Final program

TraceSpec 2009

12th Workshop on Progress in Analytical Methodologies for Trace Metal Speciation

September 15-18, 2009
Mainz, Germany

Table of contents

Organization of TraceSpec 2009

Organizers

JoGu – University of Mainz,
Institute of Inorganic and
Analytical Chemistry

EVISA
The European Virtual Institute for
Speciation Analysis

IAEAC
The International Association of
Environmental Analytical Chemistry

International Scientific Committee

T. Hoffmann (Chair), University of Mainz, Germany
M. Sperling (Co-Chair), EVISA, Germany
M. Filella (Co-Chair), University of Geneva, Switzerland
E. Rosenberg, Technical University of Vienna, Austria
U. Karst, University of Münster, Germany
D. Klockow, IAEAC, Germany
N. Bings, University of Mainz, Germany
R. Lobinski, University of Pau, France
J. Bettmer, University of Oviedo, Spain
J. Feldmann, University of Aberdeen, United Kingdom
K. Francesconi, Graz University, Austria

Organizing Committee

N. Bings, University of Mainz, Germany
M. Frei, IAEAC, Switzerland
P. Hebenstreit University of Mainz, Germany
T. Hoffmann (Chair), University of Mainz, Germany
M. Sperling (Co-Chair), University of Münster, Germany

Sponsors

Our particular thanks go to the sponsors of the conference, who have helped to keep registration affordable.

Thermo Scientific

EVISA

IAEAC

Welcome to TraceSpec 2009 and welcome to Mainz!

On behalf of the Scientific Committee of the TraceSpec 2009 and the supporting organizations, the European Virtual Institute for Speciation Analysis (EVISA), the University of Mainz and the International Association of Environmental Analytical Chemistry (IAEAC), it is an honor and pleasure to warmly welcome you to the City of Mainz. The workshop will provide an international forum to share knowledge and to exchange ideas with colleagues from all over the world.

The TraceSpec is one of the very few conferences that is completely devoted to speciation analysis unifying research groups, scientists, interested users, legislators, industrial partners and other stakeholders from different domains. It is the major objective of the workshop to highlight the value of the enhanced information provided by speciation analysis and to demonstrate and discuss how this information can be used to tackle real-world challenges related to chemical species.

Speciation analysis is a highly interdisciplinary topic and this will be reflected by six plenary lectures, 35 contributed lectures and over 50 posters. Technologically-oriented presentations will cover the latest developments with respect to analytical separations coupled to selective spectroscopic and mass spectrometric detectors as well as electrochemical developments, just to mention a few. Applications include the fields of food analysis, proteomics, metallomics, metabolomics, characterization of materials and industrial processes. For the workshop in Mainz 2009 certainly environmental analysis will be a special focus. The technical program will be complemented by an exhibition of instrumentation by the most important manufacturers in the field.

A conference, which is focused on a specific topic like speciation analysis needs to promote interaction between the participants. Therefore, we have planned ample time for discussions after the oral presentations as well as in the poster and exhibition hall. To allow intense discussions beyond the scientific program several social events will be organized, such as a welcome reception, a city tour followed by a barbecue evening and a conference dinner.

As young scientists will be the future of our discipline, we particularly try to stimulate their participation by low conference fees for students, to recognize their important contributions by several poster prizes including the well-renowned Roland W. Frei award and to incorporate several PhD students into the lecture program.

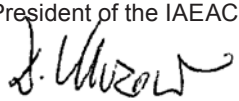
Financiation of such a conference is an important issue. Therefore, our particular thanks go to the sponsors and the exhibitors of the conference, who helped to keep registration affordable.

Let us all look forward to an event in the historically so important City of Mainz!

Thorsten Hoffmann
Chairman

Michael Sperling
Director of EVISA

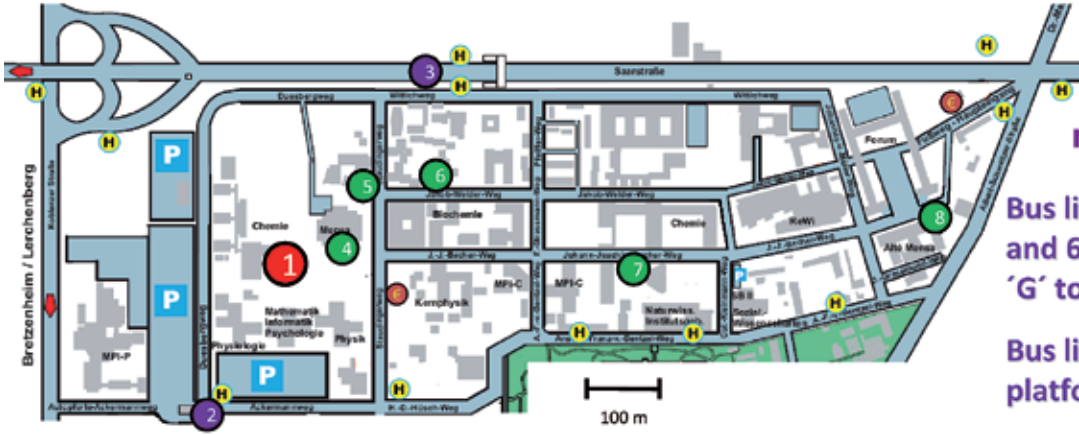
Dieter Klockow
President of the IAEAC



TraceSpec 2009

Campus Plan

JOHANNES GUTENBERG UNIVERSITÄT MAINZ



main station

Bus line 9, 54, 55, 58 and 68 at bus platform ´G´ to reach 3

Bus line 69 at bus platform ´F´ to 2

1 Conference Site

recommended Bus Stops

2 Duesbergweg

3 Friedrich-von-Pfeiffer-Weg

€ Cash dispenser

food & refreshment

4 mensaria (meals & snacks)

5 Campus Pizzeria

6 De De´s Campus Döner

7 Diwan (kebab shop)

8 Taberna academica (restaurant)

General Information

Conference Venue
Johannes Gutenberg University
New lecture hall of the Chemistry Department
Duesbergweg 10-14
55128 Mainz, Germany

How to Reach the Conference Venue?
The conference takes places in the lecture hall of the New Chemistry building (Neubau Chemie) at the Johannes Gutenberg University. A large parking lot (parking is free) is located close to the conference venue, when entering the university at Ackermannweg next to the Max Planck Institute for Polymer Research (MPI-P). The conference can be reached by the following bus lines:

Line **69** (direction "Universität/Fachhochschule") » get off at bus stop "Duesbergweg"
Line **9** (direction "Isaak-Fulda-Allee/Aareon") » get off at bus stop "F.-v.-Pfeiffer-Weg"
Line **58** (direction "Rathausplatz Wackernheim") » get off at bus stop "F.-v.-Pfeiffer-Weg"
Line **68** (direction "Klein-Winternheim") » get off at bus stop "F.-v.-Pfeiffer-Weg"
Line **55** (direction "Th.-Heuss-Str. Wackernheim") » get off at bus stop "F.-v.-Pfeiffer-Weg"
Line **54** (direction "Brucknerstraße Lerchenberg") » get off at bus stop "F.-v.-Pfeiffer-Weg" (Friedrich-von-Pfeiffer-Weg, Bausparkasse Mainz)
Lines **6/6A** (direction Mz.-Marienborn) » get off at bus stop "Universität"
Line **65** (direction Hartenberg) » get off at bus stop "Universität"
Line **64** (direction Budenheim) » get off at bus stop "Universität"

The recommended bus stop is **"Duesbergweg"** (3 minutes walk to the conference site) or the Bus stop **"F.-v.-Pfeiffer-Weg"** (8 minutes walking to the conference site). Bus stop **"Universität"** is located in a 15 minutes walking distance to the conference site. Bus tickets can be bought at the bus or at the ticket machine (ticket machines are only available at selected bus stops; ticket machine display can be switched to English). Please make sure to have cash money (preferably coins) with you. Payment by credit card or EC (Maestro) card is not possible.

Conference Office / Registration Desk
The conference office / registration desk is located in the entrance hall of the Chemistry lecture hall. Opening hours are:

Tuesday,	September 15, 2009	17:00 - 21:00
Wednesday,	September 16, 2009	8:00 - 18:00
Thursday,	September 17, 2009	8:00 - 18:00
Friday,	September 18, 2009	8:00 - 14:00

Cloakroom
A cloakroom is located in the Chemistry lecture hall. Wardrobe and luggage can be deposited there during the opening hours of the conference office.

Name Badges
TraceSpec 2009 participants are kindly requested to wear their name badges throughout the conference. In case that you should have lost your badge, a new one is available at the registration desk.

Smoking
Within the lecture hall – as a for all university buildings – smoking is prohibited. It is kindly requested to smoke outside the building.

Lectures
The single-stream lecture program will be held in the lecture hall 3 in the New Chemistry lecture hall building. Please follow the signs in the conference building. Morning speakers are kindly requested to provide their presentation on USB by the end of the day before their lecture will be given. Afternoon speakers are kindly requested to provide their presentation on USB by the beginning of the lunch break. TraceSpec 2009 staff taking care of your presentation will be available in the auditorium.

Poster Sessions
Poster sessions take place at the ground floor of the lecture hall building. All posters can be presented over the whole conference duration. Poster group I shall be mounted on Tuesday evening, but at the latest until Wednesday, September 16, 2009 at 8:30. Poster group I authors are kindly requested to be present at their posters on Wednesday, September 16, 2009 from 15:40 to 16:40. Poster group II can be mounted already on Tuesday, however, latest until Thursday, September 17, 2009 at 8:30. Poster group II authors are kindly requested to be present at their posters on Thursday, September 17, 2009 from 15:40 - 16:40. All posters should be removed on Friday, September 18, 2009 before the end of the conference.

Exhibition
TraceSpec 2009 features an exhibition of instrumentation and equipment, which provides an excellent opportunity to present the latest developments in the field of speciation analysis and to bring together customers and manufacturers. Exhibitor booths of the following companies are located in the entrance hall: Agilent Technologies, AHF analysentechnik AG, Gerstel, MLS - Milestone, PerkinElmer, PS Analytical Ltd., Shimadzu, Thermo Scientific. Exhibition is open on Wednesday and Thursday from 9:00 to 17:00, and on Friday from 9:00 to 13:00.

Coffee and Lunch Breaks
Coffee, tea and refreshments will be served next to the exhibition in the entrance hall throughout the conference. Coffee is included in the registration fee.

Internet
For the convenience of the participants, WLAN will be provided free of charge during the conference all over the campus of the university. The installation will require that participants use their own notebooks (with WLAN capability) on which they will need administrator rights for Windows XP or Windows Vista. Login, password and a short description of the installation procedure will be provided by the conference team on request.

Bus Connections from Mainz Central Station to Frankfurt-Hahn Airport (HHN)
Important notice! There are two airports which are named Frankfurt: Frankfurt-Hahn-Airport (HHN) and Frankfurt Main International Airport (FRA).

Buses regularly ride from Mainz central station to HHN airport. Buses to HHN take approx. 70 min. Shuttle busses depart from the bus stop Mainz Central Station (scheduled transfer time: 70 min). For departure times and further information please refer to the travel information of Deutsche Bahn at Mainz Central Station or in the internet: ***www.reiseauskunft.bahn.de***

Train Connections from Mainz Central Station to Frankfurt Main International Airport (FRA)
The fastest way to go to Frankfurt Main International Airport (FRA) is by train. All regional trains and S-trains (S8) to Frankfurt city stop at FRA. A ride to Frankfurt Main International Airport by train takes approximately 20 to 30 min. For departure times and further information please refer to the travel information of Deutsche Bahn at Mainz Central Station or in the internet: ***www.reiseauskunft.bahn.de***

Cash Dispensers
Cash dispensers next to the conference venue are
on campus (see also campus plan):
- Sparkasse Mainz » walking from Albert-Schweitzer-Straße to University Forum
- Mainzer Volksbank » at the corner of Johann-Joachim-Becher-Weg and Staudinger Weg

Main train station:
- Two EC cashpoints in the main station

Taxi
To call a taxi, dial: +49 6131 910 910 (“Taxi Mainz”). In case that you should need support, TraceSpec 2009 staff at the conference office will be happy to assist you.

Poster Awards

Roland W. Frei Poster Award

It is a main endeavor of IAEAC to support and stimulate young scientists' research activities. Therefore, IAEAC has established the Roland W. Frei Poster Award, which regularly goes to young researchers presenting outstanding results on their posters. At TraceSpec 2009, the best poster out of poster sessions I and II will be selected by a search committee and awarded the Roland A. Frei Poster Award. An electronic version of the awardee's poster will later be published on the IAEAC website (www.iaeac.ch).

Poster Awards for Poster Sessions I and II

Further to the Roland Frei Award, two posters out of the two sessions will be awarded poster prizes that have been sponsored by the following organizations:

2nd prize (endowed with € 500,-): Thermo Scientific
3rd prize (endowed with € 300,-): EVISA

Poster Award Session

The poster award session is going to be held on Friday, September 18, 2009 at 12:50 in the main lecture hall.

Social Program

Get-Together Mixer on Tuesday, September 15, 2009

The conference begins with an informal get-together mixer on Tuesday. All registered participants are kindly invited to join exhibitors and organizers at this event from 18:00 to 21:00 hrs in the foyer of the New Chemistry lecture hall. Drinks, refreshments and snacks will be served during this reception.

Guided Walk "Medieval Mainz" through the City Centre and Barbeque, Wednesday, September 16, 2009

The young scientists of the local Interdisciplinary Research Training Group Program "Trace analysis of elemental species: Development of methods and applications" and the members of the Bings and Hoffmann research groups invite you to a guided 90 minute walk through the historical City of Mainz along the roman and medieval sights. During this walk you will learn facts and curiosities about the city of Mainz and its importance during the era of the Roman Empire.
Following the scientific program on Wednesday, September 16, at 18:00 hrs you will be taken by bus from the Chemistry Building to the city center. After your return to the conference venue by Bus we will welcome you at 20:00 hrs with a barbecue and chilled German beer on campus. This will give you an opportunity for fruitful discussions and to meet friends and colleagues in a relaxed atmosphere.
Please register for this event at the conference office (in case not already done by Email), if you wish to participate. A participation fee of EUR 15,- will be collected.

Conference Dinner at the "Kupferbergterrasse", Thursday, September 17, 2009

Those participants having registered for this event will get the opportunity to meet at 19:00 hrs at an exceptional location, the „Kupferbergterasse" in downtown Mainz, a local champagne producer with a fine tradition since 1850. Starting with a reception you will get the possibility to discover a unique selection of sparkling wine and an international and quite remarkable collection of historical and modern champagne glasses and other extraordinary art works regarding the company's public relations and sales promotion. This exhibition is open for your visit throughout the whole evening. The Conference Dinner will begin at 21:00 hrs at the "Fürst von Bismarck Hall" after an astonishing and exploratory guided 45 min. walk through the ancient subterranean champagne cellars of "Kupferberg".
The location is within walking distance (10 min. walk) from the central station, downtown Mainz.

Paper Submissions for a Special Issue of
International Journal of Environmental Analytical Chemistry

TraceSpec 2009 organizers would like to invite all speakers and poster presenters to submit their work for publication in a special issue of the International Journal of Environmental Analytical Chemistry.

The scope of the journal comprises such subjects as original research on all aspects of analytical work related to environmental problems such as analysis of organic, inorganic and radioactive pollutants in air and water; determination of harmful substances, including their metabolic breakdown products; and analytical methods for metabolic breakdown patterns or other chemical degradation patterns in the environment and in biological samples. The journal also covers the development of new analytical methods or improvement of existing ones useful for the control and investigation of pollutants or trace amounts of naturally occurring active chemicals in the environment, or methods that help to gain more insight into our environment. Development, modification and automation of instruments and techniques with potential in environmental sciences are also part of the journal.

The journal is currently publishing the Proceedings of relevant IAEAC scientific meetings.

Manuscript submission deadline for the special issue is October 31, 2009.

All manuscripts have to be submitted electronically via: http://mc.manuscriptcentral.com/geac. “Instructions to authors” are also available on this website. Please use “TraceSpec 2009” as a key-word in order to indicate that your manuscript is for publication in this special issue.

Please note that all manuscripts submitted to International Journal of Environmental Analytical Chemistry will undergo full peer review, based on initial editor screening and anonymized refereeing by at least two expert referees.

About

IAEAC

The International Association of Environmental Analytical Chemistry (IAEAC) is a world-wide operating organization that aims to promote and maintain scientific excellence in analytical science as applied to different environmentally relevant research areas. Not only the traditional compartments soil, water, and air are included in its activities, but likewise fields such as industrial processes, human health, or quality of food. In these efforts, the IAEAC strongly collaborates with relevant disciplines other than chemistry.

In order to achieve its goals, the IAEAC provides opportunities for scientists to exchange “cutting-edge” research results significant for the environment and to become acquainted with the most advanced analytical technologies. This is successfully practiced through regularly occurring events such as symposia, workshops, and short courses, now over almost 40 years.

More information about the IAEAC can be found on: ***www.iaeac.ch***

EVISA

The European Virtual Institute for Speciation Analysis (EVISA) is a service provider in the field of speciation analysis. EVISA‘s web portal is the primary source for all those seeking information and advice about chemical species with respect to analysis, biological activity (toxicity, nutritional value, metabolism), legislation (laws, rules, standards) and research in related fields. In order to fulfill its mission, EVISA provides different services, meant to

- promote the dissemination of information and knowledge toward industry and formulate new requirements as a feed-back from industrial demands,
- help industry to install speciation related solutions fit-for-purpose to solve real world issues,
- enhance the discussion between analytical scientists,
- improve the interdisciplinary cooperation between scientists from different fields, such as toxicology, biology, medicine, nutritional science, earth sciences, environmental sciences,
- improve the quality and traceability of speciation analysis by performing different quality related actions,
- improve the education of analytical scientists for speciation analysis and quality assurance related to speciation,
- enhance the visibility of speciation related science toward policy and rule makers by adding the European dimension,
- inform policy and rule makers about the state-of-the-art of the current academic knowledge to facilitate the establishment of most effective legislation considering the characteristics of element species,
- act as a promoter of new research strategies emerging from the realization of speciation demands in industrial, food, health, and environmental issues.

More information about EVISA can be found on: ***www.speciation.net***

About

University of Mainz
Founded in 1477, Mainz University is one of the oldest German universities. In its diversity of students, its global outlook, as well as its outstanding research it is also a university of compelling change. Named after the famous fifteenth-century printer who revolutionized printing with movable types, Johannes Gutenberg University Mainz combines stimulating academic diversity with excellent research structures: About 500 professors and 2,300 members of our academic staff research and teach in our eleven departments and 150 institutes. The Johannes Gutenberg University Mainz is proud to host 12 Collaborative Research Centers, 9 Research Units, and 7 Research Training Groups, all funded by the German Research Foundation (DFG), as well as numerous research initiatives funded by other sources, both public and private. In addition, our campus is home to the Max Planck Institutes for Polymer Research and Chemistry. With degree programs available in more than ninety subjects and in numerous combinations, the range of courses we offer is extremely wide and covers all areas, be it the humanities, social studies, law, economics, or medicine. Moreover, the integration of the Academy of Fine Arts and the School of Music is unique in the German landscape of higher education. Currently, some 35,000 students, 14 percent of them from abroad, take advantage of these opportunities. An active member of the international academic community, Johannes Gutenberg University Mainz is also proud of its strong ties to the local community: The Rhine-Main area is one of the economically most powerful regions in Germany, and we actively cooperate with its businesses and industries, and participate in its political and cultural life.

