGRAM

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Polybrominated diphenyl ethers (PBDEs) were the most widely used brominated flame retardants. They can be released from the host plastic or textile and released into the environment since they are not chemically bound to the plastics or textiles. Due to increased health concern, the use of some PBDEs (penta- and octa-BDE) has been banned since 2004 for use e.g. in new electronics [1] within the EU and has also been included since 2009 in the Stockholm convention on POPs [2]. Furthermore the penta- and octa-BDE has been proposed to be added to the POPs Protocol to the UN ECE Convention on Long Range Transboundery Air Pollution [3]. Additionally the production of penta- and octa-BDE was voluntarily suspended in the US in 2005.

Once introduced into a food chain especially low brominated PBDEs are toxic and display endocrine behavior. Marine ecosystems act as sinks for PBDEs and due to their persistency in the environment they readily accumulate within the marine food web. PBDEs have been determined in pelagic and aquaculture fish around the world and their occurrence in the high Artic [4] suggests a long range transport. Since fisheries and aquaculture are important industry sectors in Norway, the National Institute of Seafood and Nutrition Research (NIFES) monitors PBDEs in both pelagic and farmed fish.

Conventionally PBDEs are analysed via GC-MS [5], however the selectivity and sensitivity of the ICP-MS for heteroatoms makes the ICP-MS an attractive detector for PBDEs analysis [6]. Here we show the comparison of GC-NCI-MS and GC-ICP-MS for analysis of 11 PBDEs. Furthermore a fast chromatographic method is presented allowing analysis time below 12 min for determination of 11 PBDEs by GC-ICP-MS. PBDE data on marine samples from the NIFES monitoring program analyzed with both methods is presented and the figures of merits are discussed.

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MP-45

DETERMINATION OF THE BROMINATED FLAME RETARDANT HBCD BY RP-HPLC-ICP-MS AND ITS APPLICATION TO ENVIRONMENTAL MONITORING

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Persistent organic pollutants (POPs) such as dioxins, PCBs and pesticides in the food are a risk for consumer's health. POPs are fat-soluble and readily bio accumulate within the aquatic food web. During the last decades Hexabromocyclododecane (HBCD) has been extensively used as brominated flame retardant (BFR) in textiles, building materials and electrical equipment. Within the EU it has been the second highest volume BFR (after TBBP-A) [1] in use until recently when the use was restricted [2]. Oily pelagic fish [3,4] and fatty farmed fish [5,6] may contain elevated levels of HBCDs. Technical HBCD consist mainly of three stereoisomers (α, β and γ-HBCD) [7] with γ-HBCD being the dominant form. In the environment however, γ-HBCD is the dominant form in sediments near an emission site, while α-HBCD is the dominant form in aquatic organisms [3]. Therefore, the analysis of the three stereoisomers of HBCD is important for identifying the HBCD pathways in food webs.

While GC-MS is only able to identify the sum of all HBCDs due to thermal conversion of β and γ-HBCDs into α-HBCD under typical GC oven conditions, RP-HPLC is able to separate α, β and γ-HBCD. ICP-MS as detector shows superior sensitivity for heteroatoms such as Br at unmatched selectivity compared to LC-MS/MS.

This contribution will demonstrate the capabilities of a RP-HPLC-ICP-MS system for the determination α, β and γ-HBCD in standards and natural marine samples. An Agilent 1260 HPLC system coupled to an Agilent 7500 ICP-MS was used in this study. Separation was done using a C_{18} column and gradient elution with a mixture of water and methanol with 2 mM NH_4Ac added.

Figures of merit of the method will be given as well as a direct comparison with an LC-MS/MS method for environmental monitoring of wild and farmed fish samples. As outlook we will discuss the possibility to use isotope dilution mass spectrometry using enriched Br compounds and the possibility to determine the different enantiomers of α, β and γ-HBCD to further aid in the identification of HBCD pathways in food webs.

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HERICIUM ERINACEUS: A MUSHROOM WITH YEAST-LIKE Se-METABOLISM

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Both yeasts and Agaricomycetes are members the kingdom of fungi, but their metabolic pathways are widely different. Each can accumulate selenium, but while yeasts are able to convert it to organic forms, even up to 2000 $\mu g \cdot g^{-1}$, *Agaricus bisporus* (champignon mushroom), the most widely researched species of Agaricomycetes merely stores the selenium in the inorganic forms. In our study *Hericium erinaceus* (hedgehog mushroom), which belongs to the same class, has been analyzed after light Se-enrichment with sodium selenite. Nearly 50% of the selenium content was found in organic form (selenomethionine) after enzymatic digestion and ion-pairing chromatography clean-up. This suggested that the metabolism of *Hericium erinaceus* is more similar to yeasts than Agaricomycetes. To confirm this, we searched for seleno-adenosyl compounds, typical for yeast metabolism, and an aqueous extraction and SEC fraction collection was executed. The primary molecule of interest was seleno-adenosyl-selenohomocysteine, one of the most abundant Se-metabolites of yeast. Three Se-adenosyl-compounds were identified after multi-dimensional chromatographic purification monitored by ICP-MS and HPLC-ESI-QTOFMS based analysis. One of the components was Se-methyl-5-selenoadenosine, which also appears in yeast metabolic pathways [1]. The oxidized form was also identified from the extract. This observation definitely opens a new group of higher mushrooms that can be directly exploited as raw materials for functional food purposes competing yeast-derived dietary supplements.

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VANADIUM SPECIATION IN SOIL AND SLAG LEACHATES BY ANION EXCHANGE HPLC-ICP-MS AFTER EDTA COMPLEXATION: THE IMPORTANCE OF SAMPLE PREPARATION

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Vanadium in soils occurs in two redox forms, i.e. V(IV) and V(V), with distinctly different geochemical properties. Under oxic and high-pH conditions V(V) is the most stable species and exists as vanadate anions (HVO_4^{2-} or $H_2VO_4^{-}$). Vanadate is more soluble than V(IV), but is strongly bound by iron oxides/hydroxides and may be reduced to V(IV) by humic substances. Vanadium(IV) typically occurs as the vanadyl oxocation VO^{2+}, which is strongly bound by different organic ligands including humic substances.

The mobility and phytoavailability of vanadium in soils depend upon its speciation and soil properties. Vanadium(V) can be phytotoxic if taken up at high concentrations, probably due to its capacity to inhibit phosphate-metabolising systems. Reduction to V(IV) in plant roots has been observed and interpreted as a detoxification mechanism since V(IV) is considered less toxic than V(V). Therefore vanadium speciation is crucial both for the entry in the food-chain and for potentially toxic effects on plants.

The low vanadium concentrations in environmental samples and the sensitivity of vanadium to pH and redox conditions make it difficult to determine vanadium speciation, as the oxidation state is easily changed during analysis. For the investigation of vanadium speciation in soil leachates a method based on the conversion of cationic and anionic tetravalent and pentavalent species into V–EDTA complexes, i.e. $[VO(EDTA)]^{2-}$ and $[VO_2(EDTA)]^{3-}$, was used [1]. The V–EDTA complexes are then effectively separated on a short anion-exchange column in <6 min.

An important feature of the method is the pre-column EDTA complexation, which is used to prevent species interconversion [2]. Maintaining the intact species composition is especially important in complex experiments such as those investigating vanadium leaching from by-products from the steel industry. These waste materials are reused for various applications such as for soil amendment and they often contain potentially toxic elements, e.g. vanadium, at high concentrations. To be able to predict the fate of vanadium in soils subjected to application of slag from the steel manufacturing process it is necessary to know the speciation of the dissolved vanadium that leaves the particles of the solid phase. Critical issues of sample preparation in order to obtain meaningful speciation results in this application are highlighted.

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MP-48

OFF-LINE MALDI AND ICP MS DETECTION OF A SINGLE RECORD OF METALLOTHIONEIN SEPARATION

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It is estimated that one third of all proteins require metals to carry out their functions. Therefore, the analyses of native metal-protein and metal-metabolite complexes by hyphenated techniques that combine separation with a specific detection is of growing importance.

A new concept of an off-line multidetection platform for metalloprotein/metallopeptide analysis of fractions collected from a single run of capillary electrophoresis (CE) or liquid chromatography (LC) is presented. The separation record, i.e. fractions collected on a target, are analyzed sequentially with matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) and substrate-assisted laser desorption inductively-coupled plasma mass spectrometry (SALD ICP MS). Thus, a single separation can yield both proteomic and metallomic information. Moreover, the off-line nature of the analysis provides further possibilities, such as laser-induced fluorescence detection or on target digestion.

Here, the approach is demonstrated on the successful reverse phase HPLC-ESI/MALDI/SALD ICP MS analysis of purified rabbit liver metallothionein (MT) isoforms: The MT1a, MT2d and MT2e (1 $\text{mg}\cdot\text{mL}^{-1}$, 5 μL) were eluted out of a C18 column with ammonium acetate buffer (pH 7.5)/ammonium acetate buffer (pH 7.5) in 60% methanol at 27.8, 29.0 and 33.4 min, respectively. Using a flow splitter, the MT isoforms were detected by on-line ESI–TOF MS and the fractions of the separation were simultaneously collected on a suitable target for successive off-line detection by MALDI and SALD ICP MS.

CE was successfully coupled to both MALDI and SALD ICP MS [1,2]. It can offer enhancement of separation efficiency, modified separation selectivity and high sensitivity. On the other hand, low amount of injected samples poses a challenge for both MALDI and SALD ICP MS detection modes. Initial results of CE as a prospective method for separation of MT isoforms will be presented. The influence of liquid junction interface, fraction collector and MALDI-TOF MS settings and other analysis parameters will be discussed in detail.

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ON-LINE QUANTIFICATION STRATEGIES COMBINED WITH AF4/SF-ICP-MS FOR SPECIATION ANALYSIS OF ENMs

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Synthetic materials exhibiting a size smaller than 100 nm at least in one dimension are allocated to the class of Engineered Nanomaterials (ENMs). In comparison to the bulk material, ENMs show promising properties in different application fields, e.g., functionalized materials (e.g., dirt-repellent wall painting, clothing), medicine (e.g., anti-bacterial band-aid), cosmetics (e.g., suncream) – therefore, ENMs gained highly in importance leading to increased production during the last years.

However, up to now, the fate and behavior of ENMs in the environment is still unclear to a large extent; furthermore, techniques for collecting, preserving and storing samples containing ENMs are lacking [1]. In addition, the analysis and characterization of ENMs is challenging and only feasible when a set of different analytical techniques is applied.

A promising tool, offering the separation of ionic fractions from different size-fractions of nanomaterials on the one hand and element-specific detection on the other hand is the coupling of asymmetric flow-field-flow-fractionation (AF4) with inductively coupled plasma-sector-field-mass spectrometry (SF-ICP-MS).

On the poster strategies for quantifying silver nanoparticle (AgNP) size-fractions after AF4 separation relying on on-line SF-ICP-MS detection will be presented; it turned out that depending on the concentration of the AgNP fractions, a varying amount of ionic silver is present in the sample. Due to this, authentic standards are not feasible for (external) quantification. Therefore, an ("post-channel") on-line isotope dilution (on-line ID) approach combined with AF4/SF-ICP-MS was developed and investigated.

Given the fact that AF4 separations were carried out under acid-free aqueous conditions the ICP-MS response of AgNPs in comparison to that of ionic silver was investigated adding different amounts of acid "post-channel" – a decreased response was observed after injecting AgNPs without acid.

When carrying out speciation analysis, a quantitative mass balance is of high importance – therefore, the fraction of ionic silver in AgNP samples was determined and correlated to the respective fractograms.

On-line ID AF4/SF-ICP-MS seems to be a promising approach for the speciation analysis and on-line quantification of AgNP counteracting possible signal fluctuations.

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PILOT STUDY ABOUT NANOPARTICLES IN MOUTHWASHES REGARDING TO SIZE AND ELEMENTAL COMPOSITION

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The characterization of daily used personal care products is of great interest. Within this pilot study, commercial mouthwashes are chosen as complex matrices. They consist of mixtures of water, alcohol, dyes, flavorings, and other compounds like possibly nanoparticles.

Within this approach, the asymmetric flow field flow fraction (AF4) technique in combination with several detectors (dynamic light scattering (DLS) resp. UV with multiple angle light scattering (MALS) and ICPMS) is applied and optimized for the identification and further characterization of nanoparticles.

Next to the composition of mouthwashes also questions about the distribution of nanoparticles are investigated. By washing the mouth, it is of interest if the nanoparticles stay in the mouth and might be further distributed in the body, or if they are spat after using the mouthwash. The first results are presented.

MP-51

Sn SPECIATION IN OYSTER’S ORGANS: USE OF STABLE ISOTOPIC TRACERS TO TRACK METABOLIC PATHWAYS

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Tributyltin (TBT) is considered a pollutant of major concern. During years, it was extensively used as antifoulant in marine structures that consequently became an important source of such organotin compound in aquatic ecosystems. Despite being recognised by its endocrine-disruption actions in aquatic organisms, the mechanisms of uptake and biotransformation remain unknown.