For further information, please visit: ***www.uni-mainz.de/eng/***

The capital of Rhineland Palatinate – Mainz
Mainz is located on the west bank of the river Rhine across from Wiesbaden, in the western part of the Frankfurt Rhine-Main Region. Up until the twentieth century, Mainz was usually referred to in English as Mayence. The population 2008 was 200,000. It can easily be reached by car, train and plane. Frankfurt airport (FRA) is only about 35km away from the city center. The city hosts the University of Mainz and the University of Applied Sciences. Altogether 50,000 students are currently educated in Mainz. Furthermore several established research institutes that are part of the Max-Planck Society are situated in Mainz.
Mainz is the Capital of the German federal state of Rhineland-Palatinate, the most famous wine region in Germany. Due to the importance and history of the wine industry for the federal state, Rhineland-Palatinate is the only state to have a wine minister. The city is well-known in Germany as the seat of Zweites Deutsches Fernsehen (literally, „Second German Television“, ZDF), one of two federal nationwide TV broadcasters. Mainz is famous for its Carnival, the Mainzer Fassenacht or Fassnacht, which has developed since the early 19th century. Carnival in Mainz has its roots in the criticism of social and political injustices under the shelter of cap and bells; today, the uniforms of many traditional Carnival clubs still imitate and caricature the uniforms of the French and Prussian troops of the past. The height of the carnival season is on Rosenmontag („rose Monday“) when there is a large parade in Mainz, with more than 500,000 people celebrating in the streets.

Conference History

Since 1983, IAEAC together with local organizers has held a series of workshops related to trace metal speciation. To date, eleven meetings of this type have been organized throughout Europe and in Canada. Starting in 2000, with the eighth meeting of the series, analytical chemistry was made the focal point of the workshop as indicated by the change of its title into „Progress in Analytical Methodologies for Trace Metal Speciation“. TraceSpec 2009 is also following this concept and presents the most recent research results in the field of speciation analysis as well as future strategies suited to face upcoming challenges.

Chronology of Trace Metal Speciation Workshops:

1983	1st Workshop:	Carcinogenic and/or Mutagenic Metal Compounds (Environmental Chemistry, Analytics, Biological Effects), Geneva/Switzerland
1986	2nd Workshop:	Carcinogenic and/or Mutagenic Metal Compounds, Villars-sur-Ollon/Switzerland
1988	3rd Workshop:	Toxic Metal Compounds (Interrelation between Chemistry and Biology), Follonica/Italy
1991	4th Workshop:	Toxic Metal Compounds (Interrelation between Chemistry and Biology), Les Diablerets/Switzerland
1994	5th Workshop:	Metals and Genetics, Toronto/Canada
1995	6th Workshop:	Metal Compounds in Environment and Life, Jülich/Germany
1997	7th Workshop:	Metal Compounds in Environment and Life, Modena/ Italy
2000	8th Workshop:	Progress in Analytical Methodologies in Trace Metal Speciation, Lisbon/Portugal (part of EUROANALYSIS XI)
2002	9th Workshop:	Progress in Analytical Methodologies in Trace Metal Speciation, Dortmund/Germany (part of EUROANALYSIS XII)
2005	10th Workshop:	Progress in Analytical Methodologies in Trace Metal Speciation, Luxembourg/Luxembourg
2007	11th Workshop on	Progress in Analytical Methodologies for Trace Metal Speciation: TraceSpec 2007, Münster/Germany
2009	12th Workshop on	Progress in Analytical Methodologies for Trace Metal Speciation: TraceSpec 2009, Mainz/Germany

TraceSpec 2009: Program Overview

Tuesday, September 15	Wednesday, September 16	Thursday, September 17	Friday, September 18
	8:00 Registration desk	*8:00 Registration desk*	*8:00 Registration desk*
	***8:20* Opening of the workshop**		
	8:40 **Plenary lecture PL1**	*8:30* **Plenary lecture PL3**	*8:30* **Plenary lecture PL5**
	9:20- 10:20 Contributed presentations: Tools for speciation analysis	*9:10-10:10* Contributed presentations: Speciation analysis in proteomics, metallomics and metabolomics	*9:10-09:50* Contributed presentations: Speciation analysis for the characterization of materials and industrial processes
	10:20-11:00 Coffee break in the exhibition area	*10:10-11:00* Coffee break in the exhibition area	*09:50-10:30* Coffee break in the exhibition area
			10:30-11:10 **Plenary lecture PL6**
	11:00-12:20 Contributed presentations: Tools for speciation analysis	*11:00-12:20* Contributed presentations: Speciation analysis in proteomics, metallomics and metabolomics	*11:10-12:50* Contributed presentations: Speciation analysis for the food and health sector
	12:20-14:00 Lunch break and exhibition	*12:20-14:00* Lunch break and exhibition	***12:50*** **Announcement of Poster awards**
	14:00 **Plenary lecture PL2**	*14:00* **Plenary lecture PL4**	***13:00*** **Closing ceremony**
	14:40-15:40 Contributed presentations: Environmental speciation analysis	*14:40-15:40* Contributed presentations: Environmental speciation analysis	
	15:40-16:40 Coffee break / **Poster session 1**	*15:40-16:40* Coffee break / **Poster session 2**	
17:00-21:00 Entrance hall, Registration desk: On-site registration	*16:40-18:00* Contributed presentations: Environmental speciation analysis	*16:40-17:40* Contributed presentations: Environmental speciation analysis	
18:00-21:00 **Foyer of the Chemistry Building Get-together mixer**	*18:10* **Meeting at the main entrance: "Medieval Mainz" tour**	*19:00* **Conference dinner at "Kupferberg-terrasse"**	

Tuesday, September 15, 2009

Late Afternoon: Informal Get-Together

The conference begins with an informal get-together mixer on Tuesday. All registered participants are kindly invited to join exhibitors and organizers at this event from 18:00 to 21:00 hrs at the conference site (neues Hörsaalgebäude Chemie). Drinks, refreshments and snacks will be served during this reception.

Wednesday, September 16, 2009

Morning session 1: Tools for speciation analysis
Chairman: Jörg Feldmann (University of Aberdeen)

8:20 Opening of the workshop:
Thorsten Hoffmann, Dieter Klockow, Michael Sperling

8:40 **PL 1** Plenary lecture: *Pascal Salaün, Kristoff Gibbon-Walsh and Stan van den Berg (Department of Earth and Ocean Sciences, University of Liverpool, UK)*
Stripping voltammetry for metals and metalloids speciation in natural waters

9:20 **OP 1.1** *Michael Sperling, Thorben Pfeifer and Wolfgang Buscher (Institute for Inorganic and Analytical Chemistry, University of Münster, Germany)*
Inductively Coupled Plasma Mass Spectrometric Detection for Speciation-analytical Applications at only 1 L/min Total Argon Consumption

9:40 **OP 1.2** *Birgit Vallant, Monika Denner, Andrea Hanus-Illnar and Claudia Gundacker (Department of Inorganic Analysis, Environmental Agency Vienna, Austria)*
Determination of mercury species in human tissue samples after liquid chromatographic separation – cold vapour generation – and ICPMS detection

10:00 **OP 1.3** *Georg Raber, Reingard Raml, Linda Kuenstl, Walter Goessler and Kevin A. Francesconi (Karl-Franzens University Graz, Austria)*
Quantitative speciation analysis using organic solvent gradients in HPLC-ICPMS

10:20 Coffee break and exhibition

Wednesday, September 16, 2009

Morning session 1: Tools for speciation analysis
Chairman: Jörg Feldmann (University of Aberdeen)

11:00 **OP 1.4** *B. Alan Wood, Toshikazu Kaise, Shinichi Miyashita, Andrea Raab and Jörg Feldmann (University of Aberdeen, UK)*
Does the edible seaweed Hijiki deal with its arsenic burden via complexation with phytochelatins?

11:20 **OP 1.5** *Peter Planitz and Ed McCurdy (Agilent Technologies)*
Introducing the New Agilent 7700 Series ICP-MS; Improved Performance for Speciated Analysis

11:40 **OP 1.6** *Ayşen Höl and Latif Elci (Department of Chemistry, Pamukkale University, Turkey)*
Simultaneous Determination of Co(II), Ni(II) and Fe(II) as 4-(2-pyridylazo) resorcinol complex by RP-HPLC

12:00 **OP 1.7** *F. Pena-Pereira, M. Costas, S. Gil, I. Lavilla and C. Bendicho (Departamento de Química Analítica y Alimentaria, Universidad de Vigo, Spain)*
Single-drop microextraction as a powerful tool for trace element analysis and speciation

12:20 *Lunch break and exhibition*

Afternoon session 2: Environmental speciation analysis I
Chairman: Michael Sperling (EVISA)

14:00 **PL 2** Plenary lecture: *Eva Krupp (University of Aberdeen, UK)*
Mercury speciation in environment and life – from MeHg to Hg biomolecules

14:40 **OP 2.1** *Peter B. Stockwell, Warren T. Corns, Bin Chen, Nicholas V. C. Ralston and Laura Raymond (PS Analytical Ltd, Kent, UK)*
The role of atomic fFluorescence spectrometry in determining levels of mercury and selenium species in the environment

15:00 **OP 2.2** *Romain Bridou, Zoyne Pedrero, Sandra Mounicou, Remy Guyoneaud, Mathilde Monperrus and David Amouroux (Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, Université de Pau et des Pays de l'Adour, Pau, France)*
Study of the transformation and localization of Hg species in different sub-cellular fractions of Desulfobulbus propionicus

15:20 **OP 2.3** *Roland A. Diaz-Bone and Tom Van de Wiele (Institute of Environmental Analytical Chemistry, University of Duisburg-Essen, Germany)*
Metabolism of metal(loid)s by intestinal microorganisms

15:40 *Coffee break and poster session I*

16:40 **OP 2.4** *Burkhard Knopf, Elisabeth Kaschak and Helmut König (Institute of Biology, University of Mainz, Germany)*
Alkylation of mercury by isolated microorganisms from the gut of Eisenia foetida

17:00 **OP 2.5** *Kalle Uroic, Pascal Salaun and Jörg Feldmann (University of Aberdeen, UK)*
Arsenic uptake and translocation via xylem sap – the cucumber model

17:20 **OP 2.6** *Birgit Daus, Holger Weiss and Rolf Altenburger (Helmholtz Centre for Environmental Research, Leipzig, Germany)*
Uptake and toxicity of hexafluoroarsenate in aquatic organisms

17:40 **OP 2.7** *Montserrat Filella (University of Geneva, Versoix, Switzerland)*
Antimony: the facts – or maybe not

18:00 *End of first part of the session 'Environmental speciation analysis'*

18:10 *Meeting at the main entrance for the "Medieval Mainz" tour*

Thursday, September 17, 2009

Morning session 3: Speciation analysis in proteomics, metallomics and metabolomics
Chairperson: Ryszard Lobinski (University of Pau)

8:30 **PL 3** Plenary lecture: *Spiros A. Pergantis (University of Crete, Greece)*
Analytical Approaches for Investigating the Function of Elemental Species in Biological Systems

9:10 **OP 3.1** *Daniel Pröfrock and Andreas Prange (GKSS Research Centre, Geesthacht, Germany)*
Combined ESI and ICP-MS approach for the quantification of biomolecules using natural element tags

9:30 **OP 3.2** *Daniel J. Kutscher and Jörg Bettmer (University of Oviedo, Oviedo, Spain)*
Absolute and Relative Protein Quantification with the Use of Isotopically Labelled p-Hydroxymercuribenzoic Acid and Complementary MALDI- and ICP-MS Detection

9:50 **OP 3.3** *Lena Telgmann, Jens Künnemeyer, Faruk Tokmak and Uwe Karst (University of Münster, Germany)*
Analysis of Gd-based MRI contrast agents and potential transmetallation products in human body fluids

10:10 *Coffee break and exhibition*

11:00 **OP 3.4** *Jörg Feldmann (University of Aberdeen, UK)*
Speciation of labile metal biomolecule complexes – not always a job for hyphenated mass spectrometric techniques

11:20 **OP 3.5** *Susanne Bomke, Anja Bräutigam, Thorben Pfeifer, Wolfgang Buscher, Dirk Wesenberg, Gerd-Joachim Krauss and Uwe Karst (University of Münster, Germany)*
Determination of ferrocene-derivatized phytochelatins by LC/ESI-MS and LC/ICP-MS

11:40 **OP 3.6** *J. Diederich and B. Michalke (Helmholtz Zentrum München, Neuherberg, Germany)*
Size characterized manganese - and iron species in sprague-dawley rats exposed to $MnCl_2 \cdot 4\ H_2O$ (i.v.)

12:00 **OP 3.7** *Björn Meermann, Stefan Trümpler, Wiebke Lohmann, Michael Sperling, Wolfgang Buscher and Uwe Karst (University of Münster, Germany)*
Mercury speciation analysis for the investigation of the interaction of thimerosal with blood components

12:20 *Lunch break and exhibition*

Thursday, September 17, 2009

Afternoon session 4: Environmental speciation analysis II
Chairman: Thorsten Hoffmann (University of Mainz, Germany)

14:00 **PL 4** Plenary lecture: *Alex Baker (University of East Anglia, UK)*
Iodine speciation in atmospheric aerosols and rainwater

14:40 **OP 4.1** *Ru-Jin Huang and Thorsten Hoffmann (Institute of Analytical Chemistry, University of Mainz, Germany)*
Development of a Coupled Diffusion Denuder System Combined with GC–MS for the Separation and Quantification of Molecular Iodine and Activated Iodine Compounds (ICl, HOI) in the Marine Atmosphere

15:00 **OP 4.2** *Oliver Baars and Peter L. Croot (IFM-GEOMAR, Kiel, Germany)*
Application of stripping voltammetry to the speciation of dissolved Zinc and Cobalt in the Southern Ocean

15:20 **OP 4.3** *Ralf Kautenburger (Saarland University, Saarbrücken, Germany)*
Influence of metal concentration and the presence of competing cations on europium and gadolinium speciation with humic acid analysed by CE-ICP-MS

15:40 *Coffee break and poster session II*

16:40 **OP 4.4** *S. Raeder, S. Fies, K. Wendt, N. Trautmann and J. V. Kratz (Institute of Physics, University of Mainz, Germany)*
Detection of the ultra trace Isotope U-236 using High Resolution Resonance Ionisation Mass Spectrometry

17:00 **OP 4.5** *Nongrat Issaro and Alain Bermond (Laboratoire de chimie analytique, AgroParisTech, Paris, France)*
Soil mercury speciation: Chemical reagents applied for the metal extraction

17:20 **OP 4.6** *T. Reich, S. Amayri, S. Dierking, B. Baeyens, R. Dähn, M. H. Bradbury and A. C. Scheinost (Institute of Nuclear Chemistry, University of Mainz, Germany)*
Speciation and surface complexation modelling of Np(V) sorption on montmorillonite

17:40 *End of session*

19:00 *Conference dinner at “Kupferbergterrasse”*

Friday, September 18, 2009

Morning session 5: Speciation analysis for the characterization of materials and industrial processes
Chairman: Dieter Klockow (IAEAC)

8:30 **PL 5** *Jorma Jokiniemi (VTT Technical Research Centre of Finland, Espoo, Finland)*
Physico-chemical characterisation of particle emissions from various industrial sources

9:10 **OP 5.1** *Shona McSheehy, Torsten Lindemann and Meike Hamester (Thermo Fisher Scientific, Bremen, Germany)*
Conforming to Legislation on Chromium Speciation in Toys

9:30 **OP 5.2** *Manuela D. Machado, Eduardo V. Soares and Helena M. V. M. Soares (Department of Chemical Engineering, Porto University, Portugal)*
The knowledge of metal chemical speciation is of paramount importance on removing and recovering metals from industrial effluents

9:50 *Coffee break and exhibition*

Friday, September 18, 2009

Morning session 6: Speciation analysis for the food and health sector
Chairman: Kevin Francesconi (University Graz)

10:30 **PL 6** Plenary lecture: *Mihaly Dernovics and Ryszard Lobinski (University of Budapest, Hungary)*
ESI-MS^n in selenium speciation: focus on structure assessment

11:10 **OP 6.1** *Martijn van der Lee, Elly Wijma and Hans Mol (Institute of food safety, Wageningen, the Netherlands)*
Speciation of Arsenic species in marine products by HPLC-ICP-MS

11:30 **OP 6.2** *GuiDi Yang, JinHua Xu, LiangJun Xu, JinPing Zheng and FengFu Fu (Key Laboratory of Analysis and Detection Technology for Food Safety of Ministry of Education, Fuzhou University, China)*
Determination of triorganotin compounds in Sea Foods by using CE-ICP-MS

11:50 **OP 6.3** *Christine Brauckmann, Björn Meermann and Uwe Karst (Institute of Inorganic and Analytical Chemistry, University of Münster, Germany)*
Species Analysis of Platinum Based Cytostatic Drugs

12:10 **OP 6.4** *Francesco Cubadda, Federica Aureli, Silvia Ciardullo, Marilena D'Amato, Andrea Raggi, Cristina Sola-Larrañaga, Raghunath Acharya, and Tejo Prakash Nagaraja (Department of Food Safety and Veterinary Public Health, Rome, Italy)*
Speciation and bioaccessibility of selenium in wheat grain from a seleniferous area and derived products

12:30 **OP 6.5** *Carl P. Verdon, Christopher G. K. Freedman, Cynthia D. Ward, Mark Fresquez, Kathleen L. Caldwell and Robert L. Jones (National Center for Environmental Health, Atlanta, USA)*
Arsenic and Mercury Speciation: Chromatographic ICP-MS Methods for the U.S. National Biomonitoring Program, Centers for Disease Control & Prevention (CDC)

12:50 *Poster awards*

13:00 *Closing ceremony*

Poster session I: Environmental speciation analysis
(authors are asked to be present at the posters, 15:40-16:40)

PO 1.1 CE-DAD-ICP-MS for determination of complex formation constants for the complexation of lanthanides and actinides with humic substances
E. Gromm, R. A. Buda and J. V. Kratz
Institute for Nuclear Chemistry, Johannes Gutenberg University, Mainz, Germany

PO 1.2 Trace Analysis of Neptunium with Resonance Ionization Mass Spectrometry
Nils Stöbener[1], Tina Gottwald[2], Sebastian Raeder[2], Gerd Passler[2], Tobias Reich[1], Norbert Trautmann[1] and Klaus Wendt[2]
[1] Institute of Nuclear Chemistry, Johannes Gutenberg University, Mainz, Germany
[2] Institute of Physics, Johannes Gutenberg University, Mainz, Germany

PO 1.3 Speciation analysis of antimony (III) and antimony (V) in water samples by dispersive liquid-liquid microextraction (DLLME) combined with electrothermal atomic absorption spectrometry
Seyed Reza Yousefi[1], Farzaneh Shemirani[1] and Mohammad Reza Jamali[2]
[1] School of Chemistry, University College of Science, University of Tehran, Tehran, Iran
[2] Department of Chemistry, Payam Noor University, Behshahr, Iran

PO 1.4 Iodine speciation in marine aerosols along a 30,000 km round-trip cruise path from Shanghai, China to Prydz Bay, Antarctica
Senchao Lai[1], Thorsten Hoffmann[1] and Zhouqing Xie[2]
[1] Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University, Mainz, Germany
[2] Institute of Polar Environment, University of Science and Technology of China, Hefei, China

PO 1.5 Speciation analysis and preconcentration of Tl in water samples using solid phase extraction by cation exchange resin and electrothermal atomic absorption spectrometry
Ján Medved'[1], Peter Matúš[1], Milan Kališ[1], Ingrid Hagarová[1], Marek Bujdoš[1], Jana Kubová[1] and Pavel Diviš[2]
[1] Comenius University in Bratislava, Faculty of Natural Sciences, Bratislava, Slovakia,
[2] Brno University of Technology, Faculty of Chemistry, Brno, Czech Republic

PO 1.6 Speciation analysis of inorganic antimony in natural waters using the combination of extraction procedures and electrothermal atomic absorption spectrometry

Ingrid Hagarová[1], Peter Matúš[1], Jana Kubová[1], Marek Bujdoš[1] and Pavel Diviš[2]

[1] Comenius University in Bratislava, Faculty of Natural Sciences, Bratislava, Slovakia

[2] Brno University of Technology, Faculty of Chemistry, Brno, Czech Republic

PO 1.7 CE-ICP-MS as speciation technique to analyze the complexation behavior of Europium, Gadolinium and Terbium with organic ligands

Christina Möser, Ralf Kautenburger and Horst P. Beck

Institute of Inorganic and Analytical Chemistry and Radiochemistry, Saarland University, Saarbrücken, Germany

PO 1.8 Development of an on-line method for the determination of I2 by using time-of-flight aerosol mass spectrometry

Michael Kundel, Mathias Schott, Marco Ries and Thorsten Hoffmann

Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University, Mainz, Germany

PO 1.9 A preliminary study of a DGT-labile trace metals distribution in the stratified Krka River estuary (Croatia)

Ana-Marija Blatarić[1], Cédric Garnier[2], Dario Omanović[1], Véronique Lenoble[2], Neven Cukrov[1], Stéphane Mounier[2], Jean-Louis Gonzalez[3] and Ivanka Pižeta[1]

[1] Ruđer Bošković Institute, Center for Marine and Environmental Research, Zagreb, Croatia

[2] Laboratoire PROTEE, Université du Sud, Toulon La Garde, France

[3] IFREMER, Département Biogéochimie et Ecotoxicologie, La Seyne/mer cedex, France

PO 1.10 Identification of volatile metal(loid) compounds formed by intestinal microorganisms by use of simultaneous EI-MS and ICP-MS detection after gas chromatographic separation

Roland A. Diaz-Bone, Markus Hollmann, Oliver Wuerfel and Dominik Pieper

Institute of Environmental Analytical Chemistry, University of Duisburg-Essen, Germany

PO 1.11 Determination of 13C/12C isotopic ratios of biogenic organometal(loid) compounds in complex matrices

Oliver Würfel[1], Roland A. Diaz-Bone[1], Manuel Stephan[2] and Maik A. Jochmann[2]
[1] Institute of Environmental Analytical Chemistry, University of Duisburg-Essen, Duisburg, Germany
[2] Instrumental Analytical Chemistry, University of Duisburg-Essen, Germany

PO 1.12 Towards the in vitro methylation of metals and metalloids: Capability of corrinoid-dependent methyltransferases from Methanosarcina mazei to volatilize metal(loid)s

Frank Thomas[1], Britta Huber[1], Roland A. Diaz-Bone[2] and Reinhard Hensel[1]
[1] Microbiology I, University of Duisburg-Essen, Essen, Germany
[2] Institute of Environmental Analytical Chemistry, University of Duisburg-Essen, Germany

PO 1.13 Gaseous and particulate mercury in ambient air of the Upper Silesia, Poland

Halina Pyta[1], Ewa Szmyd[2] and Marianna Czaplicka[2]
[1] Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze, Poland
[2] Institute of Non-Ferrous Metals, Gliwice, Poland

PO 1.14 Determination of Nitro-PAHs in Total Suspended Particles of Urban Atmosphere

Hongwei Chen[1], Qun Luo[1], Kin-Fai Ho[2] and Jingqi Tao[3]
[1] School of Chemistry & Environmental Engineering, Dongguan University of Technology, Dongguan, China
[2] Department of Civil & Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
[3] School of Chemistry & Environment, South China Normal University, Guangzhou, China

PO 1.15 Determination of arsenic species in algae by microwave-assisted extraction and high performance liquid chromatography-inductively coupled plasma-dynamic reaction cell- mass spectrometry

Syr-Song Chen, Che-Lun Hsu, Ya-Min Kao and Yang-Chih Shih
Bureau of Food and Drug Analysis, Department of Healt, Taipei, Taiwan

PO 1.16 Selenium isotope ratios of volatile organoselenium species as an indicator of the conditions of biomethylation

Kathrin Schilling and Wolfgang Wilcke
Geographic Institute, Johannes Gutenberg University, Mainz, Germany

PO 1.17 Solid-phase speciation and surface binding of nickel in serpentine soils from the North-east of Portugal

Sheila Alves[1], *Maria de Lurdes Simões Gonçalves*[1], *Maria Ascensão Trancoso*[2] *and Margarida M. Correia dos Santos*[1]
[1] Centro de Química Estrutural, Instituto Superior Técnico, Lisboa, Portugal
[2] Instituto Nacional de Engenharia e Tecnologia Industrial, Lisboa, Portugal

PO 1.18 Determination of Tributyltin (TBT) at Sub-ppt Level in Whole Water Samples

Christian Piechotta, Thomas Sommerfeld, Tin Win and Irene Nehls
Federal Institute for Materials Research and Testing, Organic Trace Analysis and Reference Materials, Berlin, Germany,

PO 1.19 Isotopic fractionation of Cu and Zn in the soil system

Moritz Bigalke[1]*, Stefan Weyer*[2] *and Wolfgang Wilcke*[1]
[1] University of Mainz, Geographic Institute, J.J. Becher-Weg 21, 55128 Mainz, Germany
[2] University of Frankfurt, Institute of Geoscience, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

PO 1.20 Arsenic speciation in whelks (Buccinum undatum)

Dagmar Urgast, Andrea Raab and Jörg Feldmann
TESLA (Trace Element Speciation Laboratory), University of Aberdeen, College of Physical Science, Chemistry, Aberdeen, Scotland, UK

PO 1.21 Sorption and speciation of neptunium(V) on Opalinus Clay

Daniel Fröhlich, S. Amayri, J. Drebert and Tobias Reich
Institute of Nuclear Chemistry, Johannes Gutenberg University, Mainz, Germany

PO 1.22 Characterization of resin gels used for determination of different mercury fractions in natural waters by DGT technique

Pavel Diviš, Roman Szkandera and Hana Frišhansová
Faculty of chemistry, Brno University of Technology, Brno, Czech Republic

PO 1.23 Copper exportation from glaciarised catchments

Damiano Monticelli, Andrea Pozzi and Carlo Dossi
Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, Como, Italy

PO 1.24 Assessment of accuracy and precision in speciation analysis by CLE–CSV: application to Antarctic samples

Alessio Castelletti, Carlo Dossi and Damiano Monticelli
Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria, Como, Italy

PO 1.25 Speciation of Hg on three mining districts by XANES techniques

José María Esbrí[1], Anna Bernaus[2], Eva MªGarcía-Noguero[1], Marta Avila[2], David Kocman[3], Beatriz Guerrero[2], Xavi Gaona[2], Rodrigo Alvarez[4], Gustavo Perez-Gónzalez[2], Pablo Higueras[1], Jorge Loredo[4], Milena Horvat[3] and Manuel Valiente[2]

[1] Department of Mining and Geological Engineering, University of Castilla-La Mancha, Almadén, Spain,

[2] Department of Chemistry, Autonomous University of Barcelona, Bellaterra, Spain

[3] Jozef Stefan Institute, Ljubljana, Slovenija.

[4] Department of Mining and Mines Exploration, University of Oviedo, Oviedo, Spain

PO 1.26 Reactive' extraction of arsenosugars from brown alga Wakame (Undaria pinnatifida)

Jürgen Mattusch[1], Peggy Landsmann[2] and Regina Walter[2]

[1] UFZ-Helmholtz – Centre for Environmental Research, Department Analytical Chemistry, Leipzig, Germany

[2] Department of Engineering and Natural Sciences, University of Applied Sciences, Merseburg, Germany

PO 1.27 Microbiological alkylation and volatilization of inorganic selenium immobilized by goethite, Se-LDH, and ferroselite

Mirko Peitzsch[1,2] and Michael Kersten[1]

[1] Geosciences Institute, Johannes Gutenberg University, Mainz, Germany

[2] Division of Medical Microbiology, Dept. of Laboratory Medicine, Lund University, Lund, Sweden

PO 1.28 Sulphur speciation in marine submicron aerosol particles using on-line thermal-desorption aerosol mass spectrometry

Sören R. Zorn[1,2], Frank Drewnick[1], Mathias Schott[3], Thorsten Hoffmann[3] and Stephan Borrmann[1,2]

[1] Particle Chemistry Department, Max-Planck-Institute for Chemistry, Mainz, Germany

[2] Institute for Atmospheric Physics, Johannes Gutenberg University, Mainz, Germany

[3] Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University, Mainz, Germany

PO 1.29 Investigation of the source, behavior, toxicity, mobility and speciation of arsenic in soil

Ka Hei Lui and Michael Kersten

Environmental Geochemistry Group, Institute for Earth Sciences, Johannes Gutenberg University, Mainz, Germany

Poster session II A: Tools for speciation analysis
(authors are asked to be present at the posters, 15:40-16:40)

PO 2.1 **Speciation and preconcentration of iron by cloud point extraction combined with fiber optic linear array detection spectrophotometry**
Elahe Kazemi[1], Nader Shokoufi[2] and Farzaneh Shemirani[1]
[1] Department of Analytical Chemistry, Faculty of Chemistry, University College of Science, University of Tehran, Iran,
[2] Faculty of Analytical Chemistry, Chemistry & Chemical Engineering Research Center of Iran, Iran

PO 2.2 **Traceability in elemental speciation analysis: Se and Fe species in human serum (EMRP T2J10)**
Claudia Swart, Claudia Frank and Olaf Rienitz
Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

PO 2.3 **Trace Metals Speciation in Water Samples by Sequential Injection Anodic Stripping Voltammetry with Monosegmented Flow and On-line UV Digestion**
Watsaka Siriangkhawut[1], Kate Grudpan[1,2] and Jaroon Jakmunee[1,2]
[1] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[2] Science and Technology Research Institute, Chiang Mai University, Chiang Mai 50200, Thailand

PO 2.4 **Comparison of some reaction media for the determination of arsenites by hydride generation atomic absorption spectrometry**
Ingrid Hagarová[1], Peter Matúš[1], Jana Kubová[1], Marek Bujdoš[1] and Pavel Diviš[2]
[1] Comenius University in Bratislava, Faculty of Natural Sciences, Bratislava, Slovakia,
[2] Brno University of Technology, Faculty of Chemistry, Brno, Czech Republic

PO 2.5 **Speciation of inorganic antimony by stripping voltammetry: advantages of a gold wire electrode**
P. Salaün
Earth and Ocean Sciences Department, University of Liverpool, UK

PO 2.6 **Comparison of chemical and electrochemical hydride generation for the on-line determination of arsenic species with an atmospheric pressure glow discharge in helium**
T. Fiedler, B. Gielniak, P. Wu and J. A. C. Broekaert
University of Hamburg, Hamburg, Germany

PO 2.7 Micro-XANES: A tool for the analysis of copper impurities in photo voltaic polycrystalline silicon

Günther Buzanich[1], Denise Kreßner-Kiel[2], Thomas Kaden[2], Heinrich Riesemeier[1], Martin Radtke[1] and Uwe Reinholz[1]
[1] Federal Institute for Materials Research and Testing BAM, Berlin, Germany
[2] TU Bergakademie Freiberg, Freiberg, Germany

PO 2.8 *Drop-on-demand* aerosol generator for ICP-MS analysis

J. N. Schaper, J. Maßmann and N. H. Bings
Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University, Mainz, Germany

PO 2.9 Fundamental characterisation of a new drop-on-demand aerosol generator: introduction of single droplets into plasma excitation and ionization sources

J. H. Petersen, J. Massmann, J. N. Schaper and N. H. Bings
Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University, Mainz, Germany

PO 2.10 Development and characterisation of a drop-on-demand-generator for sample introduction of very small volumes for plasma-spectrometry

J. Massmann, J. H. Petersen, J. N. Schaper and N. H. Bings
Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University, Mainz, Germany

PO 2.11 Ion chromatography-Inductively coupled plasma mass spectrometry used for speciation analysis

ZuLiang Chen, Mallavarapu Megharaj and Ravendra Naidu
University of South Australia, Australia

PO 2.12 Elemental imaging in thin sections of mouse aortas

Dagmar Urgast[1], Andrea Raab[1], John Beattie[2] and Jörg Feldmann[1]
[1] TESLA (Trace Element Speciation Laboratory), University of Aberdeen, College of Physical Science, Chemistry, Meston Walk, Aberdeen AB24 3UE, Scotland, UK
[2] Rowett Institute of Nutrition and Health, University of Aberdeen, Greenburn Road, Bucksburn, Aberdeen AB21 9SB, Scotland, UK

PO 2.13 Determination of superoxide dismutase (SOD) by using species-specific isotope dilution (SS-IDMS) analysis using GE-LA-ICP-MS

Sandra Braukmann, Christian L. Deitrich, Andrea Raab and Jörg Feldmann
TESLA (Trace Element Speciation Laboratory), University of Aberdeen, College of Physical Science, Chemistry, Meston Walk, Aberdeen AB24 3UE, Scotland, UK

Poster session II B: Speciation analysis in proteomics, metallomics and metabolomics
(authors are asked to be present at the posters, 15:40-16:40)

PO 3.1 Investigations of mercury interaction with human blood components by means of static high sensitivity ICP (SHIP)
Sascha Nowak[1], Stefan Trümpler[1], Björn Meermann[1], Gerhard A. Wiesmüller[2], Wolfgang Buscher[1], Michael Sperling[1,3] and Uwe Karst[1]
[1] Institute of Inorganic and Analytical Chemistry, University of Münster, Münster, Germany
[2] Environmental Specimen Bank for Human Tissues, University Hospital, Münster, Germany
[3] European Virtual Institute for Speciation Analysis, Münster, Germany

PO 3.2 Analytical approaches to selenium speciation in eggs
Elżbieta Lipiec[1,2], Katarzyna Bierla[1], Grzegorz Siara[1,2] and Joanna Szpunar[1]
[1] Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, Pau, France
[2] Katedra Chemii Analitycznej, Wydział Chemii, Warszawa, Poland

PO 3.3 Speciation analysis of glutathionine peroxidase, selenoprotein P and selenoalbumin in human serum by tandem affinity HPLC and on-line isotope dilution ICP-MS in a healthy Greek population
Sophia Letsiou[1,2], Tzortzis Nomikos[2], Demosthenes Panagiotakos[2], Christos Pitsavos[3], Christodoulos Stefanadis[3], Smaragdi Antonopoulou[2] and Spiros A. Pergantis[1]
[1] Department of Chemistry , University of Crete, Voutes, Greece
[2] Harokopeio University, Athens, Greece
[3] First Cardiology Clinic, School of Medicine, University of Athens, Athens, Greece

PO 3.4 Arsenolipids in cod liver tissue
U. Arroyo[1], M.-P. lizalde[1], J. Mattusch[2], S. Mothes[2], M. Möder[2], R. Wennrich[2] and F.-M. Matysik[3]
[1] Centro de Química, Universidad Autónoma de Puebla, Puebla, Pue., Mexico
[2] Helmholtz Centre for Environmental Research – UFZ, Department of Analytical Chemistry, Leipzig, Germany
[3] Institute of Analytical Chemistry, Chemo- and Biosensors, University of Regensburg, Regensburg, Germany

PO 3.5 EC/LC/ICP-MS Analysis of Amiodarone and Its oxidation products
Björn Meermann, Wiebke Lohmann, Ines Möller and Uwe Karst
Institute for Inorganic and Analytical Chemistry, University of Münster, Münster, Germany

Poster session II C: Speciation analysis for the food and health sector
(authors are asked to be present at the posters, 15:40-16:40)

PO 4.1 Arsenic speciation in Hungarian wheat by HPLC- ICP- MS
Eva Sugar[1] and Eszter Sugar[2]
[1] Central Agricultural Office Food and Feed Safety Directorate, Budapest, Hungary
[2] Agricultural Research Institute of the Hungarian Academy of Sciences, Martonvásár, Hungary

PO 4.2 Engineered nano materials in food with LC-ICP-MS
Elly Wijma, Martijn van der Lee and Ruud Peters
RIKILT- Institute of Food Safety, Wageningen, The Netherlands

PO 4.3 Elemental analysis and soil speciation of citrus plant of Khanpur (Pakistan)
Uzaira Rafique and Shazia Akhtar
Department of Environmental Sciences, Fatima Jinnah Women University, Rawalpindi, Pakistan

PO 4.4 Arsenic-containing hydrocarbons are natural constituents of sashimi tuna
Mojtaba S. Taleshi[1], John S. Edmonds[1], Walter Goessler[1], Maria José Ruiz-Chancho[1], Georg Raber[1], Kenneth B. Jensen[2] and Kevin A. Francesconi[1]
[1] Institute of Chemistry–Analytical Chemistry, Karl-Franzens University Graz, Universitätsplatz 1, 8010 Graz (Austria)
[2] Institute for Physics and Chemistry, University of Southern Denmark, 55 Campusvej, 5230 Odense, Denmark

PO 4.5 Analytical approaches to comparative metabolomics of selenized yeast
Sandra Gil Casal, Johann Far, Katarzyna Bierla, Hugues Preud'homme and Joanna Szpunar
Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, Pau, France

PO 4.6 Detection of Ni(II) and Co(II) in fibroblasts using CLSM
Yvonne Scheller and Heinz Duschner
Institute of Applied Structure- and Microanalysis, University medical centre of the Johannes Gutenberg University, Mainz, Germany

PO 4.7 Quantitative Determination of ‚Organic Germanium' in Nutritional Supplementations
Erwin Rosenberg
Vienna University of Technology, Institute of Chemical Technologies and Analytics, Vienna, Austria

PL 1

Stripping voltammetry for metals and metalloids speciation in natural waters

Pascal Salaün, Kristoff Gibbon-Walsh and Stan van den Berg

Marine Electrochemistry Group, Earth and Ocean Sciences, University of Liverpool,
4 Brownlow Street, L69 3GP, Liverpool, UK

Stripping voltammetry is a unique tool for detection and speciation of heavy metals and metalloids in natural waters. This analytical method consists of two stages: a deposition step where the metals of interest are accumulated at the electrode surface followed by a stripping step which removes them from the electrode. The signal is obtained during the stripping step but is largely dependent on the experimental parameters used during the deposition step. In natural conditions, the different stripping techniques are mainly responsive to the free metal ion and complexes that are both mobile (high diffusion coefficient) and voltammetrically labile (high dissociation rate). In contrast with chromatographic techniques where the signal is characteristic of one species, the voltammetric signal is a combination of several species. However, these species all have a fast dissociation rate, which, makes them highly reactive in the environment and knowledge of their concentration is important to assess the potential toxicity of a given sample.