The main aim of this study was the determination of the predominant uptake pathway and potential biotransformation of TBT in oysters’ organs by isotope dilution GC-ICP-MS. Two different pathways were evaluated: trophic and water dissolved, assisted by the addition of isotopically enriched TBT (^{117}TBT) to the oyster cultures (during 14 days). A noticeable difference of Sn species distribution in oyster organs was observed depending on the uptake mechanism. Finally, size exclusion chromatography-ICP-MS screening revealed that TBT added to the oyster culture, is associated to different biomolecules than endogenous Sn species.

2D-UPLC (HEART CUTTING/COMPREHENSIVE) IN REAL TIME AND SPECTRAL ACCURACY IMPROVEMENT FOR SPECIATION OF COMPLEX SAMPLES BY ICPMS: AN ORIGINAL MASS SPECTROMETRY STRATEGY

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This presentation gives a brief introduction of 2D-UPLC in Real Time (Heart cutting and Comprehensive) of well-identified selenium containing metabolites from Yeast based on water-soluble extract fingerprinting. In the last decade, numerous papers are dedicated to the speciation of Se compounds with firstly combination of chromatography and elemental mass spectrometry and more recently with molecular mass spectrometry.

A 2D-UPLC Acquity (WATERS SAS, France) was used as 2D liquid chromatography media. A XevoTQD was used as a tandem mass spectrometer and the 7700 series ICPMS (Agilent Technologies, France) was used as elemental mass analyser. Data from both instruments were used also for Spectral Elucidation (identification of compounds composition/interferences, isotopic ratio corrections).

Today, the speciation of whole selenium containing molecules from complex matrices such as yeast (saccharomyces cerevisiae) is still challenging (identification, interferences, origin…). We note similar difficulties with arsenic speciation in biological media. Because trace element speciation is tedious and time consuming (very low concentration, various adsorption, high reactivity, very high matrix effect, Peak capacity, request of many chromatographic separation...). An automation in Real time of Orthogonal Separative Techniques (2D-UPLC) with high peak capacity in combination with mass spectrometry detection, is one of the much promising tool which allow us a friendly access to a representative and global fingerprint with in perspective some new frontiers for Speciation. The coupling with high-speed instrument such ICPMS is required. But even if quadrupole mass spectrometer suffers of a low mass resolution, in the opposite with its long term stability, spectral accuracy (in comparison of many high resolution instruments) and its good sensitivity, we can achieve successively the detection of presence, identification and software correction of polyatomic interferences.

Here, we opened new area in instrumentation with the coupling of 2D-UPLC with the specificity and performance of ICPMS/ESIMSMS (next ICPMSMS) to achieve more than thousands peak capacity with an original computer spectral elucidation for interference allocation and molecular identification with help of spectral accuracy correction and elucidation.

Spectral and Mass Accuracy, 2D-UPLC, Peak Capacity, ESIMS, ICPMS: an exciting combination for tomorrow.

INVESTIGATIONS ON ORGANOTIN COMPOUNDS REACTIVITY USING ENRICHED ISOTOPIC TRACERS IN POLLUTED COASTAL SEDIMENTS FROM THE EASTERN ADRIATIC, CROATIA

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Croatian Adriatic Coast is still widely polluted with organotin compounds as a consequence of its long-term use in antifouling paints [1,2]. Even more, distribution of butyltin compounds in mussels and seawater suggested that TBT-based antifouling paints may be still in use [2]. As polluted sediments represent a permanent source of organotin compounds for the whole ecosystem, it is of great importance to estimate their persistence and mobility in sediment.

The proposed work allowed studying the main environmental factors affecting the persistence and degradation of Sn organometallic contaminants in sediments sampled at three polluted locations (marinas and ports) characterized with different sediment types. A complete methodology combining field incubations with the addition of species-specific isotopically enriched tracers (^{117}TBT, ^{119}DBT, ^{116}TPhT) and a mathematical approach based on the deconvolution of isotopic patterns was used [3]. The methodology has been applied for the study of environmental reactivity of Sn compounds in the total sediment and in isolated porewater and to investigate their transformations mechanisms under controlled conditions (anoxic condition, temperature and light control). Oxic/suboxic surface layer and anoxic bottom layer were incubated in order to assess organotin transformation processes under different biogeochemical conditions (redox potential, organic matter reactivity, bacterial community).

Such experimental in situ incubations have allowed to evaluate the reactivity of these compounds in highly polluted coastal sediments and to determine the half live of each compounds.

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MP-54

NOVEL STRATEGY FOR THE ACCURATE QUANTIFICATION AND IDENTIFICATION OF CHROMIUM SPECIES IN FOOD SUPPLEMENTS

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Due to the increasing consumption of chromium (Cr) food supplements by the general population in efforts to prevent the development of type 2 diabetes and achieve weight loss there is a large number of products available without prescription. However, the different Cr forms existing |on the European market are poorly characterised and, in some cases, their food safety has been questioned. Reference methods for Cr species are essential to the development of safe and effective dietary sources of high Cr content. Such methods, particularly for Cr(III) and toxic Cr(VI) species, are scarce and there is no certified reference material available for quality control.

This work presents the development of a novel strategy for accurate quantification of Cr(III) and Cr(VI) in Cr-enriched food supplements, being Cr-enriched yeast the model sample. It is based on alkaline hydrolysis of the solid sample with HPLC-ICP-MS and double spiking species-specific isotope dilution mass spectrometry (IDMS) calibration. Significant improvement, in terms of chromatographic selectivity and retention of Cr species in presence of the real matrix and compatibility between extractant and chromatographic conditions, compared to previously reported methodology [1] was achieved by using tetrapropylammonium hydroxide for alkaline sample hydrolysis and as ion pairing reagent for reversed phase HPLC. Improved preparation and in house characterisation of isotopically enriched spike solutions containing ^{50}Cr(III) or ^{53}Cr(VI) were also achieved. Published isotope deconvolution equations [2] were used to correct for the effect of species transformation occurring during extraction and separation on the Cr species mass fractions in the solid yeast. Spiking experiments were performed for method validation; recoveries for spiked Cr(III) were in the range 88-94%. The determined Cr(III) mass fraction in the yeast sample did not significantly differ from the total Cr mass fraction, both obtained using IDMS calibration.

The potential of reversed phase HPLC combined with ICP-MS and ESI MS/MS was investigated for the characterization of water soluble organo-Cr species in the Cr-enriched yeast sample. Several Cr-containing fractions were detected by HPLC-ICP-MS; one of them was found to elute at the same retention time as a Cr-Nicotinamide adenine dinucleotide phosphate (Cr-NADP) standard, prepared in house according to a published procedure [3]. HPLC-ESI MS/MS in selected reaction monitoring (SRM) mode was applied to non-spiked extracts and extracts spiked with the Cr-NADP standard to further verify the presence of these Cr species in Cr-yeast.

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ELEMENTAL LABELING AND ISOTOPE DILUTION ANALYSIS FOR THE QUANTIFICATION OF THE PEPTIDE HEPCIDIN-25 IN SERUM SAMPLES BY HPLC-ICP-MS

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Hepcidin-25 has been proposed as the key biomarker for the diagnosis and monitoring of iron disorders. The small peptide-hormone inhibits ferroportin which transports iron out of the cell and is strongly expressed by the enterocytes and liver macrophages [1]. As body iron increases, hepcidin-25 is induced in the liver which then inhibits the efflux of iron through ferroportin binding. Thus, by modulating hepcidin-25 biosynthesis, an organism controls intestinal iron absorption, iron release from the macrophages, and mobilization from stores to meet the body iron need. Structurally, hepcidin-25 is a S-rich peptide (with 8 cysteines and 1 methionine) that contains a metal binding motif in the N-terminus. That domain binds preferably Cu(II) ion forming a stable complex [2]. Such selective binding can be used as mean to determine hepcidin-25 in biological fluids by highly sensitive Cu measurement using elemental mass spectrometry (e.g. inductively coupled plasma mass spectrometry).

Thus, the synthesis of the metal-labeled peptide was conducted by optimizing the incubation conditions in order to address its stoichiometry and stability by electrospray-MS (ESI-q-TOF). It was found that Cu:hepcidin-25 complex is stable under physiological conditions and shows an equimolar stoichiometry (1:1). The collisional induced dissociation (CID) experiments confirmed the specific binding of Cu to the N-terminal motif. Therefore, we could apply liquid chromatography coupled to ICP-MS (LC-ICP-MS) to perform hepcidin-25 determination via Cu detection.

For hepcidin-25 quantification via Cu detection, two different quantitative Cu speciation methods, based on isotope dilution analysis (IDA) in combination with HPLC-ICP-MS have been investigated. The first one, included the post-column addition of a ^{65}Cu spike and the second, the synthesis of the labeled ^{65}Cu:hepcidin-25 complex as tracer (species-specific). Both methods have been optimized and critically compared in different samples. Finally, post-column IDA was chosen for the quantification of hepcidin-25 concentration in serum samples. The determination of hepcidin-25 in different serum samples from healthy individuals based on Cu monitoring showed a mean value of 20.2 $\mathrm{ng \cdot mL^{-1}}$ which is in good agreement to previously published data. Furthermore, the developed hepcidin-25 quantification methodology [3] was compared to a commercially available ELISA kit by analyzing a set of serum samples.

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MP-56

USING AsFlFFF-ICP-MS AND XAS FOR THE STUDY OF COLLOIDAL ARSENIC SPECIATION IN MINE SOILS

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Colloidal matter present in natural acuatic systems consists of a heterogeneous mixture of polidisperse inorganic and organic components, with sizes between a few nanometers to 1 µm. Colloids mobility and their role as metal nanovectors in natural soil systems are recognized as important phenomena in the pollution processes of the environment. Because of their high reactivity attributed to their large surface area, high mobility, explained by their small size, and electrochemical stabilization, that makes colloidal particles persist in suspension for a long time, colloids are able to bind contaminants and facilitate their transport. Consequently, colloidal systems control metal and metalloid distribution, speciation, bioavailability and toxicity in freshwater systems.

In this work, colloidal fractions from mine waste rocks, sediments and soils samples impacted by mine activities have been characterized using Asymmetrical-Flow Field-Flow Fractionation (AsFlFFF) coupled ICP-MS. In particular, a procedure has been developed to study the transport and speciation of As associated to colloids for both sample preparation and X-ray absorption (XAS) spectroscopy data collection. The colloidal suspensions were obtained mixing 40 g of soil sample with 400 mL of ultrapure water for 24 hours. The fraction smaller than 1 µm was isolated by centrifugation, and the colloidal size and elemental distribution studied by AsFlFFF-ICP-MS. Those separation conditions affecting the sample recoveries in AsFlFFF (membrane and mobile phase composition) and overloading effects (mass injected) were studied and optimized so reliable results could be obtained. Size distribution was obtained by calibration with SiO_2 size standards injected under the same conditions that soil samples. The elemental (Al, Ca, Fe, As, Cu, Zn and Pb) size distribution indicated metal association to colloidal particles of 30 nm in sediments from a stream that seasonally collects surface runoff from an arsenic bearing waste pile. Bigger colloidal particles (55 and 175 nm) were observed in samples from the subsoil under the riverbed layer and in sediments from a downstream pond (55 and 100 nm), suggesting colloidal aggregation. Arsenic, Fe and Al concentration were mainly found in the colloidal fraction indicating As association with Fe and Al colloidal particles.

The speciation in the colloidal fraction of As and Fe was studied by XAS. Colloids between 10 nm and 1 µm were isolated onto ultrafiltration membranes with a pore size selected according to the size distribution obtained by AsFlFFF-ICP-MS. XAS analysis indicated that scorodite is the main colloidal mineral phase in the waste pile. Arsenic adsorbed on Fe-oxyhydroxides was the main As specie found in the rest of the samples, suggesting the stability of these colloidal Fe oxyhydroxides-arsenic interactions under different geochemical conditions, and the potential role of Fe-oxyhydroxides phases as nanovectors of As transport in natural systems.

Acknowledgement

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MASS SPECTROMETRY BASED METHODOLOGIES FOR STUDYING THE DNA BINDING PROPERTIES OF NEW CYTOSTATIC RUTHENIUM COMPLEXES

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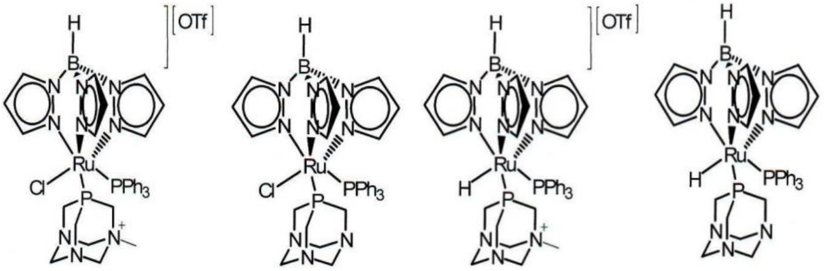
The clinical success of cisplatin as chemotherapeutic agent remains a stimulus for the development of new transition-metal complexes that address the downsides associated with cisplatin, especially the systemic toxicity and (intrinsic or acquired) resistance. In this field, ruthenium complexes appear particularly promising, since they offer the potential over cisplatin of reduced toxicity, a novel mechanism of action, the prospect of non-cross-resistance and a different spectrum of activity. In fact, two Ru(III) complexes (KP-1019 and NAMI-A) are currently undergoing clinical trials in phase II [1] and some Ru(II) arene complexes shown promise for future development.

It is known that the anticancer activity of cisplatin arises from their ability to damage DNA, with adducts forming various types of crosslinks. Although the pharmacological target for anticancer ruthenium drugs has not been unequivocally identified, it seems that the cytotoxicity of many ruthenium complexes correlates with their ability to bind DNA. Therefore, by analogy to cisplatin, DNA interactions of new potential anticancer ruthenium complexes are of a great interest.

In this vein, the main objective of this work is to study the DNA –binding properties of four new ruthenium complexes (see Fig. 1) that have proved to be cytotoxic in cell culture [2]. For that purpose, they will be incubated with individual nucleotides, a custom oligonucleotide and commercial Calf Thymus DNA. The products of this incubation will be analyzed and characterized using HPLC-ICP-MS, MALDI-TOF-MS and ESI-MS techniques.



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MP-58

STUDY OF ABSORPTION/BIOAVAILABILITY AND DISTRIBUTION OF ^{57}Fe FROM SUPPLEMENTED ^{57}Fe-LACTOFERRIN FORMULA MILK BY IPD-ICP-MS

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Iron is an essential micronutrient involved in multiple biochemical and physiological processes. Iron deficiency can lead to anemia characterized by low hemoglobin, decreased iron stores (ferritin) and low serum iron levels. According to the World Health Organization (WHO), iron deficiency is considered the first nutritional disorder in the world.

The main route of supply of trace elements is through food. For the newborn, breast milk is the ideal food because it provides all macro- and micro- nutrients in adequate concentrations along the lactacting pediod. Human milk contains rather low levels of iron (0.2–0.4 $mg \cdot L^{-1}$). However, the high bioavailability of iron contained in breast milk results in a lower incidence of iron deficiency in breastfed infants. Non-breastfed children should be fed with iron-fortified formula to prevent iron deficiences and anaemia. In general iron absortion from formula is very low compared with maternal milk.

Since the bioavailability of iron depends on its physicochemical form, it is convenient to evaluate the bioavailability (and/or absorption) of physicochemical forms of Fe different from those used today ($FeSO_4$). Perhaps other species offer higher bioavailability and so its potential for fortification of alternative and advantageous formula milks should be investigated.

Lactoferrin, a protein found in human milk, is added recently to milk formulas to protect the newborn against gastrointestinal infections. Moreover, lactoferrin appears to be involved in the metabolism of Fe, and previous studies showed that an iron fraction in breast milk eluted in the same region that lactoferrin [1].

In this work, iron enriched stable isotopes, in combination with isotope pattern decovolution (IPD) and ICP-MS [2] previouly developed, are used to investigate the iron absortion/biodisponibility and distribution in the body compartments of Fe, from ^{57}Fe-lactoferrin supplemented formula milk, in lactating rats in order to elucidate the possible use of Fe-lactoferrin as an efficient iron supplement for non-breastfed infants.

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SPECIATION OF METAL COMPLEXES IN SOIL AND PLANT RELATED SAMPLES WITH ELEMENTAL AND MOLECULAR MASS SPECTROMETRY

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Our analytical developments regarding the quantification and identity confirmation of metal complexes in soil/plant related samples and in the rhizosphere (root/soil interface) are addressing two different research topics.

In the first study the iron selectivity of 2’-deoxymugineic acid (DMA), a hexadentate non-proteinogenic amino acid ligand out of the family of phytosiderophores is investigated. The compound is released by graminaceous crop plants (such as barley, wheat, corn) into the rhizosphere in order to overcome iron limitation in soil. DMA facilitates the scavenge of iron in the oxidation status of Fe(III) from iron-bearing soil minerals [1]. Chelation of Fe^{3+} forms water-soluble stable iron-complexes to provide the plant with Fe trough the root plasma membrane by specific protein transporters, described as “strategy II” [2].

We will present sensitive and selective methods, which support the understanding of Fe-solubilization and -absorption processes, the influence of soil bacteria/micro-organisms as well as the behavior of Fe exudations rates in consequence of defined release patterns and on iron acquisition processes.

The second study focusses on the development of speciation methods for analysis and quantitation of bacterially produced secondary metabolite chelators involved in metal solubilization. We want to investigate the interaction of bacteria and plant roots in association with metal mobilization in soil and metal enrichment by plant hyperaccumulators [3,4]. Initial LC-ICP-MS and CE-ICP-MS based method development employs several separation and selectivity principles and will be performed using metallophore ligands from xylem sap. The methods will further be adapted for analysis of soil related metallophore metabolite extracts, containing the organic acids and siderophores produced by specific bacteria/microorganisms out of the family of Microbacteriaceae in the rhizosphere. Moreover, a method for identity confirmation of the metallophores will be developed by transfer of the ICP-MS based separations to an accurate mass ESI-TOF-MS system. First data will be presented and critically discussed.

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MP-60

GOLD AS AN ACTIVITY-BASED PROBE TO ADDRESS THE ACTIVE THIOREDOXIN REDUCTASE CONCENTRATION IN CELL CULTURE BY HPLC-ICP-MS

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Mammalian Thioredoxin Reductase 1 (TrxR1) is a cytosolic enzyme containing a selenenylsulfide/selenolthiol redox active site which catalyzes the reduction of a variety of disulfide containing substrates. Therefore, the enzyme plays a critical role in regulating cellular redox homeostasis and signaling pathways, and it is involved in cell proliferation, antioxidant defense, apoptosis induction and many metabolic pathways [1].

Levels of TrxR1 are altered in a variety of diseases such as asthma, hepatitis, HIV infection, rheumatoid arthritis and cancer. An increase in TrxR1 activity seen in many human primary cancers compared to normal tissue appears to contribute to increased cancer cell growth and resistance to chemotherapeutic drugs such as cisplatin [2]. Therefore, the determination of the levels of the enzyme may be useful to predict the response to cisplatin chemotherapy and can be correlated with cancer progression and outcome.

Since most analytical methods for TrxR1 determination are based on relative activity measurements using spectrophotometric assays, here we propose the absolute quantification of this protein in culture cancer cell lines through the measurement of the Se present in their structure using isotope dilution-ICP-MS after anion exchange HPLC separation. Moreover, the determination of the active form of the enzyme was also conducted by using auranofin as an activity-based probe. This electrophilic gold compound react with the selenolthiol residue of the active enzyme. Once optimized this reaction, the derivatized active form of the enzyme was quantified by HPLC with ICP-MS detection of both Au and Se

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MP-61

NEW STRATEGIES FOR THE MEASUREMENT OF GLOBAL DNA METHYLATION IN CISPLATIN SENSITIVE AND RESISTANT CELL LINES USING ICP-MS

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The development of cancer cells that are resistant to chemotherapeutic agents is a major clinical obstacle to the successful treatment of cancer. Acquired drug resistance is a multifactorial phenomenon, involving multiple mechanisms. Presently, two hypotheses, genetic (the occurrence of random mutational events that leads to the formation of drug-resistant cells from sensitive cells) and epigenetic (involving DNA methylation and chromatin modifications), have been proposed to explain mechanisms of acquired cancer drug resistance. In fact, a number of studies have indicated substantial alterations of epigenetic mechanisms in drug-resistant cancer cells, including changes in DNA methylation and histone modification patterns.

DNA methylation is a biochemical process that is important for normal development in higher organisms. It involves, mainly, the addition of a methyl group to the 5 position of the cytosine pyrimidine ring. This modification can be inherited through cell division and provides an epigenetic mechanism for the regulation of gene expression and cellular differentiation. DNA methylation is an important regulator of gene transcription. However, methylation changes constitute potentially sensitive molecular markers to define risk states, monitor prevention strategies, achieve early diagnosis, and track the prognosis of cancer.

With the aim to compare global methylation of DNA in sensitive and cisplatin resistant cell lines, we have developed different analytical strategies based on mass spectrometric measurements. We describe the use of high performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC–ICP-MS) as a novel approach for the evaluation of DNA methylation, by using the ^{31}P signal present in the phosphate group of the nucleotides.

Alternatively, in order to develop more sensitive strategies we will illustrate the use of selective labeling of 5-methylcytosine in ssDNA by two different methods: first using potassium osmate (K_2OsO_4) in the presence of strong oxidant ($K_3Fe(CN)_6$) and N,N,N`,N`-tetramethylethylenediamine (TEMED) [1] and on the other hand using lithium bromide (LiBr) in the presence of sodium periodate ($NaIO_4$) [2].

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MP-62

GLUTATHIONE PEROXIDASE LEVELS IN BIOLOGICAL FLUIDS: A POTENCIAL BIOMARKER FOR GLAUCOMA

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Selenium is an essential trace element present in numerous selenoproteins, including several enzymes with physiological key roles, such as the glutathione peroxidases (GPx), the deiodinases and the thioredoxin reductases (TR). Se in selenoproteins is contained in the form of the amino acid selenocysteine. The functions of many of selenoproteins are still unknown and there are indications of the existence of some further forms of selenoproteins that have not been identified yet.

Glutathione peroxidase (GPx) is the general name of an enzyme family with peroxidase activity. This enzyme, together with catalase, superoxide dismutase and vitamin E are an essential part of the cellular defense mechanisms against oxidative damage [1].

Oxidative stress can be defined as an increase over physiological values of the intracellular concentrations of reactive oxygen species(ROS), ROS includes superoxide anion (O_2^-), hydrogen peroxide (H_2O_2), hydroxyl radical ($OH^·$), peroxyl radical ($ROO^·$) and oxygen. The biochemical function of glutathione peroxidase is to reduce lipid hydroperoxides to their corresponding alcohols and to reduce free hydrogen peroxide to water. On the other hand, oxidative stress has been implicated in the possible pathophysiology of some ocular diseases, such as retinopathy of prematurity, glaucoma, macular degeneration, and uveitis [2].

The glaucoma is an optical neuropathy characterized by specific structure alteration of the optic nerve accompanied by progressive damage to the visual field. Untreated glaucoma can lead to permanent damage of the optic nerve and resultant visual field loss, which over time can progress to blindness.

The aim of this particular study is to investigate the possible role of the selenoprotein glutathione peroxidase in the pathogenesis of glaucoma. So speciation of selenium in biological fluids (serum, erythrocytes and vitreous humor) has been performed by HPLC-ICP-MS. Quantification of selenium and of glutathione peroxidase levels in the fluids under study was carried out by isotope dilution analysis. Total selenium and/or glutathione peroxidase observed levels in serum, erythrocytes and vitreous humor will be compared for healthy, cataracts and glaucoma suffering individuals.

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AN ISOTOPE DILUTION STRATEGY FOR THE QUATIFICATION OF PLATINUM-GG ADDUCTS INCANCER LUNG CELLS EXPOSED TO CARBOPLATIN

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Platinum-containing compounds have widely been used for cancer treatment over the past decade. The cytotoxic activity of anti-cancer drugs is derived from their ability to interact with DNA to form stable adducts which disrupt cellular processes. Measuring these adducts in *in vivo* and *in vitro* cancer models is essential to optimising cancer therapy.

Methods for the identification and accurate quantification (e.g. based on species-specific ID-MS) of ‘mediating’ elemental species in cancer treatment are essential for quality control of existing mass spectrometric assays intended for clinical use. Efforts to develop IDMS calibration approaches for the quantification of DNA adducts formed with Pt drugs, in particular with highly reactive cisPt, have been made so far [1]. However, the lack of fully characterised primary analytical methods that can be applied successfully to *in vivo* models with very limited samples and adduct concentrations at the low picogramme levels (as those produced by lower reactivity or second generation drugs including carboplatin) is a remaining challenge. Moreover, the lack of Pt-DNA adduct traceable standards, needed for calibration and quality control purposes, is also a remaining problem.