Although the identification of the ligand cannot be determined by voltammetry, titration of the sample with the metal of interest gives insight on the complexing capacity (ligands concentration and corresponding stability constants) allowing an estimation of the free metal ion concentration. In addition, due to the deposition step, stripping techniques are very sensitive with detection limits often in the low ppt range. Analysis can often been done with minimum or no sample perturbations, thus preserving the original speciation. Finally, the complete analytical system is compact and can be miniaturised for in-situ analysis, i.e. directly in the water column.

This talk will first introduce the fundamentals of stripping voltammetry and will exemplify the advantages and limitations of some of the different techniques through environmental studies taken from the literature. The second part will focus on recent advances in the inorganic speciation of As and/or Sb in groundwater and seawater. A new method for the As(III) detection which has been tested in the laboratory on different groundwaters and used on-site in West Bengal (India) will be introduced. In sea water, levels of As(III) and Sb(III) determined at natural pH and without any reagent addition will be presented for the first time.

PL 2

Mercury speciation in environment and life – from MeHg to Hg biomolecules

Eva M. Krupp[1,2]

[1] University of Aberdeen, Chemistry, Meston Walk, AB24 3UE Aberdeen, Scotland, UK
e.krupp@abdn.ac.uk
[2] ACES Aberdeen Centre for Environmental Sustainability, 23 St. Machar Drive, AB24 3UU Aberdeen, Scotland, UK

Mercury is an intriguing element, especially due to its occurrence in many different species in environment and biota. Therefore, mercury speciation analysis has been a major research effort for the past 50 some years, with the analytical chemists' focus mainly being put on the development of ever more accurate and precise methods for mercury speciation analysis. The main objective has usually been to distinguish inorganic from organic mercury compounds (mostly in the form of of methylmercury), and the use of sophisticated methods including isotope dilution with isotopically labelled mercury species (species-specific isotope dilution).

Despite the bulk of work done in the past 50 some years on mercury speciation, many phenomena connected with mercury toxicity or its behaviour in the environment (namely bioaccumulation and latent toxicity of methylmercury) is not yet fully understood. A key to a better understanding may lie in the fact that in biota, metals are often bound to and transported as complexes with larger molecules, i.e. biothiols or proteins. But, during the common speciation analysis using invasive extraction and often derivatisation procedures, these Hg biomolecules are broken down, so that important information is lost.

This lecture will provide an overview of modern analytical techniques for mercury speciation used today, and recent developments including the determination of mercury biomolecules in plants and the use of precise mercury isotope determination.

PL 3

Analytical Approaches for Investigating the Function of Elemental Species in Biological Systems

Spiros A. Pergantis

Environmental Chemical Processes Laboratory, Department of Chemistry,
University of Crete, Voutes Campus, Heraklion 71003, Crete, Greece
spergantis@chemistry.uoc.gr

Information about the function of metals and metalloids is currently obtained through a series of elemental speciation analysis techniques which have been developed over the last two decades. These are mainly high-performance liquid chromatography (HPLC) – inductively coupled plasma (ICP) – mass spectrometry (MS) based methods, along with HPLC-electrospray (ES) – tandem MS (MS/MS) which has been used with success in several cases. However, these approaches have several limitations, including limitations in monitoring relatively labile elemental species, detecting non-covalent interactions of elemental species with biomolecules and also characterising unknown elemental species.

This presentation will focus on new mass spectrometric methods and techniques used for arsenic speciation analysis. The aim of which is to be able to: (i) detect labile arsenic species, (ii) conduct targeted and non-targeted analysis of known and unknown arsenic species, respectively, (iii) and detect weak interactions of arsenic species with biomolecules i.e. proteins. For this purpose the three MS techniques that will be discussed are HPLC-ES-MS/MS, operated in the selected reaction monitoring (SRM) mode using a triple quadrupole analyser, as well as ES – Fourier-transform (FT) - ion cyclotron resonance (ICR) - MS used for ultra high resolution and accurate mass measurements. Finally, our latest advances in the development of a novel hyphenated technique involving the coupling of a nanoelectrospray ion mobility spectrometer on-line with ICP-MS will be discussed, with emphasis on its use to monitor weak interactions of arsenic species with biomolecules.

PL 4

Iodine speciation in atmospheric aerosols and rainwater

Alex Baker

School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
alex.baker@uea.ac.uk

The determination of iodine speciation in the atmosphere is complicated by the existence of a large number of inorganic and organic species, in several oxidation states, partitioned between the gaseous and particulate phases. Interaction between iodine and ozone chemistry, including formation of new aerosol particles, makes its speciation both interesting and environmentally significant. The techniques used to probe iodine speciation in the atmosphere include gas and liquid phase spectroscopies, electrochemistry, gas and ion chromatography, solution and aerosol mass spectrometry and neutron activation analysis. This presentation will discuss some of these techniques and explore the outlook for future developments in the field.

PL 5

Physico-chemical characterisation of particle emissions from various industrial sources

Jorma Jokiniemi[1,2]

[1] VTT Technical Research Centre of Finland, Fine Particles,
P.O.Box 1000, FI-02044 VTT, Espoo, Finland
[2] University of Kuopio, Department of Environmental Sciences, Fine Particle and Aerosol Technology Laboratory, P.O. Box 1627, FI-70211 Kuopio, Finland

Fine particle emissions from combustion sources have gained attention recently due to their adverse effects on human health. Here the effects of fuel quality, boiler type and control devices on particle emissions from energy production by combustion and some other industrial sources are reviewed. Several fossil and biomass based fuels are used for energy conversion processes. Here we consider coal, peat, heavy fuel oil, biomass and waste derived fuels and their effects on fine particle formation in boilers. Boiler types considered are pulverized combustion, bubbling fluidized boilers, circulating fluidized boilers, grate fired boilers, gasification-combustion boilers and oil burners. The emission control devices have the most important effect on particle matter (PM) emissions. Several PM removal devices are used like multicyclones, scrubbers, electrostatic precipitators, fabric filters with and without sulphur removal. Measurements have been performed for boilers with fuel power from 20 kW up to several hundred MWs. Extensive particle chemical composition characterisation methods are used to understand the role of different species on emissions. Understanding all these factors helps us to design the energy production units to meet the emission regulations and to asses the environmental fate of different alternatives in energy production.

PL 6

ESI-MS^n in selenium speciation: focus on structure assessment

Mihaly Dernovics[1] *and Ryszard Lobinski*[2,3]

[1] Department of Applied Chemistry, Corvinus University of Budapest, 29-33. Villányi út, 1118 Budapest, Hungary
mihaly.dernovics@uni-corvinus.hu
[2] Laboratoire de Chimie Analytique Bio-inorganique et Environnement, UMR 5254, Hélioparc, 2 av. Pr, Angot, F-64053 Pau, France
[3] Department of Analytical Chemistry, Warsaw University of Technology, 00-664 Warszawa, Poland

Since the discovery of the essential role of selenium to mammals 40 years ago, only few selenium species were considered in selenium-speciation research (1, 2). The reasons for this limited number of target compounds include the lack of commercial authentic standards allowing the development of analytical procedures and insufficient performance of instrumentation making it possible to detect, clean-up and identify any new species discovered in environmental and food matrices.

During the recent 3-4 years, the number of detected low molecular weight (< 1.0 kDa) and water soluble selenium species has increased considerably and exceeds the cumulated number of species of arsenic, mercury and tin dealt with in speciation research. There have been above 50 identified compounds and dozens of species still requiring unambigous structure assignment. Clearly, the availability and continuous development of electrospray MS instrumentation were of crucial importance to achieve this level – however, dedicated sample preparation and orthogonal chromatographic purification protocols were as important as the progress in the ESI-MS technique itself.

Electrospray MS applied to selenium speciation research has considerably evolved from the triple quadrupole devices, through medium resolution time-of-flight instruments to the high resolution Fourier-transform MS using ion cyclotrone resonance or orbital electrostatic trap (Orbitrap). These instruments were usually applied as chromatographic detectors, because the purity of selenium species was rarely high enough for infusion-type analyses. It is evident that the requirements regarding the purity of samples to introduce into an ESI-MS instrument strongly determined the preceeding purification steps introducing the danger of modification of the selenium species.

The lecture presents a tutorial overview of the use of ESI-MS techniques in the identification of selenium species. The importance of data on collision induced dissociation and in-source fragmentation of known and unknown Se-species, accurate mass analyses, mass defect and isotopic pattern of selenium are discussed. Highlighting both successful and failed approaches in species detection and structure assignments will help to show selenium-related specific problems and solutions which may be faced when dealing with real world samples and with other elements.

References

(1) Lobinski, R.; Edmonds, J.S.; Suzuki, K.T.; Uden, P.C. *Pure Appl. Chem.*, 2000, 72, 447-461.
(2) Połatajko, A.; Jakubowski, N.; Szpunar, *J. J. Anal. At. Spectrom.*, 2006, 21, 639-654.

OP 1.1

Inductively Coupled Plasma Mass Spectrometric Detection for Speciation-analytical Applications at only 1 L/min Total Argon Consumption

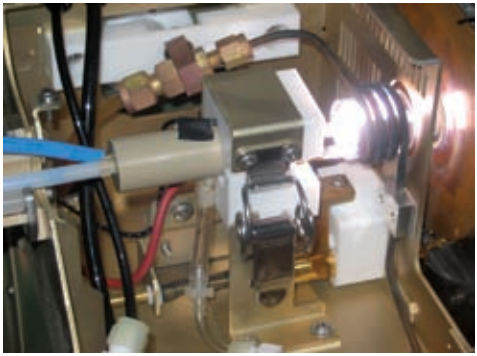
Michael Sperling[1,2], Thorben Pfeifer[1] and Wolfgang Buscher[1,2]

[1] Institute for Inorganic and Analytical Chemistry, University of Münster,
Corrensstraße 30, D-48149 Münster, Germany
Wolfgang.Buscher@uni-muenster.de
[2] European Virtual Institute for Speciation Analysis,
Mendelstraße 11 D-48149 Münster, Germany

Inductively coupled plasma mass spectrometry (ICP-MS) has proven to be a very powerful detector for separation techniques but unfortunately consumes typically 15-17 L min-1 of the noble gas argon. To circumvent this drawback, we have developed a new ICP-MS ion source that can be operated at argon gas flow rates of only 1.2 L min-1 and less. We have named this new ion source 'UMAS' for 'Universal Mass Spectrometric Detector for Speciation Analysis'.

Particularly when used as element selective detector after chromatographic separation of metal-containing (bio)molecules the UMAS source is of advantage over the conventional ICP-MS excitation source. The argon consumption per analyzed sample can be reduced substantially due to the long waiting phases in chromatography. The limits of detection (3σ) of this new ion source are comparable to those of conventional ICP-MS systems.

The UMAS ion source has successfully been coupled to both liquid and gas chromatography. For both methods it was demonstrated that this new element selective mass spectrometric detection system is well suited to be used as alternative method to current detection techniques in speciation analysis.



The UMAS ion source installed in a conventional ICP-MS system

OP 1.2

Determination of mercury species in human tissue samples after liquid chromatographic separation – cold vapour generation – and ICPMS detection

Birgit Vallant[1], Monika Denner[1], Andrea Hanus-Illnar[1] and Claudia Gundacker[2]

[1] Department of Inorganic Analysis, Environmental Agency Vienna, Spittelauer Lände 5, A-1090 Vienna, Austria
[2] Center for Public Health – Lab Ecotoxicology, Medical University of Vienna, Waehringer Strasse 10, A-1090 Vienna, Austria

A powerful procedure for the rapid determination of low levels of inorganic and methyl mercury is described by coupling of liquid chromatography with cold vapour generation inductively coupled plasma mass spectrometry. Baseline separation of mercury species is obtained within 5 minutes by cation-exchange chromatography with Hamilton PRP-X 200 and a mobile phase of 50 mM pyridine, 0.5% w/v L-cysteine, 5% v/v methanol at pH of 2.2. The separated mercury compounds are converted to mercury vapours by the use of HGX-200 vapour generation system for their introduction into the ICPMS.

The concentration of reduction agents (sodiumborohydride/hydrochloric acid) required for vapour generation was optimized for best signal to noise ratios and equal response of both species. The limit of detection for the mercury compounds studied is 0.01 ng Hg/ml and 0.25 ng Hg/g respectively; the limit of quantification is 0.02 ng Hg/ml and 0.5 ng Hg/g which makes the method suitable for speciation of mercury in human tissue samples.

The method was successfully applied for speciation of mercury in human tissue samples namely breast milk and placenta after ultrasonic assisted extraction in mobile phase. Approximately 60 samples originating from Austrian mothers were investigated with the method described, in order to reveal the major modulators of mercury exposures during pregnancy and early infancy. Via questionnaires, the medical history of women, their lifestyle and nutrition and the number of amalgam fillings were surveyed. These data were related to mercury concentrations determined in maternal and infant compartments.

OP 1.3

Quantitative speciation analysis using organic solvent gradients in HPLC-ICPMS

Georg Raber, Reingard Raml, Linda Kuenstl, Walter Goessler and Kevin A. Francesconi

Institute of Chemistry, Karl-Franzens University Graz,
Universitätsplatz 1, 8010 Graz, Austria

Accurate and species-independent quantification with HPLC-ICPMS is a challenging problem when separations are based on gradient elution using organic solvents. In the present work, the change in ICPMS response is equalized by direct introduction of a volatile organic solvent into the thermostatted spray chamber of the ICPMS. This method was tested with a newly developed chromatographic method for the simultaneous separation of anionic arsenic species, oxo- and thio-arsenosugars using a Hamilton PRP-X100 column and applying a methanol gradient from 0-50% (v/v). The accuracy of the gradient compensation method was validated with the BCR 710 oyster tissue candidate reference material.

OP 1.4

Does the edible seaweed Hijiki deal with its arsenic burden via complexation with phytochelatins?

B. Alan Wood[1], Toshikazu Kaise[2], Shinichi Miyashita[2], Andrea Raab[1] and Jörg Feldmann[1]

[1] Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, AB24 3UE, United Kingdom
b.a.wood@abdn.ac.uk
[2] School of Life Sciences, Tokyo University of Pharmacy and Life Sciences, Horinouchi 1432-1, Hachioji, Tokyo 192-0392, Japan

Edible species of seaweed, such as *Arame, Kombu* and *Hijiki*, are considered delicacies in Japan and Asia, and are gaining in popularity within the western world. Seaweeds have long been established as aquatic hyperaccumulators of the highly toxic metalloid arsenic. To deal with this burden, biotransformation of arsenic to organic species such as arsenosugars occurs, resulting in a drastically lower toxicity. However, one major exception to this is *Hijiki*, which stores arsenic mainly as the highly toxic inorganic species arsenate (As(V), $[AsO_4]^{3-}$) and arsenite (As(III), $[As(OH)_3]$). Consequently, Food Standards Agencies in countries including Canada and the United Kingdom have advised against the consumption of Hijiki.

Phytochelatins (PCs), peptides of generic structure $[\gamma\text{-Glu-Cys}]_{2\text{-}4}$-Gly, are synthesised by higher plants to bind toxic metal(loid)s such as cadmium, mercury and arsenic during cellular influx. This results in the formation of complexes such as Cd-PC, Hg-PC and As-PC, which reduces the toxicity relative to the free metal(loid). Recently, we have observed that species of brown and red algae are able to synthesise PCs. Interestingly, only one particular peptide, $[\gamma\text{-Glu-Cys}]_2$-Gly, ($PC_2$) has so far been found during our investigations.

Here, for the first time, we perform a dual chromatographic approach to determine whether As-PC complexes form *in vivo*. 1 % formic acid extraction of seaweed samples, a technique used for the analysis of As-PC complexes in terrestrial plants, was performed on fresh and As-exposed samples of *Hijiki* and *Fucus spiralis*. Speciation analysis via C_{18} RP-HPLC-ICP-MS/ESI-MS, shows that As-PC complexes do not form in vivo for seaweeds. This data is combined with the more traditional arsenosugar analysis, via AEC-HPLC-ICP-MS/ESI-MS which looks at the fate of arsenic during short-term high-concentration As-exposure.

OP 1.5

Introducing the New Agilent 7700 Series ICP-MS; Improved Performance for Speciated Analysis

Peter Planitz[1] and Ed McCurdy[2]

[1] Agilent Technologies GmbH, Hewlett-Packard-Str. 8, 76337 Waldbronn, Germany
peter_planitz@agilent.com
[2] Agilent Technologies UK Ltd., 5500 Lakeside, Cheadle Royal Business Park,
Stockport, Cheshire, SK8 3GR, UK
ed_mccurdy@agilent.com

Agilent ICP-MS systems are widely used for elemental detection in both research and routine speciation analysis, with many examples of applications combined with HPLC, GC and CE. In addition to the commonly-reported applications (such as organo-tin speciation in marine sediments, marine fauna and consumer products, arsenic speciation in food and drinking water, and chromium speciation in environmental samples and building materials), ICP-MS has also proved useful for the measurement of more unusual analytes, notably sulphur, phosphorus and the halogens. Applications include clinical, nutritional, pharmaceutical and environmental monitoring, and the improvement in the capability of ICP-MS to measure these difficult elements has been a key development goal at Agilent.

The completely redesigned, 3rd Generation Octopole Reaction System (ORS3) of the 7700 delivers vastly improved removal of interferences in helium (He) collision mode. This improved interference removal allows many previously difficult elements to be measured at significantly lower detection limits than were previously obtainable, without requiring the use of complex, single-element reaction gas conditions. In particular, the new 7700 cell provides much lower detection limits for S and Se, using the same He mode cell conditions. Significant developments to the RF generator design have also improved the tolerance of the 7700 to volatile organic solvents, allowing rapid gradient elution to be carried out with minimal disturbance of the plasma.

Software integration for speciation applications has also been improved, with fully integrated chromatographic data analysis, including advanced features such as Compound Independent Calibration, Signal to Noise calculation and real-time review during data acquisition.

OP 1.6

Simultaneous Determination of Co(II), Ni(II) and Fe(II) as 4-(2-pyridylazo) resorcinol complex by RP-HPLC

Ayşen Höl and Latif Elçi

Department of Chemistry, Faculty of Science and Art, Pamukkale University,
20017 Denizli, Turkey
aysenhol@yahoo.com

Some of metal ions are the most dangerous pollutants due to their acute toxicity and carcionogenetiy. Exposure to high concentrations of these metal ions causes lung, nasal and throat cancers. Therefore, interest and demand is increasing for metal determination in biological and environmental samples (1). Metal ions were generally determined with atomic absortion spectrophotometry or inductively coupled plasma-atomic emission spectrophotometry. But seperation and simultaneous determination of mixtures of metal ions as their metal chaletes with an organic chelating reagent by reversed-phase high performance liquid chromatography (RP-HPLC) had been accepted in inorganic analysis in recent years (2).

In this study, a reverse phase high performance liquid chromatography method for the seperation and determination of cobalt(II), nickel(II) and iron(II) with PAR chelating on a C18 column was developed. A mixture of methanol-tetrahydrofuran (THF)-water (60:5:35 v/v) containing 5x10-5 mol/L PAR and acetate buffer solution (pH:5) was selected as mobile phase. Co(II), Ni(II) and Fe(II) metal ions react very rapidly with PAR to form pink colored complexes at pH 5. The maximum absorption wavelengths of the chelates are between 483 nm and 517 nm. These metals can be determined by RP-HPLC with spectrophotometric detection at 525 nm.

In this study, the effect of mobile phase pH on the retention time of the chelates, flow rate and PAR concentration of mobile phase are investigated. The calibration curves were prepared for these analysis. The peak areas were used to prepare calibration curve. The lineer range is 50-2000 µg/L for Co(II),10-500 µg/L for Ni(II) and 100-1000 µg/L for Fe(II), respectively. The relative standart deviations for three elements were found below 5%. The chromatographic method was applied to the various samples.