This work describes a metrological approach to the accurate quantification and identification of adducts of DNA formed with carboplatin in an *in vitro* lung cancer model. It is based on the cleavage of Pt adduct to crosslinked guanosine (Pt-GG) from DNA using enzymatic hydrolysis and their quantification by HPLC-ICP-MS using species-specific double isotope dilution calibration. To achieve this, natural and ^{194}Pt-enriched Pt-GG were produced by incubation of commercially available GG with carboplatin or ^{194}Pt-enriched carboplatin, respectively. These materials were characterised for their Pt content and/or the presence of other Pt-containing compounds by using isotope dilution mass spectrometry and HPLC-ICP-MS, respectively. As a first step, method development and performance characterisation was undertaken by using calf thymus DNA incubated with carboplatin. Verification of Pt-GG formation was achieved using HPLC-ESI MS/MS. A limit of detection of 0.1 ng $\mathrm{Pt\cdot mg^{-1}}$ DNA (85 µg DNA) was achieved by using reversed phase ion pairing HPLC coupled to sector field ICP-MS. The methodology was applied to human carcinoma lung cells exposed to carboplatin (48 h); showing a cell viability of > 94%. An expanded uncertainty (k=2) of ≤ 15% was achieved for a Pt-GG mass fraction of 5.5 ng $\mathrm{Pt\cdot mg^{-1}}$ DNA.

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EVALUATION OF NEW PRE-CONCENTRATION TECHNIQUES FOR ORGANOTIN COMPOUNDS ANALYSIS IN WATER SAMPLES

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Organotin compounds are anthropogenic pollutants released directly in aquatic environments due to their extensive use as antifouling paints, biocides, and fungicides [1]. These compounds are part of the indicative list of the main pollutants in the EU Water Framework Directive [2] in which tributyltin (TBT) was identified as priority hazardous substance. As a result, laboratories should be able to identify and quantify these compounds in water samples with a quantification limit of 0.05 $ng \cdot L^{-1}$, which requires performant and sensitive analytical hyphenated techniques such as GC-ICP-MS.

However to reach such low detection and quantification limits, pre-concentration techniques must be applied. In the present work, some recent pre-concentration techniques based on solid phase extraction were tested in order to evaluate their potential when applied to organotin compounds for water samples analysis [3-5]. Silicone rods (SRs) and silicone tubes (STs) have the advantage of being inexpensive, flexible and robust and have so far been applied for the extraction/preconcentration of a large variety of organic micropollutants such as PAHs and chlorinated organic compounds. The evaluation and the optimisation of the analytical conditions (silicon material and dimensions, water sample volume, extraction time, derivatisation regnant, solvent volume) have been carried out with the help of isotopically labelled organotin compounds (^{118}DBT, ^{117}TBT, ^{116}TPT). The use of these tracers has allowed to quantify species recoveries and pre-concentration factors as well as to detect species transformations. Moreover, poor precision and reproducibility generally associated to these pre-concentration techniques have been improved with the introduction of these isotopic tracers correcting for errors due to non quantitative sample preparation, losses or transformations of the different compounds

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QUANTIFICATION OF THE MAJOR ARSENOLIPIDS IN CERTIFIED ALGAL REFERENCE MATERIAL NMIJ CRM 7405 (HIJIKI)

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Arsenic-containing organic compounds are abundant in marine ecosystems where they are thought to play a pivotal role in the cycling and detoxification of potentially toxic inorganic arsenic present in seawater. Most of the arsenic compounds identified so far have been water-soluble species, and it is only in the last few years that work has expanded to include lipid-soluble arsenicals, so called arsenolipids. Progress in this field, however, has been hampered by the lack of standard arsenolipids, or at least a standardised source of these compounds. We use HPLC/ICPMS and HPLC/molecular MS to examine the arsenolipids in the certified algal reference material NMIJ CRM 7405 (Hijiki), and report the identification and quantification of the main arsenolipids present. This algal CRM might now be used by others as source material for identifying and quantifying arsenolipids in HPLC studies employing ICPMS as the arsenic-selective detector.

MP-66

DEVELOPMENT OF AN EASY-TO-USE ANALYTICAL METHOD FOR THE DETERMINATION OF INORGANIC ARSENIC IN FOOD OF ANIMAL ORIGIN

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The application of analytical methods for arsenic speciation in food of animal origin can still be demanding to be implemented as a part of routine activities of laboratories not primarily focused on research. Most works reported in the literature deal with the identification of the variety of arsenic species typically found in marine samples, whereas only recently the interest in developing robust analytical methods focusing on inorganic arsenic (i-As), the most toxic fraction, has increased. The implementation of a relatively cheap, fast, and easy-to-use method directly applicable to real-world samples, can represent an added value for routine laboratories. One of the tasks of the European Union Reference Laboratory for Chemical Elements in Food of Animal Origin (EU-RL CEFAO), as reported in the Regulation (EC) 882/2004 [1], is to disseminate new analytical methods among the EU National Reference Laboratories.

Due to the rising interest in arsenic speciation at the level of control laboratories, EU-RL CEFAO has started developing a method based on HPLC-ICP-MS that could be applicable to incurred samples of animal origin. In particular, an effective procedure for extracting, separating and quantifying i-As has been developed so as to set an easy-to-use method with reduced sample preparation, e.g. avoiding freeze-drying. An effort has been made to develop a procedure that is less time-consuming, less expensive and more similar to the method applied on a routine basis by the laboratories.

This work was conducted on fresh samples of Mediterranean mussels containing about 3.8 $mg \cdot kg^{-1}$ of total arsenic and several procedures were tested and compared in order to obtain the highest extraction yield of i-As. Microwave-assisted procedures were investigated using three different mixtures (HNO_3/H_2O_2; HCl/H_2O_2; TFA/H_2O_2). HNO_3/H_2O_2 extraction was carried out both with and without overnight pre-digestion of samples and the usefulness of sample sonication in increasing the effectiveness of the extraction procedure was investigated. Furthermore, water bath and microwave-assisted extraction were compared using the same three mixtures of extractants.

The optimization of an HPLC-ICP-MS method for selective i-As determination was investigated and the results obtained with anion-exchange chromatography by using different columns were compared and evaluated.

The procedure optimized for fresh mussel will be tested on other matrices (*i.e.* fish and meat) in order to propose a simple and reliable method valid for most foods of animal origin.

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NOVEL SMPS-ICPMS COUPLING ALLOWS SIMULTANEOUS ANALYSIS OF SIZE DISTRIBUTION AND ELEMENTAL COMPOSITION OF AIRBORNE NANOPARTICLES

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Sensitive analytical techniques are required to characterise airborne particles in the nanometre to sub-micrometre size range in emission as well as air quality control. Size distribution and chemical composition are important nanoparticle properties for a detailed monitoring of combustion processes and for the observation of dynamic nanoparticle behaviour. However, most of the available techniques are not able to provide such physical and chemical information at the same time.

Scanning Mobility Particle Sizer (SMPS) is well established and widely used for physical aerosol characterisation. It provides size distribution and number concentration of particles in a size range from about 5 to 500 nm within scan durations of just some minutes. Depending on the specific equipment and settings this range can be shifted towards even smaller (down to 2.5 nm) or larger (up to 1 µm) particles. However, chemical composition is not directly accessible.

Inductively Coupled Plasma Mass Spectrometry (ICPMS) allows a determination of elemental composition with excellent detection limits and a wide dynamic measuring range.

The coupling of these two analysis techniques, i.e. SMPS and ICPMS will allow achieving size and chemical information at the same time. The expected full scan duration of a few minutes and the even shorter scan time for a narrower size range will enable transient particle observation, and it opens the possibility to chemically characterise an aerosol in its original condition instead of sampling particles and analysing them afterwards.

During the first period of this project the coupling of the two instruments is being realised. Due to the low oxygen tolerance of the inductively coupled plasma the SMPS has to act as a gas exchanger transferring the particles from air to an argon atmosphere. Since SMPS is normally operated with air as particle carrier gas, a new flow concept has to be developed. The SMPS components Differential Mobility Analyser DMA and Condensation Particle Counter CPC need to be arranged and calibrated for argon operation. However, argon is relatively expensive and therefore also a part-flow recycling is pursued.

In a next step, the interface will be developed to online couple both analysing instruments, followed by optimising the operation parameters of SMPS and ICPMS using standardised nanoparticle containing aerosols. The concept of the planned setup as well as first results will be presented here.

IN-VITRO STUDIES WITH GOLD NANOPARTICLES MONITORED BY HPLC-ICP-MS

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Gold nanoparticles (GNPs) are being extensively used in many biomedical applications like bioimaging, gene delivery, drug delivery and other therapeutic and diagnostic applications, thanks to their small size to volume ratio, ease of synthesis and functionalization, chemical stability, optical properties, etc [1]. Due to the increasing use of these nanomaterials, the knowledge about their toxicity in the environment and biological systems has gained great interest in the last years.

Based on a recent work [2], it is developed a hyphenated technique, HPLC-ICP-MS, to determine the presence of GNPs, their size and also the free gold ions detached from the particles if any. The technique was applied for the analysis of GNPs in cell cultures.

For this purpose, in vitro studies were carried out. GNPs of 10 and 30 nm of diameter size were incubated onto HT-29 cells. After the addition of the particles, information about the viability and proliferation of the cells were tested by MTT assay and flow cytometry. Oxidative stress evaluation of the cells was also carried out with a special kit. On the other hand, for the implemented HPLC-ICP-MS method for the GNPs analysis, an alkaline extraction procedure was needed and therefore performed in order to take the GNPs out of the cells.

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MP-69

THE ROLE OF ICP-MS AND ESI-MS IN PRODUCTION OF INTACT PROTEIN STANDARDS FOR QUANTITATIVE PROTEOMICS

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Quantitative proteomics was introduced with quantifications on a relative basis, requiring only peptide intensity ratios generated by ESI or MALDI MS. Next, methods for regular quantification (“absolute quantification”) followed, which deliver data for absolute amounts and concentrations. The optimal strategy in this context is the use of intact, stable isotope labeled proteins as internal standards, e.g. PSAQ (Protein Standard Absolute Quantification) [1]. Here, we describe an approach related to PSAQ but different both in the way of protein standard production and quantification. In the presented concept, standard protein production is achieved by cell-free synthesis. This technology allows simultaneous incorporation of selenomethionine and of selected stable isotope labeled amino acids. Standard protein quantification is performed by ICP-MS and selenium quantification. Standard proteins with these properties have been named RISQ proteins standards [2] (for Recombinant Isotope labeled and Selenium Quantified). While RISQ proteins allow highly accurate protein standard quantification due to their exclusive selenium content, their stability might be influenced by the objectionable reactivity of selenium. Therefore, to further develop the RISQ protein concept, we generated Se-quantified but Se-free standard proteins. For this purpose we introduced the two types of label into two separately expressed proteins. The Se-containing protein is quantified by ICP-MS and is then used as standard for quantification of the purely stable isotope labeled standard by LC-ESI/MS. The latter then represents the final Se-free protein to be used as internal standard. The extra quantification step by LC-ESI/MS can be performed with a relative standard deviation around 1% [3]. This new concept is demonstrated for production of an intact standard for human serotransferrin labeled with [$^{13}C_9$,^{15}N]-Phe (F+10). Standard preparation and purification, its characterization and purity control are described in detail. Accurate quantification of human serotransferrin has great importance in clinical chemistry due the key role of serotransferrin in “iron-out-of-balance” disorders.

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MP-70

FLOW FIELD-FLOW FRACTIONATION COUPLED WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (FlFFF-ICP-MS) FOR STUDY OF Pt(II) AND HEN EGG WHITE PROTEIN BINDING

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Cisplatin or platinum(II)-containing anti-cancer drug is widely used as the anticancer agents for the treatment of solid tumors however its application is still limited by its side effects. Hen egg white protein was investigated as a potential delivery system for Pt based drug in order to reduce side effect with high drug retention time.

Flow field-flow fractionation with inductively coupled plasma mass spectrometry (FlFFF-ICP-MS) is a sensitive and highly specific method to study binding efficiency of Pt and hen egg white protein by determination of platinum ($^{195}Pt^+$). The separation condition in FlFFF was optimized by using poly(regenerated cellulose acetate) membrane (molecular weight cut off of 1 kDa) and 30 mM TRIS buffer as carrier liquid. Channel flow rate of 1 $mL \cdot min^{-1}$ and cross flow rate of 2 $mL \cdot min^{-1}$ were used as separation condition. Hen egg white protein (22-26 kDa) powder was prepared by removing ovomucin and impurity from the fresh hen egg. The binding efficiency between K_2PtCl_4 and hen egg white protein was examined. The results from FlFFF-ICP-MS show binding between hen egg white protein and Pt (II) at the molecular weight of hen egg white protein around 22-26 kDa and the binding efficiency depends on the their concentrations.

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ASYMMETRICAL FLOW FIELD-FLOW FRACTIONATION COUPLED WITH ICP-MS FOR MULTI ELEMENT ANALYSIS OF PLASMA PROTEINS.

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Albumin and transferring are two main plasma proteins that are known to bind and transfer metal ions in the biological fluids. Metal-protein complexes are involved in many health studies such as metal-based drugs for cancer or diabetes treatments [1,2]. Chromatography techniques hyphenated to ICP-MS and MALDI-TOF-MS have been used to investigate metal speciation and metal binding kinetics in plasma and serum proteins [1,2].

Field-Flow Fractionation (FFF) is a chromatography like technique that uses an external field for separation. In FFF the separation takes place in an open channel (no stationary phase). As a result of sample-field interaction, different sample species (different size classes) form different sample zones which are swept out of the channel at different speeds. The order of separation in FFF is from small to large. The main advantages of FFF over other chromatography techniques are higher sample recovery and being able to use non-denaturing and less destructive carriers.

In this study Asymmetrical Flow FFF (AF4) was used to separate mixture of human serum albumin and transferrin. The FFF system was interfaced with ICP-MS to obtain metals distributions in the protein mixture. The results demonstrated that AF4-ICP-MS is a non-destructive and element selective detection technique for plasma proteins such as serum albumin and transferrin. This is mostly important for applications in which the two plasma proteins are acting as binders of the same element (Vanadium in diabetes studies).

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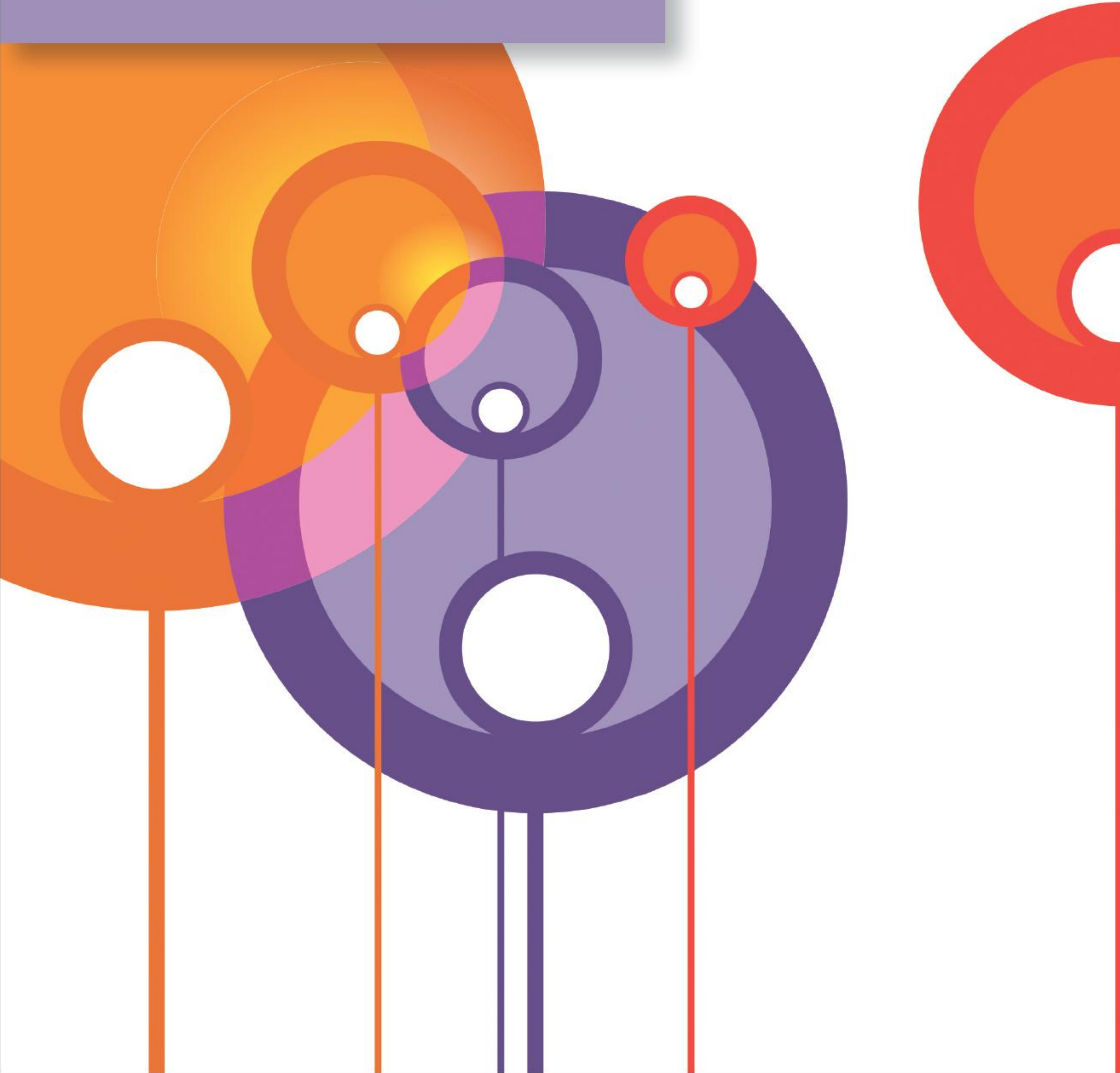

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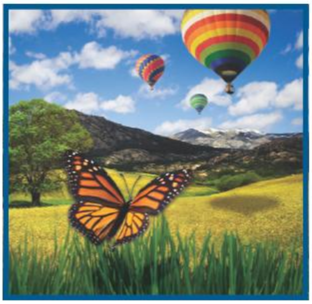

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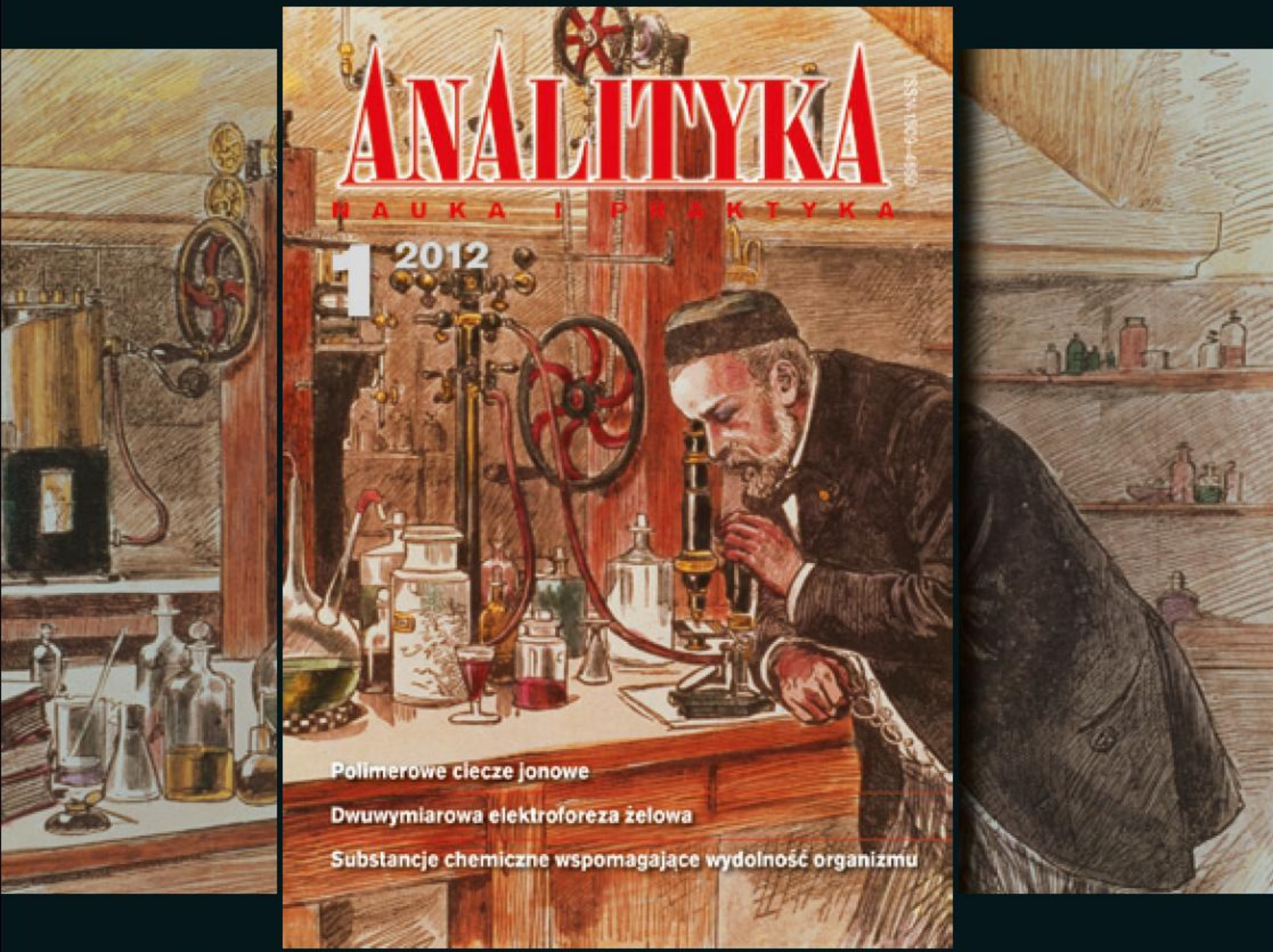
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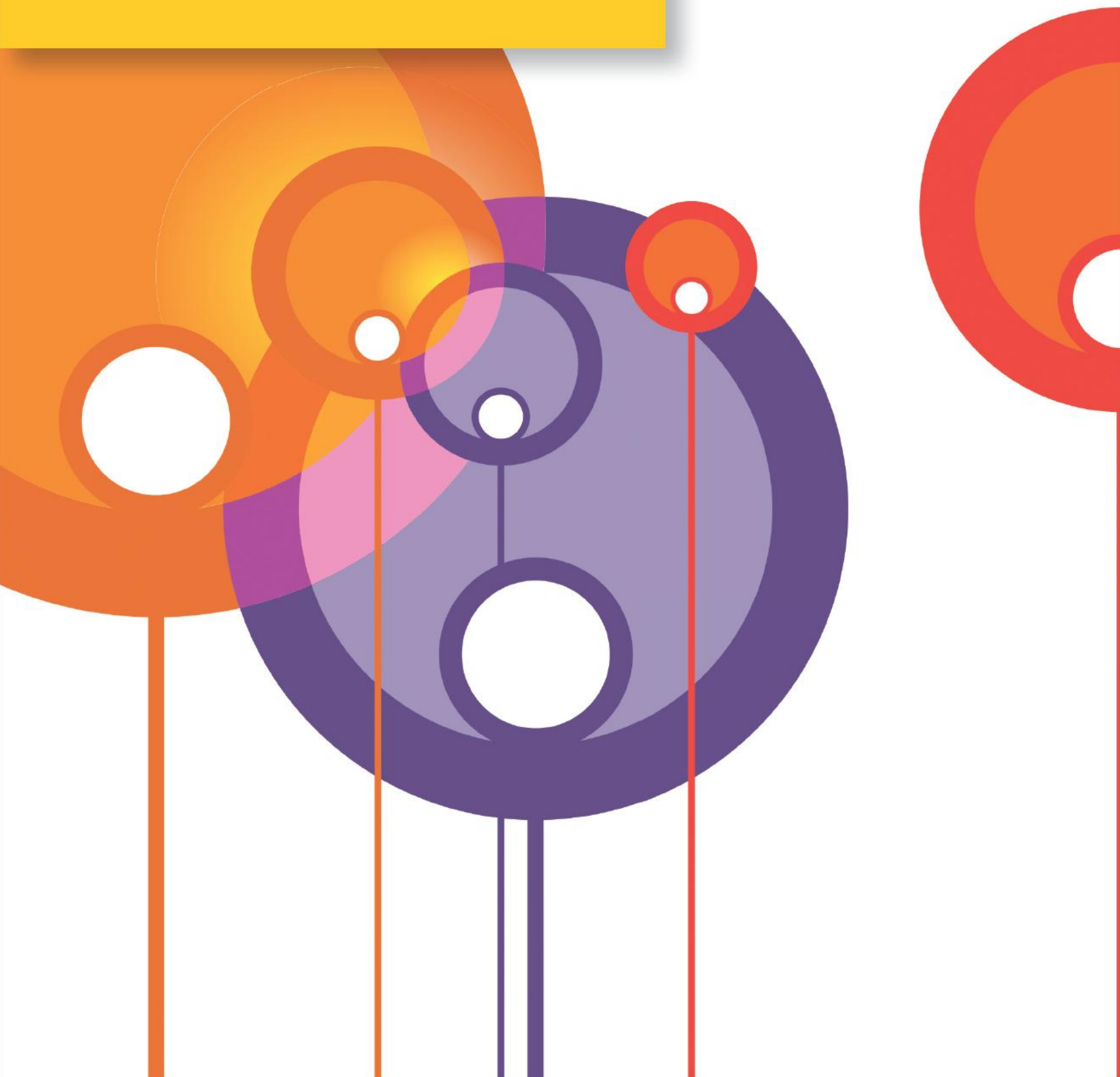

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ANALITYK

Booth No. 5

ANALITYK provides wide range of high-developed instruments for evaluating the environment, foods, pharmaceuticals, industrial processes, and biological samples. Long-term experience and close business relations with our international partners are the fundamentals of our business activity. We offer instruments, equipment, sample preparation systems, standards and consumables for spectroscopy and molecular biology. ANALITYK is the sole distributor of Teledyne Leeman Labs (ICP-OES spectrometers, mercury analyzers), Hitachi High-Technologies (atomic absorption spectrometers), Berghof Products + Instruments (microwave digestion systems, reactors), Inorganic Ventures (inorganic standards), Illumina Inc. (sequencing and arrays), SII Nanotechnology (X-ray fluorescence spectrometers), Titan instrument (atomic fluorescence spectrometers). We provide full support including installation, service and trainings for our whole product portfolio.