References

(1) Kaur, V., Malik, A. K., A New Method for Simultaneous Determination of Co(II), Ni(II) and Pd(II) as Morpholine-4-Carbodithioate Complex by SPME-HPLC-UV System, *Talanta*, 73, 425-430, 2007.
(2) Chung, Y., Chung, W., Determination of Co(II) Ion as 4-(2-Thiazolylazo) resorcinol or 5-Methyl-4-(2-thiazolylazo) resorcinol Chelate by Reversed-Phase Capillary High-Performance Liquid Chromatography, Bull. *Korean Chem Soc*., Vol. 24, No.12, 1781-1784, 2003.

OP 1.7

Single-drop microextraction as a powerful tool for trace element analysis and speciation

F. Pena-Pereira, M. Costas, S. Gil, I. Lavilla and C. Bendicho

Departamento de Química Analítica y Alimentaria, Área de Química Analítica, Facultad de Química, Universidad de Vigo, As Lagoas-Marcosende s/n, 36310 Vigo, Spain
bendicho@uvigo.es

During last decade, miniaturization of classical approaches for separation and preconcentration has been proposed with the aim of decreasing the volume of the extractant phase. Thus, through miniaturization of classical liquid-liquid extraction (LLE), several techniques have emerged, such as single-drop microextraction (SDME), being the most important, hollow-fibre liquid-phase microextraction (HF-LPME) and dispersive liquid-liquid microextraction (DLLME). Several operations needed for accomplishing applications in speciation analysis such as derivatization, separation, preconcentration and clean-up can be performed in an integrated manner, thus eliminating tedious sample treatments and minimizing errors by losses and contamination.

SDME is a simple, low-cost, fast and virtually solvent-free sample preparation technique based on a great reduction of the extractant phase-to-sample volume ratio. SDME is not exhaustive, and only a small fraction of analyte(s) is extracted/preconcentrated for analysis. This technique can be accomplished in two main modes, i.e. immersed or direct and headspace (HS). Direct-SDME requires the use of a water-immiscible extractant phase, whereas, in principle, HS-SDME allows the use of organic, ionic and aqueous solvents. Volatile analytes or suitable derivatization procedures yielding volatile species are required for the successful application of HS-SDME.

In this work, several examples of SDME methods for ultratrace analysis and speciation using both headspace and immersed approaches along with detection techniques such as ETAAS, ETV-ICPMS, GC-MS, HPLC-UV and UV-Vis spectrophotometry will be discussed.

Acknowledgements: Financial support from the Spanish Education and Science Ministry (project CTQ2006-04111/BQU) is gratefully acknowledged.

References

(1) F. Pena-Pereira, I. Lavilla, C. Bendicho, Miniaturized preconcentration methods based on liquid–liquid extraction and their application in inorganic ultratrace analysis and speciation: A review, *Spectrochim. Acta Part B*, 64 (2009) 1-15.

OP 2.1

The Role of Atomic Fluorescence Spectrometry in Determining Levels of Mercury and Selenium Species in the Environment

Peter B. Stockwell[1], Warren T. Corns[1], Bin Chen[1], Nicholas V. C. Ralston[2] and Laura Raymond[2]

[1] P S Analytical Ltd, Arthur House, Crayfields Industrial Park, Main Road, Orpington, Kent BR5 3HP, UK
[2] Energy & Environmental Research Center, University of North Dakota, Grand Forks 58202, ND, USA

Methyl mercury exposures have long been an environmental concern. The major source of human exposure to methyl mercury is from consumption of fish and shellfish. Numerous studies have reported measurements of the levels of mercury in the environment and foods in an effort to assess the risks associated with exposure. However, most of these studies have not recognised the protective effects of the essential trace element selenium. Mercury has a high affinity for selenium and high exposures to methyl mercury inhibit selenium dependent enzyme activities. Inhibition of these enzyme activities appear to be responsible for most if not all of mercury's pathologic effects, but improved dietary selenium intakes preserve their activities, thereby preventing or reversing the progressive debilitation that would otherwise occur. Reliable measurement of both the mercury exposures and selenium intakes and their resulting tissue concentrations are needed to provide meaningful risk evaluations. Atomic fluorescence spectrometry measurements are ideally suited to provide the measurements of the concentrations and molecular speciation of these elements at the levels of interest in a relatively simple and cost effective manner.

The instrumentation developed for these measurements and results from a range of collaborations with industrial and academic partners will be presented.

OP 2.2

Study of the transformation and localization of Hg species in different sub-cellular fractions of Desulfobulbus propionicus

Romain Bridou[1], Zoyne Pedrero[2], Sandra Mounicou[2], Remy Guyoneaud[1], Mathilde Monperrus[2] and David Amouroux[2]

[1] Equipe Environnement et Microbiologie, CNRS UMR 5254 IPREM, Université de Pau et des Pays de l'Adour, 2 Avenue Pierre Angot, 64053 Pau, France
[2] Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, CNRS UMR 5254 IPREM, Université de Pau et des Pays de l'Adour, 2 Avenue Pierre Angot, 64053 Pau, France

Bacterial methylation is one of the major process which transform inorganic mercury Hg(II) into toxic monomethylmercury MeHg. The methylation potential of some bacteria, as well as their MeHg assimilation potential could be directive to evaluate their impact on the ecosystem. However, the Hg methylation mechanisms by bacteria are still poorly understood and further investigations are required to better understand the fractionation of mercury species between the cellular compartments and the metabolic pathways involved. The advantages of the use of multiple isotopic tracers can be exploited in order to study the localisation (partitioning) and the origin of the different mercury compounds after incubation.

In this work, a pure bacterial strain Desulfobulbus propionicus MUD10 (DSM 6523) was incubated during 90 hours under sulphate reducing conditions in presence of isotopically labeled mercury species (100 µg g-1 of ^{199}Hg(II) and 10 µg g-1 of ^{201}MeHg). Hg speciation analyses in each sub-cellular fraction (membranes, cytoplasm) were carried out by GC-ICP-MS, and quantification was performed by reverse species-specific isotope dilution analysis. Ultrasound probe sonication and French press were used for the extraction of soluble cytoplasmic mercury-containing proteins and efficiencies of both methods were compared. Size Exclusion Chromatography-ICP-MS was investigated to obtain mercury-containing proteins patterns in cytosolic extract.

This study confirms the use of isotopically labeled Hg species as a valuable tool to follow their transformations due to metabolic process.

OP 2.3

Metabolism of metal(loid)s by intestinal microorganisms

Roland A. Diaz-Bone[1] *and Tom Van de Wiele*[2]

[1] Institute of Environmental Analytical Chemistry, University of Duisburg-Essen, Universitätsstraße 3-5, 45141 Essen, Germany
roland.diaz@uni-due.de
[2] Laboratory of Microbial Ecology and Technology, University of Gent, Coupure Links 653, 9000 Ghent, Belgium

Methylation and hydrogenation of metal(loid)s by microorganisms are widespread and well-known processes in the environment, by which mobility and in most cases toxicity are significantly enhanced in comparison to inorganic species. Though the human gut contains a highly diverse and active microbiocenosis, little is known about the occurrence and importance of this process in the human intestine. Therefore, both in vivo and in vitro studies were conducted to elucidate the metabolism of metal(loid)s by intestinal microorganisms.

First, in vivo studies with human probands were conducted. Following administration of bismuth subcitrate, trimethylbismuth was detected by GC-ICP-MS in blood, exhaled air as well as fecal matter. Both the relative distribution of trimethylbismuth as well as the kinetic of the methylation process indicated that the methylation predominantly occurs in the human intestine.

In order to compare the capability of intestinal microorganisms towards volatilization of different metal(oid)s (Ge, As, Sn, Sb, Te, Hg, Pb and Bi) as well as the nonmetal selenium, further studies were conducted using an in vitro gastrointestinal model, the Simulator of the Human Intestinal Ecosystem (SHIME), both due to both ethical and experimental considerations. Comparative experiments using fresh fecal matter were conducted. These experiments clearly showed that intestinal microorganisms are capable to volatilize As, Se, Te, Sb and Bi from inorganic species.

In dependence on the element concentration and the part of the large intestine simulated, different species were detected. In addition to methylated species of Se, Te, Sb and Bi, surprisingly the formation of the highly toxic arsine (AsH3) was found. In addition to these compounds, a range of high-boiling arsenic and selenium species was detected. By simultaneous elemental (ICP-MS) and molecular detection (EI-MS) hyphenated to gas chromatography, these compounds were identified as mixed Se/S, As/S as well as As/Se compounds. Five of these species have not been described in environmental or human matrices before.

These results suggest that the intestinal microbiota can significantly increase the mobility and toxicity of orally ingested metal(loid)s. We therefore conclude that the role of the intestinal microbial community in metal(loid) biotransformation needs to be further addressed to assess to what extent this metabolic potency may pose health hazards to the human body. Further studies are necessary to investigate the extent of this process as well as the availability of metal(loid)s from different sources for microbial transformations.

OP 2.4

Alkylation of mercury by isolated microorganisms from the gut of Eisenia foetida

Burkhard Knopf, Elisabeth Kaschak and Helmut König

Institute for Microbiology and Wine Research, Johannes Gutenberg University,
Becherweg 15, D- 55128 Mainz, Germany
e.kaschak@web.de

The qualitative speciation and determination of organomercury compounds at ultra trace levels are of special interest, because toxicity, bioavailability and detoxification depend mainly on the chemical form of this element. Alkylated mercury species can cross the blood-brain barrier and cause heavy intoxifications. Much is known about the mercury circle of aquatic systems and the microbial methylation but less about the bioavailability in soil and the effect on soil feeding invertebrates. The circle of mercury in soil is of special interest because of a high methylation potential by microorganisms. Mainly sulphate reducing bacteria are responsible for the methylation of mercury. This omnipresent of microorganism in the gut of soil living and feeding invertebrates is a way to alkylate mercury and accumulate higher concentrations of organomercury compounds. As an invertebrate model organism the annelidae Eisenia foetida was chosen. First studies of the potential alkylation of mercury by the model organism show an increase of methylmercury in the tissue of the worm.

For this reason aerobic and anaerobic microorganisms were isolated and different microbiological methods were used to produce pure cultures. Following to the isolation these cultures were screened for their potential to alkylate inorganic mercury.

The speciation of the alkylated mercury species in the biological samples were done by GC-ICP-MS. For this water soluble organomercury compounds were transferred into peralkylated by a derivatization with sodium tetra-(n-propyl)-borate and extracted with hexane.

OP 2.5

Arsenic uptake and translocation via xylem sap – the cucumber model

Kalle Uroic[1], Pascal Salaün[2] and Jorg Feldmann[1]

[1] Department of Chemistry, University of Aberdeen,
Meston Walk, Aberdeen AB24 3UE, UK
[2] Earth and Ocean Sciences Department, University of Liverpool,
Brownlow Street, Liverpool L69 3GP, UK

Understanding the processes involved in the arsenic uptake by plants from contaminated soils to the roots and the subsequent arsenic translocation from roots to fruits are of fundamental importance either for food safety aspects or phytoremediation purposes.

In this work, cucumbers were chosen because not only they are easily and rapidly grown but they also produce high amount of xylem sap. The xylem is a tissue network that transports water from the roots up to the leaves and is thus an important pathway for metal transport. Cucumbers were grown hydroponically in a nutrient Hoagland solution for three weeks before being subjected to different concentrations (100, 500 and 1,000 µg/kg) of inorganic (As(III) and As(V)) and organic (MMA and DMA) arsenic for 24h. After decapitating the cucumbers, the excreted xylem sap was collected for 1 hour. Roots, shoots and leaves were separated and digested. Electrochemistry was used to monitor the concentration of As(III) and total inorganic arsenic in the Hoagland solution during the contamination period. The total As concentration in the Hoagland, roots, stems and leaves were measured by ICP-MS. The arsenic speciation in sap and nutrient solution was determined by anion HPLC-ICP-MS while complexes from the root extracts were analyzed by RP-HPLC-ICP-MS/ESI-MS.

When subjected to As(V), As(III) was detected in the nutrient solution after c.a. 30 minutes suggesting a reducing mechanism either within the plants by arsenate reductase and subsequent excretion or within the rhizosphere. The total arsenic concentration in the different parts of the cucumber was dependent on the arsenic species in the Hoagland solution. Inorganic arsenic was found at higher levels in the roots but less in the shoots and leaves compared to plants subjected to organic arsenic. High levels of arsenic were always found in the roots as phytochelatins PC3 and PC4 complexes when subjected to inorganic arsenic. While less organic arsenic is taken up by the roots, it is transported more into shoots and leaves than inorganic arsenic which remains immobilized as PC complexes in the roots. Interestingly, the amount of collected sap was found to decrease significantly in presence of increasing levels of inorganic arsenic in the Hoagland solution. In the sap, it was found that plants subjected to organic arsenic transport unchanged species in the sap whereas plants subjected to either As(V) or As(III) transport arsenic as As(III). In that case, no complexes but only the free As(III) were detected by HPLC-ICP-MS/ESI-MS, as observed in previous studies (1).

Is As(III) really free or is it present as weak complexes which are unstable in the chromatographic column? It is hoped that electrochemistry will shed some light on this fundamental question.

References

(1) Raab, A.; Schat, H.; Meharg, A. A.; Feldmann, J., Uptake, translocation and transformation of arsenate and arsenite in sunflower (Helianthus annuus): formation of arsenic-phytochelatin complexes during exposure to high arsenic concentrations. *New Phytologist* 2005, 168, (3), 551-558.

OP 2.6

Uptake and toxicity of hexafluoroarsenate in aquatic organisms

Birgit Daus[1], Holger Weiss[1] and Rolf Altenburger[2]

UFZ - Helmholtz Centre for Environmental Research,
Departments [1] Groundwater Remediation and [2] Bioanalytical Ecotoxicology,
Permoserstrasse 15; 04318 Leipzig, Germany
birgit.daus@ufz.de

The arsenic species hexafluoroarsenate has been described as a surface water contaminant of anthropogenic origin. A method for species analysis of this compound was developed using ion pair chromatography coupled with ICP-MS (1).

Data about the ecotoxicological effects of hexafluoroarsenate are lacking in the literature. Taking into account its use as pesticide, it can be expected to show some bioactive potential. The objective of this study therefore was to characterize the eco-toxicological effects of hexafluoroarsenate with respect to aquatic organisms. Next to performing a screening of bioactivity against standard sentinel organisms (an algal one generation reproduction assay using Scenedesmus vacuolatus, determination of luminescence inhibition in the bacterium Vibrio fischeri, disturbance of Daphnia magna motility, and effect determination on Danio rerio egg development), we were interested to study the uptake of hexafluoroarsenate and understand its ecotoxicologically relevant properties in comparison to arsenite or arsenate. In particular, possible biotransformation by species analysis and investigation on the mode of action are of interest to conclude about possible detoxification mechanisms and to assess the ecotoxicological potential of hexafluoroarsenate (2).

The observed effects were evoked at high ambient concentrations and thus the ecotoxic potential was found to be low in comparison to other arsenic compounds. The most sensitive organism was the unicellular green alga Scenedesmus vacuolatus with an EC50 value of 1.15 mmol L-1 (86 mg L-1 As). Nevertheless, the internal dose was of interest to evaluate the effect mechanism. A linear relationship between ambient and internal concentration was found for this organism with a slope of 1.63 µmol mmol-1. The uptake seems to be limited. However, the internal concentration which shows a significant effect, e.g. 20 % of inhibition of reproduction, was found to occur at a low internal dose of 0.98 µmol L-1 (73.5 µg L-1 As).

Using arsenic speciation analysis with HPLC-ICP-MS, now other arsenic species were detected inside the algae. Consequently, no biotransformation takes place by the algae.

References

(1) Daus, B., Tümpling, W. v., Wennrich, R., Weiss, H., 2007. Removal of hexafluoroarsenate from waters. *Chemosphere* 68, 253 – 258.
(2) Daus, B., Weiss, H., Altenburger, R. (2009): Uptake and toxicity of hexafluoroarsenate in aquatic organisms. *Chemosphere*, submitted.

OP 2.7

Antimony: the facts – or maybe not

Montserrat Filella[1,2]

[1] Institut F.A. Forel, University of Geneva,
Route de Suisse 10, CH-1290 Versoix, Switzerland
montserrat.filella@unige.ch
[2] SCHEMA, Rue Principale 92, L-6990 Rameldange, Luxembourg
filella@schema.lu

Antimony first attracted public attention in the mid-1990s amid claims that it was involved in Sudden Infant Death Syndrome. A substantial number of papers have now been published on the element and its behaviour in the natural environment. However, many key aspects of the environmental chemistry of antimony remain poorly understood. These include critical areas such as its ecotoxicology, its global cycling through different environmental compartments, and what chemical form it takes in different environments. Moreover, the comprehensive analysis of what has been published on antimony shows that some generally accepted facts (e.g., the relative toxicity of Sb(V) versus Sb(III)) are based on very few evidences or that studies in some areas have a limited reliability just because simple solubility-related considerations have been ignored (e.g., ecotoxicity) or speciation in culture media not taken into account (e.g., biomethylation). All these aspects will be discussed in this communication.

OP 3.1

Combined ESI and ICP-MS approach for the quantification of bio-molecules using natural element tags

Daniel Pröfrock and Andreas Prange

GKSS Research Centre, Institute for Coastal Research, Marine Bioanalytical Chemistry,
Max Planck Str. 1, 21502 Geesthacht, Germany
daniel.proefrock@gkss.de

The quantification of proteins or peptides as well as their post translational modified counterparts represents an ongoing challenge within the field of bio- analysis. The utilization of ICP-MS for the determination of covalently bound (hetero)elements, which are naturally present in nearly all proteins, or which have been introduced via chemical reactions, represents an emerging strategy within the field of absolute protein or peptide quantification.

Reversed phase LC is the method of choice for the separation of peptides. Unfortunately even at low flow rates, as used in nano or capillary-LC, changes in the elemental response with changing gradient composition due to carbon related effects on the ionization behavior of an element can be observed, which complicates accurate quantification.

Capillary LC hyphenated to ICP-MS has been used for the element specific detection of the separated peptides. The developed instrumental setup utilizes a matched reversed gradient sheath flow, which is mixed post column with the flow of the RP column. Due to the mixing of both gradients a stable elemental response over the whole chromatographic separation has been achieved, which is an essential pre-requisite for the application of ICP-MS for quantification of phosphorylated peptides via their hetero(atom) content, especially when no matched calibration standards are available or in general when utilizing mono isotopic element tags for quantification.

In addition capillary LC-ESI-QTRAP-MS has been used to identify and to elucidate the tag stoichiometry of the separated peptides.

In comparison to other techniques the developed instrumental setup helps to maintain a constant elemental response during the whole chromatographic separation and therefore eliminates gradient related effects. For the separation of a model peptide retention time and peak area RSDs of 0.05% and 7.6% respectively have been obtained (n=6). Detection limits for phosphorus of 6.24 µg L-1 which corresponds to 6.24 pg P have been realized. Simple inorganic phosphorus standards have been used for the quantification of either model peptides or tryptic protein digests. The expected as well as the quantified values were in good agreement resulting in calculate recoveries of 93 % (tryptic digests) or 102 % (model peptides) indicating the potential of the proposed setup for quantitative peptide analysis.