ANALITYK,
Surowieckiego 12,
02-785 Warsaw,
Poland

Anton Paar

Booth No. 34

Anton Paar has been developing, producing and distributing high-precision measuring and analytical instrumentation for laboratory and process applications since 1922. Anton Paar’s instruments embody decades of technical know-how. This continuously growing knowledge at the cutting edge of technological developments forms the basis for robust and reliable analytical instruments. Anton Paar’s deep understanding of each analytical method results in precise instruments with excellent performance and reproducibility. Openness towards customers’ requirements and attention to new market trends are the source of new ideas which meet the needs of customers.

Anton Paar has been working in the field of microwave technology for more than three decades. Using high-quality materials and innovative solutions, Anton Paar defines the standard for top level instruments. Multiwave PRO is designed to be a microwave reaction platform system for demanding applications in sample preparation for trace analysis professionals. The broad range of accessories for Multiwave PRO gives customers maximum flexibility in the choice of configurations. The same microwave system can be used for digestion, extraction, evaporation, leaching, oxygen combustion, drying and UV digestion.

Applied Spectra, Inc.

Booth No. 15

Applied Spectra, Inc. (ASI – http://www.appliedspectra.com) is a leading supplier of analytical instruments using laser ablation (LA) technology. Based in Fremont, California USA, ASI manufactures and services laser ablation sample introduction systems for LA-ICP-MS analysis and Laser Induced breakdown Spectroscopy (LIBS) instruments. ASI J200 Series product portfolio includes 213nm & 266nm nanosecond LA systems, Yb direct diode-pumped femtosecond LA system, a complete line of standalone LIBS instruments, and the recently introduced Tandem LA – LIBS instrument that combines Laser Ablation for ICP-MS and LIBS based on one instrument package. The J200 Tandem LA-LIBS instrument provides the analyst with unprecedented capability of simultaneous measurement of bulk and trace elements/isotopes and expands the elemental coverage into all elements in the periodic table including lighter and organic elements, traditionally difficult for ICP-MS. We've assembled a world-class scientific sales, engineering and application support team whose members are truly the experts in LA-based chemical analysis. Our customers don't just buy an instrument, they buy the very best scientific and technical support team.

Berghof Products & Instruments GmbH

Booth No. 4

For over 40 years we have been combining innovative ideas with experience and knowledge to develop market-oriented products. We use to advantage the outstanding properties of modern flouropolymers to develop new instruments. We manufacture sample decomposition and chemical reactor systems for laboratory and industrial applications employing PTFE-materials. Our established product line comprises pressure digestors, microwave digestion systems, acid purification systems, water detection instruments and high pressure chemical reactors. The most important product is the speedwave microwave digestion system, boasting several features which are unique on the market. Apart from its non-contact temperature measurement, it also offers patented, non-contact pressure measurement in all vessels. Hence each vessel is under control at all times, thus significantly raising both the user’s safety and the reproducibility of the digestion processes. It is extremely easy to handle as no sensors need to be connected to the pressure vessel and the vessels comprise only a few elements and are locked and opened manually. All of the products are developed and produced in Germany. Typically they have innovative technologies and at least one unique selling proposition which guarantees the customer an additional benefit; for example they are easier and safer to operate. Global sales, services, and applications support is assured by a network of specifically trained specialist.

Berghof Products + Instruments GmbH, Harretstrasse 1, 72800 Eningen, Germany

Bruker Daltonics GmbH

Booth No. 16&17

Bruker Daltonics provides a broad range of high performance, easy to use Mass Spectrometry (MS) and analytical separation systems. Bruker delivers a series of innovative, fully integrated systems for use in the Pharmaceutical, Life Science, Applied Analytical, and Clinical Research areas, including: Protein Characterization and Quantification, Drug Research and Development, Environmental, Forensics and Doping Analysis, Biomarker Discovery & Tissue Imaging, Metabolomics and Chemical Analysis.

Utilizing a product and technology portfolio which includes MALDI-TOF MS, ESI-TOF and qTOF MS, Ion Trap MS, FTMS, ICP-MS, and GC/MS as well as LC and GC systems, Bruker provides the best solutions for the very latest analytical questions.

CETAC Technologies

Booth No. 25&26

CETAC Technologies, headquartered in Omaha, Nebraska, USA, is a worldwide leader in sample introduction and sample handling equipment for elemental analysis. For 25 years CETAC has been supplying high quality products that help atomic spectrometrists do more with their atomic absorption, inductively coupled plasma atomic emission and inductively coupled plasma mass spectrometry equipment, expanding the scope of possible measurements and pushing the boundaries of productivity. CETAC offers specialist automation products, including autosampling and analysis acceleration devices; advanced sample introduction systems, including high-efficiency and desolvating nebulizers; solid sample introduction devices, including 266, 213 and 193 nm laser ablation systems; and complete mercury analyzer systems based on both atomic absorption and atomic fluorescence. In recent years CETAC has been focusing on innovation to support a continuous stream of new products in these categories and we are proud to be exhibiting new laser ablation and mercury analyzer products at this year's Winter Conference.

For more information, please visit us at booth 25-26,
visit our website at www.cetac.com or e-mail us at sales@cetac.com.

Claisse, Corporation Scientifique

Booth No. 22

Claisse is the world leader in sample preparation by fusion for AA, ICP and Wet Chemistry analysis.

Fusion consists in the mixing an oxidized sample with a lithium borate flux. This mix is heated to around 1000°C. At this temperature, the flux melts and dissolves samples to form a perfectly homogeneous mass. Finally, the molten material is poured, into an acid to be analyzed by AA, ICP or any Wet Chemistry method.

Typical samples include silica, silicates, abrasives, catalysts, ceramics, glass, sulfides, fluorides, bauxites, alumina, inorganic pigments, graphite, coal, fly ash, polymers, synthetic rubbers, lime, alloys, pure metals, cosmetics, pharmaceutical, environmental, mining and geological materials.

Claisse manufactures gas and electric fusion instruments, ultra-pure, fused borate fluxes and high-quality platinum accessories. Claisse offers high-quality products and outstanding services. We are committed to providing 100% satisfaction to our customers. Our professional customer support and friendly approach are our hallmark.

www.claisse.com

CPI International

Booth No. 33

CPI was established by two college roommates in their dorm room in 1986 to provide carbon TOX columns to various laboratories. Shortly thereafter, CPI moved to a garage in order to increase manufacturing capacity. Always the entrepreneurs, the pair recognized other substantial opportunities to offer additional innovative products to the environmental testing laboratories. After years of continuous growth and market expansion, CPI was acquired by a group formed by Unique Investment Corporation, a private equity firm located in Southern California.

CPI is now recognized as a manufacturing leader for quality, service, and innovation in key categories, including specialized products for spectroscopy, chromatography, mass spectrometry, and microbiology. CPI operates in the Analytical Chemistry, Microbiology, and Semiconductor testing markets, is a key manufacturer for many of the world's largest OEM's, and has a customer list that contains several Fortune 500 companies.

ESI New Wave Research Division

Booth No. 13

The global leader in laser-based analytical solutions......

ESI is a leading supplier of innovative, laser-based, analytical solutions for the chemical analysis industry. Notably, we are the global leaders in design and manufacture of laser ablation instrumentation for ICP-MS and ICP-OES. ESI systems enable accurate and precise elemental charecterisation of a wide variety of solid sample types.

Recent innovation to our laser ablation product line include the new NWR193UC and NWRFemtoUC laser ablation units – the most rugged, reliable and compact instruments available. Further examples of innovation include ESI's TruLine™ technology, providing the fastest signal washout (<250 ms) of ANY commercially available ablation cell, and its IVA and XYR beam shaping technology for enhanced application flexibility and analytical performance. ESI look forward to welcoming you at our booth during EWPC.

Elemental Scientific

Booth No. 20&21

Elemental Scientific (ESI) is an inter-nationally recognized leader in developing innovative sample introduction systems for trace metal analysis of a wide variety of samples by ICP-MS, ICP and FAA. Our product line ranges from consumables to fully automated inline dilution systems that increase samplethroughput & improve data quality resulting in reduced per sample costs.

GBC Scientific Equipment Pty Ltd, Australia

Booth No. 7

GBC Scientific Equipment designs, manufactures and markets a range of scientific instruments comprising Atomic Absorption Spectrometers (AAS), UV-Visible Spectrometers (UV-Vis), Inductively Coupled Plasma Optical Emission Spectrometers (ICP-OES), Inductively Coupled Plasma Time of Flight Mass Spectrometers (ICP-TOF-MS), High Performance Liquid Chromatographs (HPLC), X-ray Diffractometers (XRD) and Rheometer (MFR).

For over 30 years GBC has been at the forefront of scientific technological development. The most acclaimed and the award winning product OptiMass 9500 ICP Time of Flight Mass Spectrometer which is a true simultaneous ICP-MS is an example of GBC's technological excellence.

GBC has always placed a strong emphasis on quality in all aspects of our operation, from design and manufacture to the provision of service and support to our customers, and are fully committed to continuous evaluation and improvement in all areas.

For enquiries please contact over e-mail: gbc@gbcsci.com or phone: +61-3-95886666.
Website: www.gbcsci.com

ICP Information Newsletter

Booth No. 32a

ICP Information Newsletter, Inc. is a nonprofit corporation established to foster science education, research, and study in spectroanalytical chemistry. The corporation includes the ICP Information Newsletter, a monthly publication now in its 38th year with international distribution that gathers conference and published information related to plasma spectrochemistry; the Winter Conference on Plasma Spectrochemistry, a biennial meeting with international participation featuring state-of-the-art research developments in plasma spectrochemistry, and the University Research Institute for Analytical Chemistry.

The 2014 Winter Conference will be held Monday, January 6 through Saturday, January 11, 2014, on Amelia Island, Florida (www.ameliaisland.com) at the Omni Amelia Island Plantation Resort (http://www.omnihotels.com/FindAHotel/AmeliaIsland.aspx). The 2014 conference, eighteenth in the series, highlights plasma spectrochemical analysis fundamentals and developments with inductively coupled plasma (ICP), microwave plasma, glow discharge, and laser sources. Continuing education short courses and manufacturers' seminars will be offered Friday through Monday, January 3-6. Spectroscopic instrumentation and accessories will be shown during a three-day exhibition, and workshops on New Plasma Instrumentation, Clinical ICP-MS, and Elemental Speciation methodology will be presented.

Visit http://icpinformation.org or contact wc2014@chem.umass.edu for subscription and conference details.

Inorganic Ventures

Booth No. 3

Inorganic Ventures is a chemical Certified Reference Material (CRM) producer that specializes in preparing custom inorganic standard solutions designed for a variety of applications. These include ICP, ICP-MS, Ion Chromatography, and Atomic Absorption. Additionally, they produce a wide selection of QC water standards, as well as reference materials for wet chemical applications.

A family-owned and operated company, Inorganic Ventures has been turning out a higher class of standards for nearly a quarter of a century. A rigorous code of quality controls governs every step of CRM preparation, from conception to certification. Their detailed four-page Certificate of Analysis accompanies all single and multi-element blends. This certificate includes assigned values obtained using two independent methods, traceability to specific NIST SRMs and lot numbers, and elemental uncertainties calculated using both random and systematic errors.

For almost a decade, Inorganic Ventures has been fully registered to ISO 9001, ISO 17025, and ISO Guide 34. These key international accreditations have helped Inorganic Ventures to excel in both the caliber of their products and the quality of their customer service.

In 2009, Inorganic Ventures relocated its USA corporate facilities to Christiansburg, VA, where a state-of-the-art "green" manufacturing center was constructed. The European office and distribution center is located in Madrid, Spain.

LECO Polska Sp. z o.o.