This approach helps to overcome the problems related with the application of mono-isotopic element-tags and ICP-MS for bio-molecule quantification.

OP 3.2

Absolute and Relative Protein Quantification with the Use of Isotopically Labelled p-Hydroxymercuribenzoic Acid and Complementary MALDI- and ICP-MS Detection

Daniel J. Kutscher and Jörg Bettmer

University of Oviedo, Department of Physical and Analytical Chemistry,
C/ Julián Clavería 8, E-33006 Oviedo, Spain
bettmerjorg@uniovi.es

Chemical labelling with subsequent mass spectrometric detection represents a common approach for protein quantification. Whereas most methods make use of stable isotope labels from naturally elements like ^{2}D, ^{13}C, ^{15}N, or ^{18}O, artificially introduced metals have gained interest as alternative markers. This work presents the application of p-hydroxymercuribenzoic acid (pHMB) as labelling reagent for cysteine-containing proteins. As proof of concept, insulin was chosen as model protein and two different workflows were employed to its absolute and relative quantification with the use of complementary MALDI-MS and ICP-MS. Based on the synthesis of isotopically labelled ^{199}Hg-pHMB, and thus, on the label-specific isotope dilution concept, a differential labelling procedure can be either applied to the comparative study of two different samples (relative quantification) or to the absolute quantification of insulin. In both cases, final detection by MALDI-MS followed by isotope pattern deconvolution was applied to extract the quantitative data from the mass spectra. Good agreement with the expected values was obtained for the relative insulin quantification, and the recovery for insulin applying the absolute quantification workflow was between 90 and 110 % with a RSD better than 5 % in the fmol and pmol range.

OP 3.3

Analysis of Gd-based MRI contrast agents and potential transmetallation products in human body fluids

Lena Telgmann[1], Jens Künnemeyer[1], Faruk Tokmak[2] and Uwe Karst[1]

[1] Institute of Inorganic and Analytical Chemistry, University of Münster, Corrensstr. 30, 48149 Münster, Germany
[2] Marienhospital, KfH-Nierenzentrum, University of Bochum, Cruismannstr. 37, 44807 Bochum

Contrast agents for magnetic resonance imaging based on Gadolinium (Gd) are complexed with polyaminocarboxylic acid chelating agents. These complexes have very high thermodynamic stability constants, but a connection between the medication with Gd-based contrast agents and a newly observed disease called nephrogenic systemic fibrose has been proposed. It has been postulated that transmetallation reactions with parental iron or oral chromium supplements play a role in its pathogenesis. A separation technique for Gd chelates and potential transmetallation products is presented. The separation efficiency of capillary electrophoresis for ionic compounds is combined with the high resolution of time-of-flight mass spectrometry. In blood plasma three ionic Gd-based contrast agents Gd-DTPA, Gd-BOPTA and Gd-DOTA have each been added to different iron supplements, iron salts or chromium salts respectively. The samples were analysed by CE/ESI-ToF-MS. Iron transmetallation products have been detected in the samples that contained one of the iron salts and either of the contrast agents Gd-DTPA or Gd-BOPTA, but not in the samples with iron supplements. A transmetallation reaction is in general possible, but a direct connection between the medication with parental iron supplements after the treatment with Gd-based contrast agents and NSF cannot be proven. Gd-DOTA showed no transmetallation at all. Its macrocyclic structure leads to a higher stability compared to complexes based on linear ligands (Gd-DTPA and Gd-BOPTA). The samples containing chromium picolinate or chromium chloride did not lead to transmetallation as well. A connection between a medication with chromium in any binding form and NSF cannot be shown at all.

Speciation of labile metal biomolecule complexes – not always a job for hyphenated mass spectrometric techniques

Jörg Feldmann

TESLA (Trace Element Speciation Laboratory)
University of Aberdeen, College of Physical Science, Chemistry, Meston Walk
Aberdeen AB24 3UE, Scotland ,UK

The determination of biomolecules containing metals using chromatography coupled to elemental mass spectrometry is very attractive. The reason for that is the species-unspecific response of ICP-MS. The problem is however, if the metals are not covalently bound to the biomolecules.

In this lecture a couple of new quantification and identification strategies for metalloproteins in real samples will be presented.

The first study is generating a copper and zinc isotopically-enriched superoxide dismutase (SOD) which has been used to quantify SOD in liver homogenates using 2 D chromatography ICPMS (1) and GE-LA-ICPMS. It will be made clear that this approach is only feasible when worked under non de-naturing conditions.

The second study is highlighting that hyphenated techniques are not always successful for the detection of metal protein complexes. This will be demonstrated for metal complexes of calprotectin, the most abundant protein in neutrophils. Here the imaging of metals and proteins in addition to the structural features give first identification of the impossible involvement of such metal complexes in biota. Techniques such as 2 D imaging using laser ablation ICPMS and MALDI-TOF-MS as well as histopathology will be shown for an infection caused by the antibiotic-resistant Staphyllococcus aureus (2).

References

(1) C.L. Deitrich, A. Raab, B. Pioselli, J. Thomas-Oates, J. Feldmann, Chemical preparation of an isotopically enriched superoxide dismutase and its characterisation as a standard for species-specific isotope dilution analysis, *Anal. Chem.* (2007) 79, 8381-8390.

(2) BD Corbin, EH Seeley, A Raab, J Feldmann, MR Miller, VJ Torres, KL Anderson, BM Datillo, PM Dunman, R Gerads, RM Caprioli, W Nacken, WJ Chazin, ER Skaar, Metal chelation as a defence strategy to prevent bacterial growth in tissue abscesses, *Science*, (2008) 319, 962-965.

OP 3.5

Determination of ferrocene-derivatized phytochelatins by LC/ESI-MS and LC/ICP-MS

Susanne Bomke[1], Anja Bräutigam[2], Thorben Pfeifer[1], Wolfgang Buscher[1], Dirk Wesenberg[2], Gerd-Joachim Krauss[2] and Uwe Karst[1]

[1] Institute for Inorganic and Analytical Chemistry, University of Münster, Corrensstrasse 30, 48149 Münster, Germany
[2] Institute of Biochemistry and Biotechnology, Ecological and Plant Biochemistry, Martin-Luther University Halle-Wittenberg, Kurt-Mothes-Strasse 3, 06120 Halle/S., Germany

Plants evolved numerous strategies to deal with heavy metals that represent both essential nutrients (e.g. Zn, Cu, Fe) and toxic agents (e.g. Cd, Pb, Hg). Plants react to Cd stress by synthesis of metal coupling thiol rich peptides, so called phytochelatins (PCs).

PCs are glutathione-derived peptides with the general primary structure (γ-Glu-Cys)n-Gly. The amount of γ-Glu-Cys units depends on the organism and metal exposure time. The peptides are able to bind metals such as Cd via coupling by thiol groups, according to the HSAB concept. Thus, toxicity as well as the detoxification of the metal is connected to its affinity to sulfhydryl groups.

Former studies have shown a broad variety of PC and iso PCs synthesized in C. reinhardtii after Cd exposition (Bräutigam et al. Analytical and Bioanalytical Chemistry, submitted). Up to now, a suitable method for the precise quantification of phytochelatins does not exist. Therefore, a new method for the quantitative determination of phytochelatins in the green alga Chlamydomonas reinhardtii is presented. This alga appears in fresh water and soil. The polar peptides were derivatized using a ferrocene-based derivatizing agent. Hereby, the cysteine residues react quantitively with a maleimide group to form the corresponding stable thioethers. Through this derivatizing process unpolar reaction products are formed which are suitable for the separation on reversed phase columns.

The labeled biomolecules are characterized by liquid chromatography (LC) coupled with electrospray ionization (ESI) and inductively coupled plasma (ICP) mass spectrometric (MS) detection. Several PCs and PC Isoforms extracted from C. reinhardtii could be derivatized, separated and identified using RP-HPLC with coupled ESI-MS. As complementary data, ICP-MS measurements show a high potential for absolute quantification.

OP 3.6

Size characterized manganese- and iron species in sprague-dawley rats exposed to $MnCl_2 \cdot 4\ H_2O$ (i.v.)

J. Diederich[1,2] and B. Michalke[1]

[1] Helmholtz Zentrum München, Institute of Ecological Chemistry,
Ingolstädter Landstraße 1, D-85764 Neuherberg, Germany
[2] Universität Münster, Institute of Food Chemistry,
Corrensstrasse 45, D-48149 Muenster, Germany

Continuous manganese (Mn) exposure leads to damage of the central nervous system and finally to a Mn dependent Parkinsonism, also called “manganism”. However, the exact mechanism, how Mn can enter the brain without using the transferrin-receptor mediated transport, is still unknown. Excessive Mn load can cause an overflow of the liver and an overload of the original Mn carriers (e.g. transferrin or serum albumin). In that case, low molecular mass (LMM) compounds can act as ligands and form stable Mn-complexes. These LMM Mn species (above all Mn-citrate) probably cross the blood-brain barrier and accumulate in the brain (basal ganglia). Iron (Fe) is discussed as a co-factor of the manganese dependent neurodegeneration specifically because it represents the main competitor in the formation of Mn species.

The rat is a well established experimental animal for exposure experiments and the adequate analogy of the blood-brain barrier is quite sufficient to investigate its characteristics regarding the permeability of Mn- and Fe species. The current research therefore investigated the size distribution of the Mn- and Fe species of the original Mn- and Fe carrier of unexposed rats fed with a high manganese and iron standard diet as the first characterization step. Subsequently Mn- and Fe species analysis of exposed sprague-dawley rats (one-time i.v. injection of up to 1 mg Mn per kg body weight and four days incubation) fed with a low Mn- and Fe special diet (2 weeks pre-feeding) are supposed to improve the understanding of the homeostasis of allegedly harmful LMM Mn species. The special diet provides comparable low Mn- and Fe body levels and accordingly an enhanced Mn absorption in all rats. Unexposed animals (controls) were analyzed after injection of the same infusion solution without Mn. In all experiments the animals were anesthetized and killed painless. The organs and body fluids were frozen in liquid nitrogen for further investigations. After homogenizing under liquid nitrogen and cleaning up the samples under inert gas (Ar), the different rat tissue extracts and sera were size-characterized (eluent pH=7.4). These methodical parameters were found to be the optimum conditions with regard to species stability and quality assurance. The size exclusion chromatography coupled on-line to an inductively coupled plasma – dynamic reaction cell - mass spectrometer (SEC-ICP-DRC-MS) offers a valuable tool for speciation analysis of labile Mn- and Fe species. The recovery was determined by ICP-optical emission spectroscopy (ICP-OES).

The investigation of different tissues (e.g. brain, kidney, liver and lung) and sera could assign the organic Mn- and Fe species to a molecular mass between 80-160 kDa. However, nearly each sample showed a minor signal at the retention time according to probably harmful LMM-Mn-species (<1000 Da) and inorganic Mn and Fe respectively. This finding may be discussed either due to a chemical equilibrium between high- and low molecular mass species in the sera and accordingly tissue extracts, or due to a degradation of native Mn species. However, polyatomic interferences (e. g. Ar-N-H, Ar-O, Ar-O-H according to the mass ^{55}Mn, ^{56}Fe, ^{57}Fe) which are removed to a large extent by DRC cannot be completely excluded.

OP 3.7

Mercury speciation analysis for the investigation of the interaction of thimerosal with blood components

Björn Meermann[1], Stefan Trümpler[1], Wiebke Lohmann[1], Michael Sperling[1,2], Wolfgang Buscher[1] and Uwe Karst[1]

[1] Institute for Inorganic and Analytical Chemistry, University of Münster, Corrensstrasse 30, D-48149 Münster, Germany
[2] European Virtual Institute for Speciation Analysis, Mendelstrasse 11 48149 Münster, Germany, MS@speciation.net

We investigated the interaction of thimerosal, an ethylmercury-containing preservative used in some vaccines, with blood components. For this reason we incubated physiological simulation solutions and model proteins with thimerosal, methyl mercury and mercury (II) chloride. Speciation analysis, using the hyphenated techniques LC/ICP-MS and LC/ESI-MS was applied to gain element-selective and molecular information. The complementary use of element-selective and molecular speciation techniques allowed the identification of EtHg-biothiol adducts under physiological conditions (1).

References

(1) Trümpler S., Lohmann W., Meermann B., Buscher W., Sperling M., Interaction of Thimerosal with proteins-ethylmercury adduct formation of human serum albumin and ß-lactoglobulin A, *Metallomics* **2009**, 1, 87-91.

OP 4.1

Development of a Coupled Diffusion Denuder System Combined with GC–MS for the Separation and Quantification of Molecular Iodine and Activated Iodine Compounds (ICl, HOI) in the Marine Atmosphere

Ru-Jin Huang and Thorsten Hoffmann

Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany
t.hoffmann@uni-Mainz.de

This study concerns the development of a coupled diffusion denuder system capable of separating and quantifying gaseous molecular iodine (I_2) and two other highly reactive iodine species, ICl and HOI, which are collectively named activated iodine compounds (AIC). Both I_2 and AIC are key species in the atmospheric chemistry of iodine. 1,3,5-trimethoxybenzene (1,3,5-TMB) and α-cyclodextrin/$^{129}I^-$ (α-CD/$^{129}I^-$) coated denuders proved to be suitable for the collection of gaseous AIC and I_2, respectively. The experimental collection efficiencies for AIC (tested as ICl) and I_2 agreed well with the theoretical values for gas flow rates in the range between 300 and 1800 mL min^{-1}. The coupled denuder system (1,3,5-TMB-coated denuder as front-denuder coupled upstream of an α-CD/$^{129}I^-$-coated denuder) was applied successfully to separate test gas mixtures of ICl and I_2 at various mixing ratios in the laboratory. The operation of both denuder systems was demonstrated to be independent of relative humidity (0–100%) and storage period (at least 2 weeks prior to and after sampling). Detection limits were achieved at sub parts-per-trillion-by-volume (sub-pptv) level. The presented method provides a reliable and practical approach for the speciation of gaseous iodine compounds. In addition, we report for the first time ambient air measurements of AIC mixing ratios, carried out at the atmospheric research station in Mace Head, Ireland. A maximum concentration of AIC of 30.2 pptv was observed for nighttime measurements and 6.0 pptv for daytime measurements. A similar diurnal pattern was found for I_2 with an average concentration level of 23.2 pptv during daytime and 85.1 pptv during nighttime, indicating a strong correlation with AIC.

Application of stripping voltammetry to the speciation of dissolved Zinc and Cobalt in the Southern Ocean

Oliver Baars and Peter L. Croot

IFM-GEOMAR, FB2: Marine Biogeochemistry,
Düsternbrooker Weg 20 24105 Kiel, Germany
obaars@ifm-geomar.de

We report the application of voltammetric stripping analysis to the chemical speciation of the bio-essential trace metals (1) Zinc and (2) Cobalt in seawater samples from the Southern Ocean. The samples were collected from February – April 2008 on transects along the Zero Meridian south of Africa and through the Drake Passage during the Polarstern expedition ANT24-3 as part of the IPY project GEOTRACES.

Zn speciation information was obtained by anodic stripping voltammetry (ASV) with a thin mercury film rotating glassy carbon disc electrode (TMF-RGCDE). Zn ligands and their complex stability constants were determined by Zn titration of the sample. Complementary Pseudopolarograms were recorded with unaltered seawater from selected bottles. Overall we analysed the Zn speciation from 6-8 bottles distributed over the whole water column at each of 8 stations along the two transects. Labile Zn (Zn') along with free Zn (Zn2+) was high and unlikely to limit primary productivity during the time of study. In the Zn rich Southern Ocean waters the major fraction of Zn binding ligands was present as Zinc complexes.

For Co speciation a modification of an existing catalytic cathodic stripping voltammetry (CSV) detection with Dimethylglyoxime (DMG) was developed. The new method represents an alternative to the conventional catalysis with Nitrite opening a way around the large amount of Nitrite salts needed (e.g. 0.5 mol/L) thus reducing the risk of metal contamination and additionally alleviating experimental uncertainty caused by a change of the ionic strength. Currently experiments are being performed concerning the catalysis mechanisms. We are working towards a full mechanistic understanding of the processes involved in the catalytic Co determination with CSV. Results of this ongoing work shall be presented at this time.

Influence of metal concentration and the presence of competing cations on europium and gadolinium speciation with humic acid analysed by CE-ICP-MS

Ralf Kautenburger

Institute of Inorganic and Analytical Chemistry and Radiochemistry, Saarland University, Campus C4.1, 66123 Saarbrücken, Germany
r.kautenburger@mx.uni-saarland.de

Nowadays, there is a broad consensus on the technical merits of the disposal of high-level nuclear waste (HLW) in deep and stable geological formations. For the safety assessment of a waste disposal it is important to understand the radionuclide migration in the near- and far-field of a repository caused by an incident. In this environment, natural organic matter such as humic substances can play an important role by their complexation behaviour for metal ions.

Capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry (CE ICP-MS) has been used to study the complexation behaviour of Eu and Gd (as homologues of the actinides americium and curium) with humic acid. The influences of lanthanide concentration as well as the presence of competing cations like Ca, Mg and Al on the HA-complexation have been analysed (1).

The lanthanide speciation by CE-ICP-MS reveals weak and strong HA binding sites for the used trivalent lanthanides subject to the given lanthanide concentration. The influence of the competing alkaline earth ions can be assumed as relevant at very high concentrations only while aluminium at already low concentration represents a strong competitor to Eu and Gd in HA-complexation, and may affect toxic metal speciation and thus metal mobility in the geological barrier of a future disposal.

The author thanks the BMWi for financial support (grant no. 02 E 9683 and 02 E 10196).

References

(1) R. Kautenburger (2009) *J. Anal. At. Spectrom.* DOI: 10.1039/B904107A.

Detection of the ultra trace Isotope U-236 using High Resolution Resonance Ionisation Mass Spectrometry

S. Raeder[1], S. Fies[1], K. Wendt[1], N. Trautmann[2] and J. V. Kratz[2]

[1] WA LARISSA, Institute of physics, Johannes Gutenberg University, D-55099 Mainz
[2] Institute of nuclear chemistry, Johannes Gutenberg University, D-55099 Mainz

The detection of the ultra trace isotope ^{236}U in uranium containing samples provides information about origin and history of the contamination. The long living radionuclide ^{236}U is produced from ^{235}U by neutron capture and the low natural neutron fluxes results in natural isotope ratios ^{236}U / $^{238}U < 10^{-10}$. A significant enhancement of this isotope indicates a neutron exposition and therefore an anthropogenic origin of the sample. The determination of the ^{236}U / ^{238}U – ratios by selective mass spectrometry in a region with anthropogenic uranium contamination allows for the study of the migration behaviour of elemental uranium species in the environment.

The method of High Resolution Resonance Ionization Mass Spectrometry (HR-RIMS) combines a selective laser-ionization with the mass resolution of commercial mass spectrometers. Due to the electron structure of the atomic shell it is possible to ionize evaporated uranium atoms isotopes selective using narrow bandwidth cw-lasers. For ^{236}U an optical three step excitation and ionization scheme is applied and a quadrupol mass filter is used for mass selection an suppression of surface ions. The method competes in abundance sensitivity with AMS.