Booth No. 29

A Global Leader in High-Quality Analytical Instrumentation, Mass Spectrometers, Metallography/Optical Equipment, and Consumables. Over the past 75 years, customers around the world have trusted LECO to provide analytical solutions for a variety of applications and markets, including mined materials and metals, environment and agriculture, energy and fuels, foods and beverages, and life sciences (pharmaceuticals, metabolomics, forensic science/toxicology, and flavor/fragrance analysis). With a global reputation for rapid, accurate analysis in iron, steel, alloys, refractory metals, and ores, LECO instruments have become the brand leader for these markets. Instrumentation includes the CS744 and CS844 Carbon Sulfur, ONH836 Oxygen/Nitrogen/Hydrogen, RC612 Carbon and Water, DH603 Hydrogen, and GDS500A and GDS850A Glow Discharge Atomic Emission Spectrometers. A number of sample preparation and microstructural analysis solutionsfor the metallography industry are also available, such as the MSX-Series Sectioning Machines, Micro- and Macroindentation Hardness Testing Systems, Automatic and Rockwell-type Hardness Testing Systems, and the IA44 Image Analysis/Management System.

Please don’t hesitate to visit us on Plasma Conference or at www.leco.com.pl
(soon pl.leco-europe.com)
LECO Polska Sp. z o.o., ul. Czarna 4, 43-100 Tychy,
Tel.+48 322000760, Fax.+48 322000536

Milestone

Booth No. 30

Milestone has been active since 1988 in the field of advanced microwave sample preparation. With over 15000 instruments installed worldwide covering large and small research institutions, as well as universities and industrial laboratories, we are the acknowledged industry leader in microwave technology. Milestone vision is to help chemists by providing the most technologically advanced microwave instrumentation for research and quality control. By listening to our customers, we have established a history of developing unique solutions in analytical laboratories around the world. Our products offer a wide range of applications, such as microwave acid digestion, acid purification, microwave solvent extraction and ashing, mercury determination, and microwave assisted synthesis. Furthermore, we truly offer our customers the highest level of application support, building up over the years a relationship based on trust and commitment. Milestone is operative all over the world through a network of very reliable partners; USA headquarter is located in Shelton, Connecticut. The presence of Milestone in Japan is assured by Milestone General KK, near Tokyo, and in Korea by Milestone Korea, located in Seoul. All these branches have sales and technical assistance departments, as well as applications laboratories supporting our customers. Besides this, Milestone is present through over 70 exclusive distributors, who guarantee everywhere high standards of quality and assistance.

Nu Instruments

Booth No. 14

Nu Instruments is a British high technology manufacturing company specialising in the design and manufacture of high precision mass spectrometers. All our products are both technically advanced and proven to be very reliable. Our instruments are used by scientists in Material Science, Geo Chemistry and Nuclear Industry and have been installed in Universities and Research Laboratories around the world. Our dedicated R&D team of skilled scientists, engineers and application chemist are committed to innovation and enhancement of our products to meet our customer’s needs.

We take pride in providing our customers a personal service, supporting them at every stage of the specification, procurement, test and installation process and beyond.

The Nu Instruments range of high performance range of products including MultiCollector ICP-MS, High Resolution ICP-MS, Glow Discharge MS, Stable Isotope MS and Noble Gas MS.

Our market leading Plasma Source products are The Nu Astrum – Glow Discharge MS, The Nu Attom High Resolution ICP-MS, The Nu Plasma II Multi Collector ICP-MS, the Nu Plasma 1700 Multi Collector ICP-MS MS and Noble Gas MS.

PerkinElmer

Booth No. 10&11

PerkinElmer, Inc. is a global leader focused on improving the health and safety of people and their environment. Engaged in a proactive fight against illness, including contamination and other threats to our well-being, PerkinElmer conceives and delivers scientific solutions to meet society's ever-changing needs. From critical therapeutic and disease research and prenatal screening to environmental testing and industrial monitoring, we are actively engaged in improving health and advancing quality of life all around the world.

ENVIRONMENTAL HEALTH – PerkinElmer is dedicated to the quality and sustainability of the environment. With our analytical instrumentation and leading laboratory services, we focus on improving the integrity and safety of the world we live in.

Our Environmental Health business develops analytical instrumentation and laboratory services which include: Atomic Absorption, ICP, ICP-MS, SP-ICP-MS, GC, GC/MS, Headspace Sampling, Thermal Desorption, Liquid Chromatography, UHPLC, LC/MS, Infrared (FTIR & NIR), UV/Vis & UV/Vis/NIR, Raman, Thermal Analysis, Elemental Analysis, Informatics, Consumables, Trainings and OneSource Services.

PerkinElmer has more than 50 years of experience with innovation in inorganic analysis. We are ready to help you select the right instrument and the right options for your application. Plus, with factory-trained service and support experts in 150 countries, we will be at your side to ensure you get the great results you demand.

Postnova Analytics

Booth No. 37

Postnova Analytics are the experts in Field-Flow Fractionation (FFF) and Light Scattering technologies – the modern alternative to chromatography. FFF can separate and fractionate Nanoparticles (1nm into the µm range) and is ideal to couple with ICP-MS to achieve size-based elemental distributions. Found in 1997 by Dr. Thorsten Klein in Munich, Germany, the company introduced the first commercial Asymmetrical Flow FFF (AF4) instrument. This system brought a new level of automation and separation performance to the market. In 2001 Postnova Analytics acquired FFFractionation – founded by Prof. Giddings the inventor of FFF, a company based in Salt Lake City, Utah that had been a pioneer for the commercialization of FFF technology, and Postnova Analytics USA was formed. The new company became the sole provider of all variants of Field-Flow Fractionation.

Postnova Analytics continues to innovate, and now offers 'the FFF-Platform' a broad range of Field-Flow Fractionation and Light Scattering solutions, which are ideally suited for gentle, high resolution and matrix-free separations of large molecules and particles, which traditional chromatographic techniques cannot perform. FFF coupled to Multi-Angle Light Scattering (MALS) is the modern alternative to liquid chromatography (LC) and size exclusion SEC techniques, especially when it comes to separation, characterization and fractionation of nanoparticles, proteins, antibodies, biomacromolecules, polymers, adhesives, elastomers, rubbers and other large molecules or particles.

Pulse Instrumentation

Booth No. 35

Pulse Instrumentation is the leading manufacturer of flared tubing, supplying a comprehensive range of standard and bespoke tubing. We have developed specia-list know-how and expertise to flare PVC, silicone, santoprene, viton/acidflex and solvaflex tubing to meet your exact requirements and specification. Flared tubing provides a simple solution to the problems encountered when inserting sample tubes into the peristaltic pump tubing of ICP-MS. It is particularly effective where the peristaltic pump tubing has a small internal diameter (ID) and so is difficult to work with. For example, pump tubing used for the internal standard usually has an ID of only 0.2 to 0.4mm and is incompatible with the sample tubing OD of 1.3mm.The flared end of this pump tubing allows the larger sample capillary tubing to be easily inserted. Pulse Instrumentation can design any pump tubing with flared ends to meet your specific need; this includes 2-shoulder and 3-shoulder with a choice of lengths, diameters, shoulder pitches and material specifications. We can manufacture pump tubing to your specifications. We specialize in custom lengths, tube flaring sizes and tubing harness assembly. Pulse Instrumentation provides a one stop source for standard and flared peristaltic pump tubing and carries an extensive stock of tubing products. We pride ourselves on our customer service and provide a fully comprehensive range of peristaltic pump tubing products.

www.flaredtubing.com
www.pulseinstrumentation.com

Royal Society of Chemistry Journal of Analytical Atomic Spectroscopy

Booth No. 31

The Royal Society of Chemistry (RSC) is the largest organisation in Europe for advancing the chemical sciences, supported by 45,000 members worldwide and an internationally acclaimed publishing business. The Analytical Division of the RSC advances analytical chemistry and science by providing a forum for analytical chemists and scientists to exchange information and ideas. It organises meetings and via, the Analytical Chemistry Trust Fund, finances studentships, Schools Analyst competitions, awards, lectureships and VSO students. RSC Publishing is one of the largest and most dynamic not-for-profit publishers of chemical science information in the world. Our analytical portfolio of journals features wide coverage across all areas of analytical science, from fundamental developments in Analyst, early applied demonstrations of new analytical methods in Analytical Methods and the application of analytical techniques to probe the role of metals in biological systems in Metallomics. Journal of Analytical Atomic Spectroscopy (JAAS) publishes innovative research on the fundamental theory, instrumentation, practice and application of spectrometric techniques to elemental and isotopic analysis. JAAS is publishing a themed issue from the 2013 European Winter Conference and welcomes submissions up to 1st April 2013. For more information, please visit our website or drop by the stand to meet JAAS Editor, May Copsey

www.rsc.org/jaas.

SCP SCIENCE

Booth No. 23

SCP SCIENCE is a privately owned manufacturer and distributor of analytical equipment, supplies, reagents and certified reference material for the inorganic analytical laboratories market especially involved in Atomic Spectroscopy: AAS, ICP-AES, ICP-MS, and XRF.

SCP SCIENCE proposes: Sample digestion and distillation DigiPREP equipment as well as microwave digestion NOVAWAVE systems and their respective consumables (DigiTUBES and Racks), Automatic Sample preparation systems EasyPREP and AutoCHEM, Inorganic standards (PlasmaCAL) or metallo-organic standards (CONOSTAN) as well as certified reference material (EnviroMAT), SCP SCIENCE offers single, multi-element and custom blends for both PlasmaCAL and CONOSTAN, Reagents, acids and ultra-pure acids, Glassware, nebulization systems, sample introduction systems, for elemental analysis (ICP-OES and ICP-MS), consumables (pomp tubing, etc.) SPE cartridges (DigiSEP), XRF consumables (sample cells, thin film windows, standards, fusion fluxes) and Rotrod consumables (electrodes, rods, etc.) or AAS.

SCP SCIENCE production process is certified ISO 9001:2000 and ISO 17025. Our standards are manufactured following the ISO 17025 and ISO Guide 34 rules.

Lately, CONOSTAN, the world leader in metallo-organic and sulfur and chlorine standards in oil has been acquired by SCP SCIENCE, giving the company a worldwide leading position in Standards manufacturing.

Shimadzu

Booth No. 18&19

Shimadzu is one of the worldwide leading manufacturers of analytical instrumentation. Its equipment and systems are used as essential tools for quality control of consumer goods and articles of daily use, in health care as well as in all areas of environmental and consumer protection. For more than 135 years, Shimadzu has been at the service of science ensuring precise, reliable diagnoses and analyses in medicine, chemistry and pharmacy. In 1934, Shimadzu developed Japan’s first spectrograph. The first UV-VIS spectrophotometer was presented in 1952. These events were followed by numerous other world premières, such as capillary electrophoresis on a single chip in the year 2000. In 2002 the Shimadzu engineer Koichi Tanaka was awarded the Nobel Prize for Chemistry. Spectroscopy, chromatography, environmental analysis, balances, biotechnology and material testing make up a homogeneous yet versatile offering. Customers may select from a wide range in order to obtain the solution which has been tailored to their individual needs. In this way, Shimadzu has become the only supplier of the whole range of analytical instruments whose product offering has grown constantly. At the same time, Shimadzu is the market- or technological leader in almost all areas. As a Global Player, Shimadzu operates production facilities and distribution centers in 76 countries. Shimadzu’s success is based on more than 10,000 employees worldwide.

SPECTRO Analytical Instruments GmbH

Booth No. 36

SPECTRO is one of the worldwide leading suppliers of analytical instruments for optical emission and X-ray fluorescence spectrometry. As a member of the AMETEK Materials Analysis Division, SPECTRO manufactures advanced instruments, develops the best solutions for strongly varying applications and provides exemplary customer service. SPECTRO's products are exemplified by unique technical capabilities that deliver measureable benefits to the customer. From its foundation in 1979 until today, more than 30,000 analytical instruments have been delivered to customers around the world. Product range:

ICP-OES spectrometers – for the rapid analysis of elements in a variety of matrices including aqueous, organic, geological, metallurgical and slurries, ICP-MS spectrometers – for the fully simultaneous measurement of the complete, inorganically relevant, mass range, Stationary metal analyzers – for the elemental analysis of all kinds of metals in process control, Portable and mobile on-site metal analyzers – for fast and reliable identification (PMI), sorting and analysis of metals, XRF spectrometers – for the elemental analysis of solids, powders and liquids, XRF handheld analyzer – for metal analysis and sorting, compliance screening, environmental testing and mining applications. On-line Systems – for the fully automatic analysis of liquid streams, powders and coatings.

Boschstr. 10, 47533 Kleve, Germany

www.spectro.com

Spetec GmbH

Booth No. 24

Spetec GmbH is your partner of choice for Pumps, Stand allone versions and OEM versions. Unique to Spetec peristaltic pumps is the fact that there are no series. Every pump consists of a set of standard parts like the roller head, the pressure brackets and tube holders. The color of these parts can be selected to match the surrounding equipment. The pump may be powered by different types of motors, such as AC, DC or multiphase (stepper) motors.

Spetec engineering also offers clean room products and products for the modern laboratory, such as pump tubings made to meet the most stringent specifications. In partnership with you, the Spetec GmbH also delivers custom products exactly to your specifications. Spetec GmbH will also present a very brand new product – the Symax Syringe pump.