First analytical measurements with synthetic samples demonstrate a selectivity > 10^8 and an efficiency > $5 \cdot 10^{-7}$ for the whole system. In a linear arrangement of ion optic and quadrupol mass filter the selectivity is limited by background from neutral uranium atoms at a level of 10^{-7} compared to resonant laser ions. The detection system was thus upgraded by a 90°-deflector to separate the laser ions from the remaining neutral atoms resulting in a corresponding reduction of the background. Measurements of certified samples and first measurements of environmental samples are foreseen. Furthermore the development of a direct sample injection, which allows a coupling of the RIMS-technique to chromatographic and electrophoretic methods, will be discussed. The status of the development and concepts for improvement of the system will be presented as well as the foreseen application.

OP 4.5

Soil mercury speciation: Chemical reagents applied for the metal extraction

Nongrat Issaro and Alain Bermond

Laboratoire de chimie analytique, AgroParisTech,
16 rue Claude Bernard 75213 Paris, France

Mercury speciation, aiming at quantitative identification of the metal species in a medium, provides useful information in toxicological, bioavailable and biogeochemical terms that are inaccessible even with only total mercury determination. We are particularly interested in soil because it is considered as a sink for punctual polluted sources and for deposited atmospheric mercury. Accordingly, this environment becomes an important provenance of mercury in plants, ground waters, rivers, and atmosphere (re-emission). However, it is crucial to note that although the “key” to speciation determination is the appropriate choice of reagent used in extraction step, neither specific extractants nor standard protocols exist for the isolation of particular soil-mercury forms. Consequently, a sequential extraction approach with its operational interpretation is widely referred in literature while a single extraction study, more specific approach, seems to be rare.

By using the single extraction approach, several reagents, based on their stability constant with the target metal, such as EDTA, DTPA, cysteine and sodium-thiosulfate, were selected for extracting mercury in our experiments. Besides, all possible interferences caused by such reagents and soil matrix had been studied. We found that the extraction of mercury was independent on the stability constant values, probably due to high organic matter content in the soil samples. Among these reagents, sodium-thiosulfate seems to be relatively the best soil-mercury extractant. As the matter of fact, we demonstrated the favoured reagent and its convenient operational conditions for soil mercury extraction. Finally, once the pertinent chemical reagent had been defined, a kinetic fractionation methodology and its associated experimental results were also applied as a specifying tool for soil mercury mobility.

Keyword: contaminated soil; kinetic fractionation; mercury; single extraction, speciation.

Speciation and surface complexation modelling of Np(V) sorption on montmorillonite

T. Reich[1], S. Amayri[1], S. Dierking[1], B. Baeyens[2], R. Dähn[2], M. H. Bradbury[2] and A. C. Scheinost[3]

[1] Institute of Nuclear Chemistry, Johannes Gutenberg Universität Mainz, 55099 Mainz, Germany
treich@uni-mainz.de
[2] Laboratory for Waste Management, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[3] Institute of Radiochemistry and Rossendorf Beamline at ESRF, Forschungszentrum Dresden-Rossendorf, 01314 Dresden, Germany

The sorption of Np(V) on Na-montmorillonite (STx-1) has been studied by batch experiments, spectroscopic measurements, and surface complexation modelling with the aim to contribute toward a better understanding of the sorption of ^{237}Np ($t_{1/2}$ = 2.1 × 10^6 a) in the near field (bentonite backfill material) and far field (argillaceous rocks) of high-level nuclear waste repositories. Batch experiments were performed in the absence of inorganic carbon and under air-equilibrated conditions with 0.1 and 0.01 M $NaClO_4$ as background electrolyte, 8 × 10^{-12} and 9 × 10^{-6} M Np(V), and 3 ≤ pH ≤ 10. At pH > 8 the presence of inorganic carbon has a strong influence on the sorption behavior of Np(V) due to the formation of aqueous Np(V) complexes with carbonate.

Neptunium LIII-edge extended X-ray absorption fine structure (EXAFS) measurements on Np(V)/montmorillonite samples with Np(V) loadings in the range of 0.3-3.5 µmol/g have been performed to determine the speciation of Np at the solid-liquid interface. The EXAFS spectra of samples prepared under ambient air conditions (p_{CO2} = $10^{-3.5}$ atm) revealed the formation of Np(V)-carbonate complexes at the montmorillonite surface.

The results of the batch experiments obtained under CO_2-free conditions could be modeled using the two site protolysis non-electrostatic surface complexation and cation exchange (2SPNE SC/CE) model described in (1). For modeling the sorption behavior of Np(V) on montmorillonite in the air-equilibrated system, the aqueous complexation of Np(V) with carbonate (2) was included and the following additional surface complexation reaction was required: $\equiv SOH + NpO_2^+ + CO_3^{2-} <> \equiv SONpO_2CO_3^{2-} + H^+$.

References

(1) M.H. Bradbury and B. Baeyens, Modelling the sorption of Mn(II), Co(II), Ni(II), Zn(II), Cd(II), Eu(III), Am(III), Sn(IV), Th(IV), Np(V) and U(VI) on montmorillonite: Linear free energy relationships and estimates of surface binding constants for some selected heavy metals and actinides, *Geochim. Cosmochim. Acta* 69, 875-892, 2005.
(2) Chemical Thermodynamics of Neptunium and Plutonium, (Eds. J. Fuger et al.) *Elsevier*, Amsterdam 2001.

OP 5.1

Conforming to Legislation on Chromium Speciation in Toys

Shona McSheehy, Torsten Lindemann and Meike Hamester

Thermo Fisher Scientific, Hanna-Kunath Str. 11, 28199 Bremen, Germany
shona.mcsheehy@thermofisher.com

Legislation is primarily implemented to protect the environment and the health of the consumer. Directives therefore often impose maximum allowable concentrations (MACs) of elements in specific matrices where higher concentrations are deemed to be a threat to the environment or the health of the population at large. With the recognition that physicochemical properties such as toxicity are strongly related to the chemical form of an element, the regulation of chemical species is becoming more commonplace. One of the most regulated species is hexavalent chromium. In European legislation alone it is regulated in automobiles, cement, workplace atmospheres, waste electrical equipment and packaging components.

Very recent legislation (European Toys Safety Directive (88/378/EEC)) is now imposing limits for hexavalent and trivalent chromium along with a number of elements and organic tin in children's toys. The limits are called migration limits and refer to the amount of element or elemental species that can migrate from the toy to the child when the toy is being used in an appropriate (not dangerous) fashion. The imposed levels for chromium species in the directive are shown in Table 1.

Species	mg/kg in dry, brittle, powder-like or pliable toy material	mg/kg in liquid or sticky toy material
Chromium (III)	37.5	9.4
Chromium (VI)	0.04	0.01

Table 1. Migration limits from toys or components of toys that shall not be exceeded

An extraction procedure was performed for a number of toy materials to establish whether the toy indeed contains any Cr species. Different 'extraction' approaches which then aim to mimic a 'migration' situation have been developed and applied. For the separation and determination of chromium species, an HPLC-ICP-CCT-MS method that had previously been tested for mineral waters was employed. The instrumental methodology was validated using a CRM and the extraction procedures were evaluated with species spike recoveries.

OP 5.2

The knowledgement of metal chemical speciation is of paramount importance on removing and recovering metals from industrial effluents

Manuela D. Machado[1,2], Eduardo V. Soares[1,3] and Helena M. V. M. Soares[2]

[1] Chemical Engineering Department, Superior Institute of Engineering from Porto Polytechnic Institute, Rua Dr António Bernardino de Almeida, 431, 4200-072 Porto, Portugal
[2] REQUIMTE-Department of Chemical Engineering, Faculty of Engineering of Porto University, Rua Dr. Roberto Frias, s/n, 4200-465 Porto, Portugal
[3] IBB-Institute for Biotechnology and Bioengineering, Centre for Biological Engineering, Universidade do Minho, Campus de Gualtar 4710-057, Braga, Portugal

One major prerequisite in the treatment procedures of matrix containing metals is the knowledge of metal chemical binding forms in solution and their impact on water technology.

With the aim to develop a clean (without residues) and low cost process for removing metals from real electroplating effluents followed by a selective recovery of metals (copper, chromium, nickel and zinc), a multistage process, which combines biosorption and chemical methodologies, was implemented. Under this context, the knowledge of metal chemical speciation on (i) removing metals from the effluent using flocculent cells of Saccharomyces cerevisiae and (ii) recovering selectively metals from the ashes of the contaminated biomass was of fundamental importance.

The influence of the real matrix of effluents on the removal of heavy metals by bioremediation with Saccharomyces cerevisiae was evaluated by analysing metals chemical speciation and validated through the bioremediation of a real electroplating effluent. From this work, we concluded that (i) carbonates, chlorides, fluorides, phosphates and nitrates in effluents do not compete with biomass for copper, nickel and zinc ions; (ii) sulphates can compete with biomass for nickel and (iii) high concentrations of fluorides, phosphates and sulphates can reduce the efficiency of bioremediation of effluents with chromium, at pH 6.0. Additionally, the importance of metal chemical speciation on the optimization of the treatment of real effluents was also demonstrated. Several guidelines for modelling the best experimental conditions for bioremediation of real effluents containing multi-elements (copper, chromium, nickel and zinc) will be presented and discussed during the communication.

Additionally, the selective recovery of the three metals was achieved, with high yield and purity, from the ashes of the contaminated biomass after acid digestion of the ashes followed by the electro deposition of Cu and then alkalinisation of the solution: (i) metallic copper (recovery: 99.9%; purity: 99.7%) (ii) nickel as nickel hydroxide (recovery: 99.98%; purity: 80.6%) and (iii) zinc as tetrahydroxozincate (recovery: 95.7%; purity: 99.98%). Here, again, the knowledge of metal chemical speciation was fundamental for designing the best experimental conditions for selective recovery of nickel and zinc.

Acknowledgment: Financial support by Foundation for Science and Technology (FCT) of Portuguese Government (Project POCTI/CTA/47875/2002) with FEDER funds, are gratefully acknowledged. Manuela D. Machado is also gratefully acknowledged for a grant scholarship financed under the same project and anothergrant from FCT (SFRH/BD/31755/2006).

OP 6.1

Speciation of Arsenic species in marine products by HPLC-ICP-MS

Martijn van der Lee, Elly Wijma and Hans Mol

RIKILT Institute of food safety, Bornsesteeg 45 – building 123,
6708 PD Wageningen, the Netherlands
Martijn.vanderlee@wur.nl

In general, speciation of arsenic species is known for several years and wide a scope of analytical methods have been developed since then. A number of publications have been written on the speciation of arsenic compounds in drinking waters, marine products and plant materials (e.g. 1-2). However the number of publications on arsenic speciation in animal feed products is limited, while e.g. seaweed and algae are often used as feed ingredient. This contribution describes the method development based on HPLC separation of the species and the ICP-MS detection of organic and inorganic arsenic species in fishery products and seaweed based animal feed products.

European legislation on arsenic species in fishery products is lacking. Maximal residue level (MRL) for fruit and vegetables is based on total amount of arsenic and is 0.1 mg/kg product. In animal feed the legislation on total and inorganic arsenic are given by EU2003/100 for compound feed based on fish and fishery products, or feed products based on seaweed. The maximal residue level for inorganic arsenic (some of As^{3+} and As^{5+}) in these feed products is 2 mg/kg.

Speciation of organic and inorganic arsenic is usually done by using an unselective extraction method combined with a LC-ICP-MS. Concentrations of the inorganic species, As^{3+} and As^{5+}, can be summed mathematically afterwards, however our preference is the chemical conversion of As^{3+} to As^{5+} by redox reaction with hydrogen peroxide during the extraction before HPLC separation. The chromatography was therefore optimized for the As^{5+} separation and the ICP-MS was used for arsenic detection. The total amount of inorganic arsenic was expressed as As^{5+}. The total As concentration was determined by a second measurement using the ICP-MS.

200 mg seaweed (or compound feed) is weighted and 10 ml 0.07 Molar HCl prepared in 10% H_2O_2 is added. The sample was placed in the microwave (600 W) at 90ºC for 25 minutes. The extract was centrifuged and 100 µl was analysed on an HPLC equipped with an anion PRP-X100 column. Eluting compounds were detected on the online coupled ICP-MS. Performance of the method and quality control was done using seaweed and fish tissue reference materials, respectively BCR-279 and TORT-2.

Organic and inorganic arsenic species in marine products were successfully extracted with 0.07M HCl prepared in 10% H_2O_2 and analysed with LC-ICP-MS. The concentrations inorganic arsenic in seaweed and compound feed were between 0.1 and 1 mg/kg, i.e. always below the MRL. Total As contents were in seaweed in the range from 20 to 40 mg/kg (n=12) and for compound feed 1 to 10 mg/kg (n=13).

References

(1) J.J. Sloth and K. Julshamn, Survey of total and inorganic arsenic content in blue mussels from Norwegian fiords: Revelation of unusual high levels of inorganic arsenic, *J. Agric. Food Chem.* 2008, 56, 1269-1273.
(2) A.A. Meharg, C. Deacon, R.C.J. Campbell, A.-M. Carey, P.N. Williams, J. Feldmann and A. Raab, Inorganic arsenic levels in rice milk exceed EU and US drinking water standards, *J. Environ. Monit.* 2008.

Determination of triorganotin compounds in Sea Foods by using CE-ICP-MS

GuiDi Yang[1,2] *JinHua Xu*[1], *LiangJun Xu*[1], *JinPing Zheng*[1] *and FengFu Fu*[1]

[1] Key Laboratory of Analysis and Detection Technology for Food Safety of Ministry of Education, and Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, China
[2] College of Life Sciences, Fujian Agriculture and Forestry University, Fuzhou 350002, China

For environmental studies, speciation is of major interest in organotin analysis, since the organotin's toxicity is strongly dependent on the species. Therefore, it is very important to develop a sensitive and accurate analytical method for the quantification of organotin compounds (OTCs) in aquatic organisms.

So far, the main techniques employed to the speciation analysis of OTCs are based on the combination of separation techniques such as GC or LC and sensitive, selective detectors. To our knowledge, no information about the use of CE-ICP-MS for the analysis of triorganotin compounds has been reported in the literature.

In this study, a microwave-assisted extraction used to extract trace triorganotin compounds from aquatic organisms, and as well as a sensitive method for the analysis of ultratrace triorganotin compounds, namely trimethyltin (TMT), triethyltin (TET), tripropyltin (TPT) and tributyltin (TBT), with capillary electrophoresis - inductively coupled plasma mass spectrometry (CE- ICP-MS) were described in this study. The CE-ICP-MS analytical method has a much lower detection limit of 0.2-0.7 ng Sn/mL for TMT, TET, TPT and TBT, and can be used to determined trace TMT, TET, TPT and TBT in aquatic organisms directly without any derivatization and preconcentration. With the help of the above methods, we have successfully determined TMT, TET, TPT and TBT in dried Mya arenaria Linnaeus and *Corbicula fluminea* within 17 min with a RSD (relative standard deviation, n=6) <5% and a recovery of 93-104%.

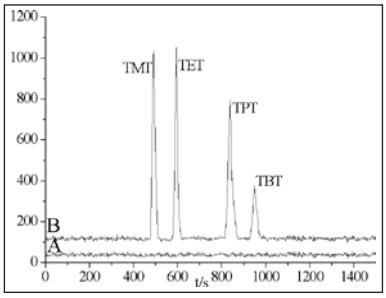


Figure 1.
Electropherograms of TMT, TET, TPT, TBT and reagent blank. (A) Blank; (B) Mixed standard solution.

Acknowledgements: We thank Fujian Provincial Department of Science and Technology for supplying our financial support (2005HZ1009, 2008Y0034).

OP 6.3

Species Analysis of Platinum Based Cytostatic Drugs

Christine Brauckmann, Björn Meermann and Uwe Karst

Institute of Inorganic and Analytical Chemistry, University of Münster,
Corrensstr. 30, 48149 Münster, Germany
christine.brauckmann@uni-muenster.de

Cisplatin is frequently used as an efficient drug in chemotherapy for germ cell tumours, osteosarcoma and neuroblastoma. Unfortunately, it also causes serious side effects like nephrotoxicity and ototoxicity. The reasons for those side effects are not associated with reactions of cisplatin with the DNA, which was thoroughly investigated in the past. It is still unclear, which interactions of cisplatin in the human body cause the toxic effects. Particular reactions with Pearson soft thiols are proposed and proven. Therefore, we investigate the interactions of cisplatin with biologically relevant thiols under different physiological conditions.

Cisplatin is a highly reactive substance. Therefore the reaction between blood constituents and cisplatin does strongly depend on the reaction conditions. Hence, the kind and concentration of buffer salts in the reaction medium and the LC mobile phase were important as well as the pH value. Yet the most important parameter is the chloride concentration in the reaction mixture, because a high chloride concentration improves the stability of cisplatin, which affects the reaction behaviour of the platinum complex.

We present a high performance liquid chromatography (HPLC) separation of cisplatin and the respective adducts, which were formed with biologically relevant thiols. We identified these adducts by means of HPLC coupled to electrospray ionization mass spectrometry (ESI-MS) detection. The coupling of HPLC to inductively coupled plasma mass spectrometry (ICP-MS) detection allows quantifying the platinum amounts matrix and species independent.

OP 6.4

Speciation and bioaccessibility of selenium in wheat grain from a seleniferous area and derived products

Francesco Cubadda[1], Federica Aureli[1], Silvia Ciardullo[1], Marilena D'Amato[1], Andrea Raggi[1], Cristina Sola-Larrañaga[2], Raghunath Acharya[3] and Tejo Prakash Nagaraja[4]

[1] Department of Food Safety and Veterinary Public Health, Istituto Superiore di Sanità, 00161 Rome, Italy
francesco.cubadda@iss.it
[2] Department of Chemistry and Soil Science, University of Navarra, Pamplona, Spain
[3] Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai, India
[4] Department of Biotechnology & Environmental Sciences, Thapar University, Patiala, India

Samples of wheat *(Triticum aestivum)* collected in the Nawanshahr-Hoshiarpur Region (Punjab, India) showed the highest selenium concentration ever recorded in grains for human consumption. The aim of this study was to assess the identity and content of the selenocompounds potentially bioavailable in wheat-based items consumed by the population of this seleniferous area.

Wheat flour and chapati bread were produced from a batch of high-Se wheat grown locally. In order to investigate the fate of the different selenocompounds along wheat processing up to simulated human digestion, total Se and Se speciation in wheat, derived products and in vitro gastrointestinal digests were assessed. The determination of selenium species was carried out after enzymatic extraction by HPLC-ICP–DRC–MS with three separation mechanisms (reversed phase, cation exchange, and anion exchange) in order to cross-check the identification of the different selenocompounds by retention time matching with authentic standards. Chapati was submitted to in vitro enzymolysis and detailed information on the different Se species released was obtained by two-dimensional chromatography. Size exclusion chromatography was used for isolation of selenium containing fractions, which were further characterized by HPLC-ICP–DRC–MS and off-line electrospray tandem mass spectrometry in an attempt to identify the selenocompounds generated during gastrointestinal digestion.

The investigation of Se speciation and bioaccessibility in wheat-based products from the seleniferous belt of the Nawanshahr-Hoshiarpur Region provided useful data for risk assessment of selenium exposure in that area. On the other hand, such information will be used to evaluate if and how local grains can be used to supplement the mammalian diet in many areas that are deficient in selenium.