Spex CertiPrep

Booth No. 6

Spex CertiPrep provides superior certified reference materials and sample preparation equipment for analytical spectroscopy. Our SamplePrep equipment is used to prepare samples for a wide range of analytical technologies including XRF, AA and ICP. Much of our sample preparation equipment is also used for cuttingedge research in pharmaceuticals, superconductors, polymers and genetics. Our products have become the industry standard for reliability and durability in the laboratory.

Today, SPEX SamplePrep continues to stay above the fold through researching of new and innovative applications for our products. We are also taking strives to protect the environment by reducing the use of hazardous materials in our products. Our expertise and products can help you achieve accurate, consistent results by ensuring reproducible samples, analysis after analysis. With over five decades of experience, let us help you stay on the cutting edge by demonstrating the SamplePrep Advantage.

From product demonstrations in our labs to unparalleled support, we are here to help you every step of the way. When you are as passionate about science as we are, breaking up is never as hard as it seems…

Springer
Analytical and Bioanalytical Chemistry

Booth No. 32

Analytical and Bioanalytical Chemistry (www.springer.com/abc) is a truly international journal with a mission to publish excellent research papers from all areas of analytical and bioanalytical science. The journal is coowned by eight prestigious European chemical societies and its latest Impact Factor for 2011 is 3.778. The journal is published by Springer, a leading global scientific publisher, providing researchers in academia, scientific institutions and corporate R & D departments with quality content via innovative information products and services. Roughly 2,000 journals and more than 7,000 new books are published by Springer each year, and the group is home to the world’s largest STM eBook collection, as well as the most comprehensive portfolio of open access journals.

Teledyne Leeman Labs USA

Booth No. 2

From its founding in 1981, Teledyne Leeman Labs has combined the best technology with superior customer service to meet the changing needs of the analytical chemistry laboratory. Today, Teledyne Leeman Labs is a leader in automated products for elemental analysis, servicing laboratories in diverse fields. Ongoing research and development on analytical instrumentation helps laboratories like yours meet the increasing demands for elemental analysis. Our diverse product lines include; Inductively Coupled Plasma AES, simultaneous with State-of-the-Art Array Detector Technology brings together high-speed array detection and high resolution Echelle spectrometry; DC Arc is simultaneous, high dispersion ICP spectrometer, for direct analysis of traces in conductive and nonconductive materials, and Automated Mercury Analyzers for analysis of trace Hg in solid and liquid samples with detection limits from 0.02ppt having specially designed early warning system to protect against contamination by samples with high mercury levels. Our family of products is geared toward a variety of applications such as: Academic/Research, Central Labs, Chemical/Pharmaceutical, Clinical, Commercial Testing, Drinking Water/Municipal, Energy/Utilities, Environmental Discovery/Enforcement/Redemption, Foods/Agriculture, Metal Production, Wear Metal Oil Analysis, Petroleum/Petrochemical, Remote Testing, and Research/Development.

Teledyne Leeman Labs,
6 Wentworth Dr. Hudson NH 03051 USA

Thermo Scientific (part of Thermo Fisher Scientific)

Booth No. 27&28

Thermo Fisher Scientific Inc. (NYSE: TMO) is the world leader in serving science. Our mission is to enable our customers to make the world healthier, cleaner and safer. With revenues of $12 billion, we have more than 39,000 employees worldwide and serve customers within pharmaceutical and biotech companies, hospitals and clinical diagnostic labs, universities, research institutions and government agencies, as well as in environmental, food safety and process control industries.

We create value for our customers through three premier brands, Thermo Scientific, Fisher Scientific and Unity™ Lab Services, which offer a unique combination of innovative technologies, convenient purchasing options and a single solution for laboratory operations management. Our products and services help accelerate the pace of scientific discovery, ranging from complex research to routine testing to field applications.

Visit www.thermofisher.com for more information on our extensive range of products and services.

UT2A – Training & Consulting - Analyses

Booth No. 1

UT2A is a spin-off of the University of Pau and the Adour Countries (UPPA) and is born from researchers' willing to share their know-how in the domains of inorganic analysis and speciation. UT2A is both a technology centre specialized in the determination of trace elements and their chemical forms in samples from different areas such as environment, food, biomedical or pharmacopoeia, and a training centre.

Analytical determinations can be proposed as analytical services if the method is well defined and validated or as short research studies when an analytical development has to be performed. One of our specificity is to propose speciation analysis to industrials allowing them to better understand their manufacturing process. Since recently, UT2A also proposes analytical services for physico-chemical characterization of nanoparticles.

Analytical instrumentation available at UT2A is ICP-AES, ICP-MS and coupled techniques (GC-ICP MS, HPLC-ICP MS, Capillary electrophoresis-ICP MS and A4F-MALLS-ICP MS for nanoparticles characterization).

Hardly with more than 10 years of experiment in the organization of training courses, and accompanied by more and more numerous experts in other analytical sciences than those who constitute our heart of business, we are also at your disposal to help you develop the field of your analytical activities.

European Winter Conference
on Plasma Spectrochemistry
10-15 February 2013, Krakow, Poland

list of authors

European Winter Conference
on Plasma Spectrochemistry
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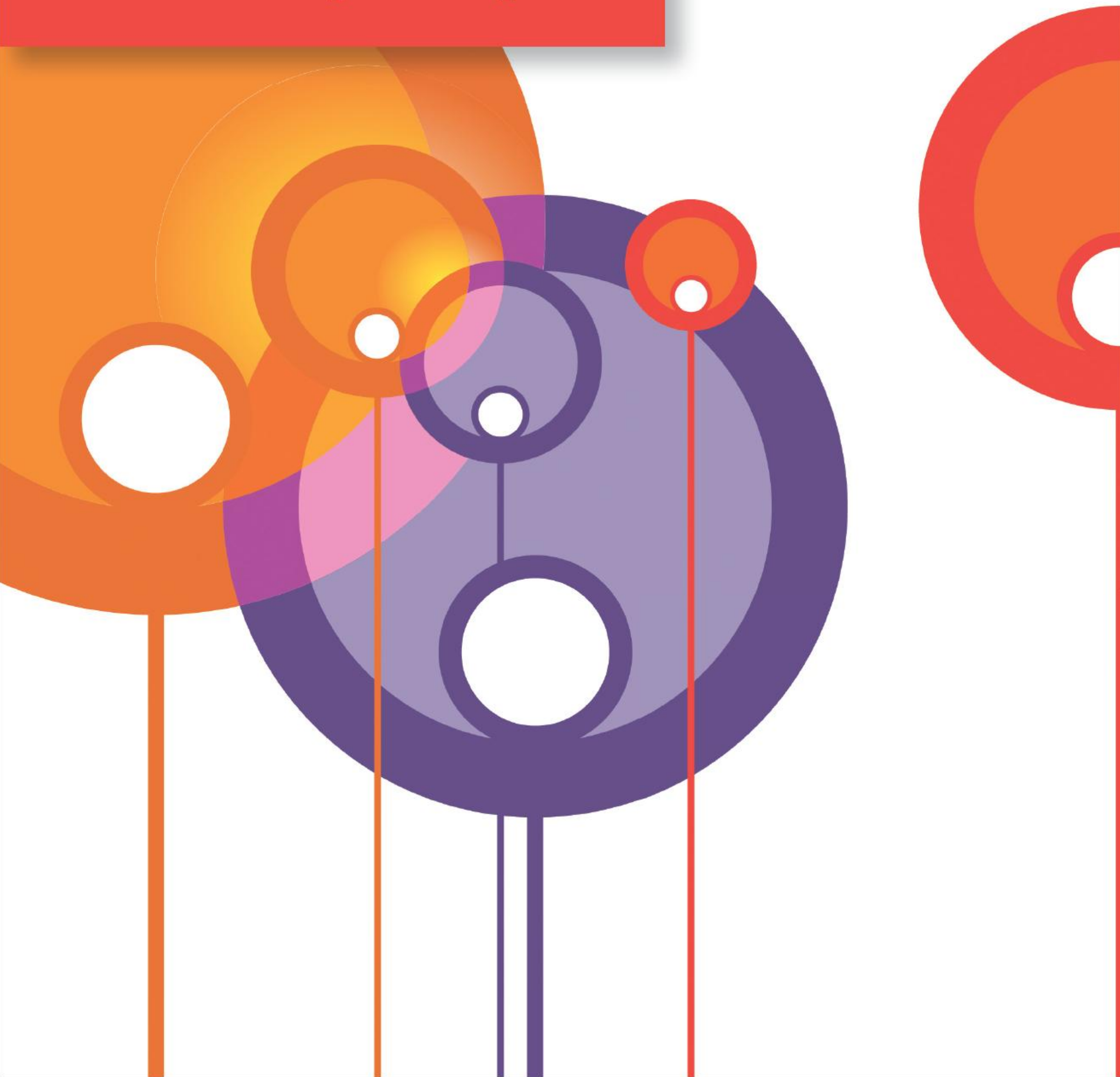
list of participants



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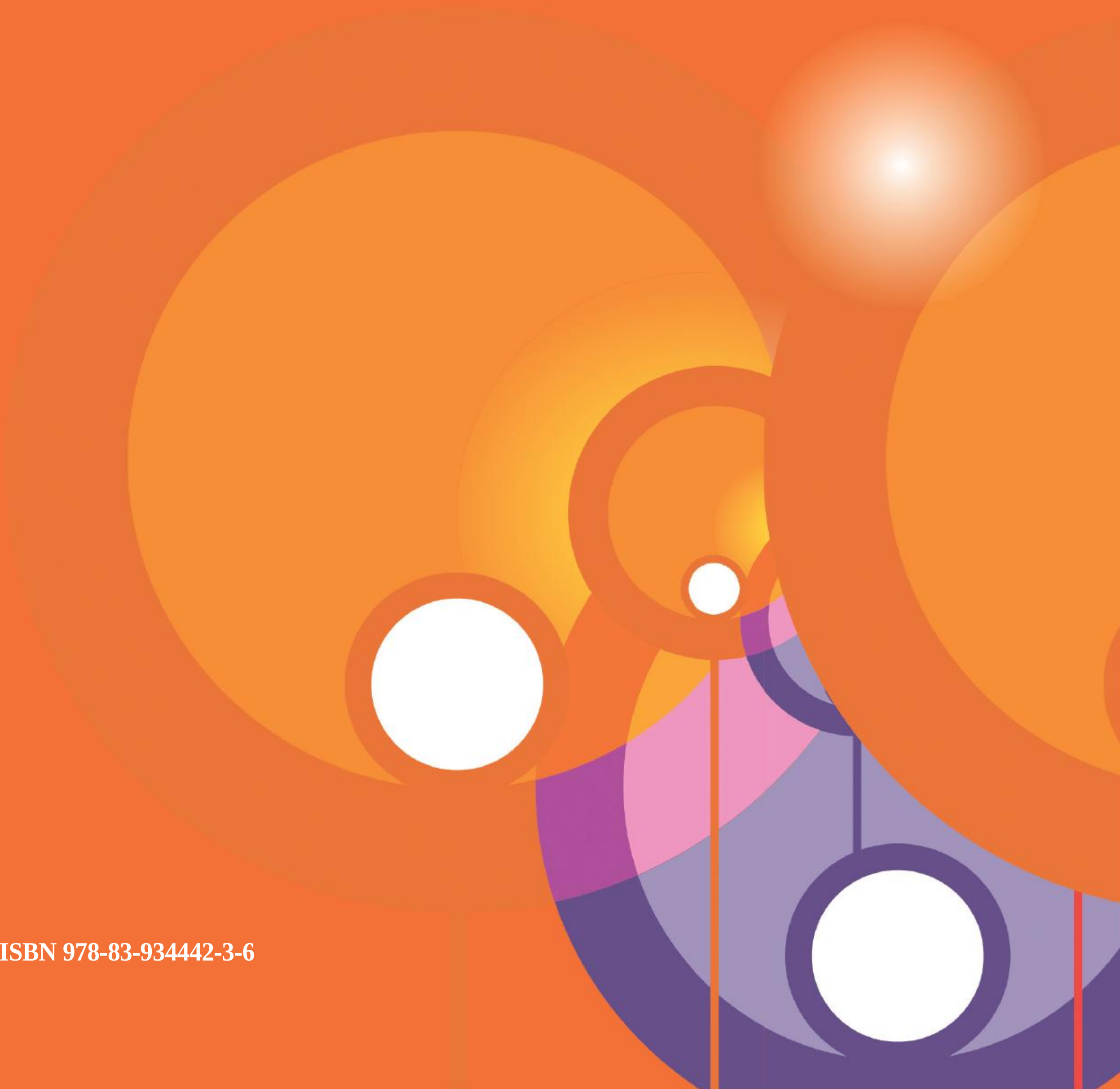

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