OP 6.5

Arsenic and Mercury Speciation: Chromatographic ICP-MS Methods for the U.S. National Biomonitoring Program, Centers for Disease Control & Prevention (CDC)

Carl P. Verdon[1†], Christopher G. K. Freedman[2], Cynthia D. Ward[2], Mark Fresquez[2], Kathleen L. Caldwell[1] and Robert L. Jones[1]

[1] Inorganic Radiation & Analytical Toxicology Branch, National Center for Environmental Health, Centers for Disease Control & Prevention (CDC)
[2] Battelle Memorial Institute, 4770 Buford Highway NE, Atlanta, Georgia 30341, USA
[†]cverdon@cdc.gov

As a member laboratory of the CDC's National Biomonitoring Program (www.cdc.gov/ exposurereport), we recently reported (Caldwell KL et al., 2009. J Expos Sci Env Epidem 19:59-68) the measurement of speciated arsenic concentrations in 2,568 human urine specimens from the National Health and Nutrition Examination Survey (www.cdc.gov/ NHANES), multi-year study whose purpose is to follow changes in the health of the U.S. population by moni¬toring hundreds of health indices including many blood and urine analytes. Our arsenic spe-ciation method (Verdon CP et al., 2009. Anal Bioanal Chem 393:939-947) measures seven spe-cies of arsenic commonly found in human urine (arsenate, arsenite, dimethylarsenite, monomethylarsonate, arsenocholine, trimethylarsine oxide, and arsenobetaine). This high performance liquid chromatography (HPLC) method uses a gradient elution anion-exchange column (Hamilton PRP-X100®) coupled to a PerkinElmer "ELAN DRCII" inductively-couple plasma mass spectrometer (ICP-MS) with a Dynamic Reaction Cell® (DRC) using 10% H_2/Ar to eliminate polyatomic interference by ArCl at m/z 75. This method has been shown to be accurate per comparisons with SRM target values, and exhibits long term reproducibility by our QA/QC program criteria (Caudill SP et al., 2009. Statistics in Medicine 27: 4094-4106). The method incorporates an external 6-port, 2-position programmatically-activated switching valve (Rheodyne) with an inline sample loop which is used for post-column injection of the arsenic-containing internal standard. This configuration allows the internal standard peak to be placed anywhere in the chromatogram. Urinary speciated arsenic data obtained from the analysis of NHANES samples showed a direct relationship between total urine arsenic and arsenobetaine concentrations. Additionally, our laboratory has two methods for speciation of inorganic mercury (InHg), methyl mercury (MeHg) and ethyl mercury (EtHg) in human whole blood. The first is a HPLC-ICP-MS method using a cation-exchange column (Phenomenex "Luna® SCX", 4.6x150 mm). The HCl digested blood sample is diluted with L-cysteine and 2-mercaptoethanol, centrifuged and the supernatant analyzed by HPLC-ICP-MS. An external switching valve introduces the internal standard (methyl mercury) in the same manner as is done with arsenic speciation. The spray chamber is replaced with a desolvation device (ESI APEX Q) to improve analyte signal intensity. Our second method uses a species-specific iso-tope dilution (SSID) technique with gas chromatography (GC) coupled to ICP-MS to analyze whole blood for InHg, MeHg and EtHg species. Blood spiked with enriched $CH_3{}^{200}Hg$, $C_2H_5{}^{201}Hg$, and ^{199}Hg is solubilized in tetramethylammonium hydroxide (TMAH) then derivatized using sodium tetra(n-propyl)borate (Na-TPB) at pH 5. Volatile propylated Hg species are adsorbed onto a solid-phase microextraction (SPME) fiber which is injected into a splitless 200°C sample port of a PerkinElmer "Claris" GC. Species are separated on a PerkinElmer "Elite-5" (crossbond 5% diphenyl/95% PDMS) 30 m column using a 2.0 mL/min He flow rate and a 75–250°C temperature ramp. A PerkinElmer "ELAN DRCII" ICP-MS con¬nected to the GC exit port by way of a 150°C transfer line (Hyphenated Solutions) detects Hg masses. Mass bias and dead-time corrected isotope peak ratios are used in a isotope ratio deconvolution algorithm (Applied Isotope Technologies) to mathematically correct for in situ species interconversion. Various problems were solved, most notable were 1) the idiosyncratic appearance of a large Hg^0 peak apparently coming from thermal depropylation of the derivatized inorganic Hg species, and 2) large amount of contaminating mercury in reagent blanks. Switching buffers (sodium acetate to ammonium citrate) and SPME fibers (carboxy-PDMS to PDMS) solved these problems. We intend to use this method to study the potential problem of Hg species interconversion during sample collection, transport and extended storage.

CE-DAD-ICP-MS for determination of complex formation constants for the complexation of lanthanides and actinides with humic substances

E. Gromm, R. A. Buda and J. V. Kratz

Institute for Nuclear Chemistry, Johannes Gutenberg University Mainz,
Fritz-Strassmann-Weg 2, 55128 Mainz, Germany

The investigation of complex formation constants for the humic acid complexation of actinides and, as model substances, lanthanides, is of interest with respect to the deep geological disposal of radioactive waste. In most aquatic systems and also in clay formations, natural organic matter such as humic substances (HS) is present. These HS can act as ligands for metal ions and thus have an influence in the speciation and migration of radionuclides.

In earlier studies, it has been shown that the CE-ICP-MS (1) as well as CE-DAD-ICP-MS (2) coupling can be applied for the investigation of the complexation behaviour of metal ions with HS. The different species are separated by CE and detected by DAD and ICP-MS. By application of pressure onto the CE capillary during the separation it is possible to detect both the cationic and anionic species at the exit of the capillary. The free metal ions and metal containing HS species can be measured with a low limit of detection by ICP-MS, whereas the HS as well as some EOF markers can be detected by DAD due to their light absorption. For calibration purposes and to identify the species, iodine marked humic acid can be used and easily detected by both detectors.

Due to the dissociation of the metal-humate complex, the interpretation of resulting electropherograms is complicated. Besides the cationic free metal ions and the anionic metal humate complex, there is another species consisting of initially complexed metal. It is supposed that these metal ions are dissociated from „weak binding sites“ of the humic substance caused by the high electric field under CE separation conditions. By lowering the concentration of metal ions, the complexation at „weak binding sites“ is likely to play a minor role. Thus, a more precise determination of complex formation constants should become possible.

For a standard (Aldrich) humic acid, a combination of ultrafiltration to determine the loading capacity LC as a function of pH, with CE is being used to obtain reliable log β values. For fulvic acid, ultrafiltration is not feasible and the aim of the present study is to determine both the loading capacity and log β values by CE.

References

(1) R. Kautenburger, K. Nowotka, H. P. Beck, *Anal. Bioanal. Chem.* **2006**, *384*, 1416-1422.
(2) E. Gromm, diploma thesis, Johannes Gutenberg-University, Mainz **2008**.

Trace Analysis of Neptunium with Resonance Ionization Mass Spectrometry

Nils Stöbener[1], Tina Gottwald[2], Sebastian Raeder[2], Gerd Passler[2], Tobias Reich[1], Norbert Trautmann[1] and Klaus Wendt[2]

[1] Institute of Nuclear Chemistry, University of Mainz, Fritz-Strassmann-Weg 2, D-55128 Mainz, Germany
[2] Institute of Physics, University of Mainz, Staudingerweg 7, D-55128 Mainz, Germany

After a storage time of more than 1000 years, the radiotoxicity of spent nuclear fuel is mainly determined by long-lived isotopes of plutonium and the minor actinides neptunium, americium and curium. Hence, safety assessments of possible nuclear waste repositories must consider the geochemical behaviour of these elements.

Under natural conditions, neptunium can occur in the tetra- or pentavalent state. Depending on its oxidation state, neptunium has different migration properties. While Np(V) has a high mobility in aquatic systems, Np(IV) is much less soluble and has a strong tendency towards sorption on host materials. Speciation studies are therefore important to understand the migrational behaviour of neptunium. Very sensitive methods for the detection of neptunium are required, since the concentrations in aquatic systems of a nuclear waste repository are expected to be less than 10-10 mol/L.

We have developed a method for the sensitive detection of the long-lived isotope ^{237}Np ($T_{1/2}$ = $2.14 \cdot 10^6$ a) applying resonance ionization mass spectrometry (RIMS). In RIMS, laser light is used to produce neptunium ions by three-step resonant excitation and ionization of neutral neptunium atoms. Because of the uniqueness of optical transitions, this ionization process is element specific. In our setup, three titanium-sapphire lasers provide light for excitation and photo-ionization of neptunium atoms. The resulting neptunium ions are detected subsequently in a quadrupole or time-of-flight mass spectrometer.

Since only few energy levels for a multi-step excitation and ionization of ^{237}Np have been known, extensive spectroscopic studies had to be carried out. These studies led to the identification of suitable energy levels for a three-step excitation and ionization of ^{237}Np and will be presented in detail.

As a future application in speciation analysis, it is planned to use capillary electrophoresis coupled off-line with RIMS for the speciation of the different oxidation states of neptunium at ultratrace level.

Two of us (N.S. and S.R.) thank the Deutsche Forschungsgemeinschaft (Graduiertenkolleg 826) for financial support.

PO 1.3

Speciation analysis of antimony (III) and antimony (V) in water samples by dispersive liquid-liquid microextraction (DLLME) combined with electrothermal atomic absorption spectrometry

Seyed Reza Yousefi[1], Farzaneh Shemirani[1] and Mohammad Reza Jamali[2]

[1] School of Chemistry, University College of Science, University of Tehran, Tehran, Iran
[2] Department of Chemistry, Payam Noor University, Behshahr, Iran

Dispersive liquid- liquid microextraction (DLLME) technique combined with electrothermal atomic absorption spectrometry (ET-AAS) was proposed for determination of antimony specie at very low concentration in water samples. N-benzoyl-N-phenylhydroxylamine (BPHA) was used as chelating agent for Sb(III), and chloroform and ethanol were used as extraction and disperser solvent, respectively. In order to determine the Sb(V) concentration, it reduced to Sb(III) by L-cysteine, then the concentration of Sb (V) was indirectly calculated by subtracting of Sb(III) from total antimony. The effect of various experimental parameters on the extraction and determination was investigated. Under the optimum conditions the calibration graph was linear over the range of 0.02- 0.8 μg L^{-1}. The relative standard deviations (R.S.Ds.) were 3.8% for Sb(III) and 4.1% for total Sb (C = 0.4 μg L^{-1}, n = 8), respectively. The enrichment factor (EF) was 188 and the detection limits (3σ) were 0.005 μg L^{-1} for Sb(III) and 0.008 μg L^{-1} for total Sb.

The developed method has been applied successfully to the determination of Sb(III) and Sb(V) in natural water samples.

Iodine speciation in marine aerosols along a 30,000 km round-trip cruise path from Shanghai, China to Prydz Bay, Antarctica

Senchao Lai[1,3], Thorsten Hoffmann[1] and Zhouqing Xie[2]

[1] Institute of Inorganic and Analytical Chemistry,
Johannes Gutenberg University, Mainz, Germany
senchao.lai@mpic.de
[2] Institute of Polar Environment, University of Science and Technology of China, Hefei, China
thoffmann@uni-mainz.de
[3] Atmospheric Chemistry Division, Max Planck Institute for Chemistry, Mainz, Germany

Iodine chemistry plays an important role in the tropospheric ozone depletion and the new particle formation in the Marine Boundary Layer (MBL). The sources, reaction pathways, and sinks of iodine in MBL are not fully understood. Therefore, it is essential to detect and characterize the various iodine species in the sea water, marine air and aerosols.

An online coupling technique of ion chromatography coupled to Inductively Coupled Plasma-Mass Spectrometry (IC-ICP-MS) and its application in water soluble iodine speciation in marine aerosol samples are present. Iodide, iodate and an unidentified iodine species were detected in the marine aerosols (Total suspended particles, TSP) samples, which were collected onboard a round-trip cruise from Shanghai, China to Prydz Bay, Antarctica from November 2005 to March 2006. ICP-MS was also used to measure the total amount of soluble iodine fraction in the samples.

The results reveal that soluble organic iodine (SOI) is the most abundant fraction, accounting for approximately 70 % of total soluble iodine (TSI) on average. One unidentified organic iodine (UOI) signal was present in almost all of the samples and was responsible for up to 38.3% of TSI. The abundance of inorganic iodine species, iodate and iodide, was less than 30% of TSI. Iodide was significantly correlated with SOI Suggesting a link between iodide formation and SOI decomposition. TSI levels varied considerably over the length of the voyage. In the coastal Antarctic enhanced level of TSI were found to be correlated with the air mass transport from the ice front sector.

PO 1.5

Speciation analysis and preconcentration of Tl in water samples using solid phase extraction by cation exchange resin and electrothermal atomic absorption spectrometry

Ján Medveď[1], Peter Matúš[1], Milan Kališ[1], Ingrid Hagarová[1], Marek Bujdoš[1], Jana Kubová[1] and Pavel Diviš[2]

[1] Comenius University in Bratislava, Faculty of Natural Sciences,
Mlynská dolina 1, 842 15 Bratislava, Slovakia
matus@fns.uniba.sk
[2] Brno University of Technology, Faculty of Chemistry,
Purkyňova 118, Královo Pole, 612 00 Brno, Czech Republic

Thallium is a heavy, very toxic metallic element, which occurs in earth´s crust in an estimated abundance from 0.1 to 0.8 $mg.kg^{-1}$. In the environment, it is mainly combined with other elements (primarily oxygen, sulfur, halogens, potassium and rubidium) in inorganic compounds. During the weathering processes it can be mobilized by aqueous media and accumulated in sediments and soils. The main sources of pollution nowadays come from anthropogenic emissions from refineries, coal-fired power stations, mining activities, metal smelters and the cement industry (1).

Thallium exists in natural waters as either Tl(I) (thallous) or Tl(III) (thallic) species. The oxidation state of Tl affects its complexation and subsequent bioavailability and toxicity in the environment. Thallium content in surface waters is within the range 1-82 ng l^{-1}. Due to this low contents of Tl in water samples, it is necessary to combine the laboratory separation, preconcentration and determination techniques for the purpose of Tl speciation analysis (1).

The scope of the presented work was to use an solid phase extraction (SPE) for the separation and preconcentration of Tl species in water samples followed by the determination using electrothermal atomic absorption spectrometry (ET AAS). In this method, Tl(III) was stabilized by formation of a Tl(III)-DTPA complex. Tl(I) species remained in its original form. These two species were then separated by using a cation exchange resin Amberlite IR120 and nitric acid as the eluent in a batch SPE protocol. The potential interferences of Fe (III), Al, Ca, Mg and other metals were investigated. The optimized experimental conditions for separation/preconcentration step (pH 2-3, time 15 min, temperature 60 °C) and Zeeman ET AAS determination (chemical modifier Pd + ascorbic acid, atomization temperature 2100 °C) (2) were used for the speciation analysis of thallium in filtered acid water samples from open quartzite mine in the Banská Štiavnica – Šobov region (Slovakia) where an acid mine drainage is present mainly as a product of pyrite oxidation (2). For both Tl species the preconcentration factor about 40 was achieved, LOD and LOQ were 25 and 90 ng l^{-1}, the calibration curve was linear from 75 ng l^{-1} to 25 µg l^{-1}, the precision expressed by a RSD ranged from 3 to 19 %. The accuracy of analytical results was checked by the analyte addition technique and by analysis of water CRM samples.

References

(1) M. Kališ, P. Matúš, M. Bujdoš, J. Medveď, *Chem.* Listy 101 (2007) 782-789.
(2) J. Medveď, M. Kališ, P. Matúš, M. Bujdoš, J. Kubová, *Chem.* Pap. 62 (2008) 168-175.

The work was supported by Slovak Research and Development Agency under the contracts No. LPP-0038-06, LPP-0188-06, SK-CZ-0044-07 and LPP-0146-09, by Scientific Grant Agency of Ministry of Education of Slovak Republic and the Slovak Academy of Sciences under the contracts No. VEGA 1/4463/07, VEGA 1/4464/07 and VEGA 1/0272/08 and by Ministry of Education, Youth and Sports of Czech Republic under the contract No. MEB 080813.

PO 1.6

Speciation analysis of inorganic antimony in natural waters using the combination of extraction procedures and electrothermal atomic absorption spectrometry

Ingrid Hagarová[1], Peter Matúš[1], Jana Kubová[1], Marek Bujdoš[1] and Pavel Diviš[2]

[1] Comenius University in Bratislava, Faculty of Natural Sciences,
Mlynská dolina 1, 842 15 Bratislava, Slovakia
matus@fns.uniba.sk
[2] Brno University of Technology, Faculty of Chemistry,
Purkyňova 118, Královo Pole, 612 00 Brno, Czech Republic

The aim of the present work was to propose an optimal procedure for the speciation analysis of inorganic antimony in drinking and natural waters prior its determination by electrothermal atomic aborption spectrometry (ET AAS).

Solid phase extraction (SPE) using nano-sized titanium dioxide (which has a high surface area/body weight ratio, high adsorption capacity, and strong coordination of titanium) was used for the separation and preconcentration of total inorganic antimony. Three different modes for the separation, preconcentration and determination of inorganic antimony can be compared: (I) direct TiO_2-slurry ET AAS sampling after adsorption of antimony onto TiO_2, (II) batch mode with the elution of antimony from TiO_2 by a mixture of EDTA and HNO_3, and (III) minicolumn system using TiO_2 with the elution by a mixture of EDTA and HNO_3. Some advantages and drawbacks of these three procedures are discussed and evaluated. Direct TiO_2-slurry sampling offers relatively easy preparation but the high attention has to be pay to the stability of TiO_2-slurry and a serious problem with the damage of a graphite tube leads to the worst reproducibility. Batch mode is the most laborious (tending to the higher risk of sample contamination) but in spite of that it offers higher reproducibility than direct TiO_2-slurry sampling mode. Minicolumn system is flexible, since different initial volumes of a sample can be used (resulting in different enrichment factors and detection limits), reuse of the column is possible after regeneration and high reproducibility is achieved. Briefly, all three procedures are effective for the separation and preconcentration of inorganic antimony in water samples.

Cloud point extraction (CPE) was used for selective separation and preconcentration of inorganic Sb(III) species. After their complexation with ammonium pyrrolidinedithiocarbamate (APDC), the analyte was quantitatively extracted to the surfactant-rich phase in the non-ionic surfactant octyl phenoxy polyethoxy ethanol (Triton X-114). Then the surfactant-rich phase separated by the centrifugation was diluted by HNO_3/ethanol to reduce its high viscosity and the concentrated analyte was introduced into graphite tube of ET AAS. The effects of pH, extraction temperature, extraction and centrifugation time, ionic strength, potential interferents and APDC, Triton X-114, HNO_3 and ethanol concentrations on obtained results were investigated also.

The accuracy of the both optimized methods was checked by certified reference material (CRM) for trace elements in riverine water SLRS-4 (for CPE, the reduction of Sb(V) to Sb(III) with L-cysteine was firstly made). Finally, the proposed methods were used for the speciation analysis of inorganic antimony in drinking and natural waters.

The work was supported by Slovak Research and Development Agency under the contracts No. LPP-0038-06, LPP-0188-06, SK-CZ-0044-07 and LPP-0146-09, by Scientific Grant Agency of Ministry of Education of Slovak Republic and the Slovak Academy of Sciences under the contracts No. VEGA 1/4463/07, VEGA 1/4464/07 and VEGA 1/0272/08 and by Ministry of Education, Youth and Sports of Czech Republic under the contract No. MEB 080813.

CE-ICP-MS as speciation technique to analyze the complexation behavior of Europium, Gadolinium and Terbium with organic ligands

Christina Möser, Ralf Kautenburger and Horst P. Beck

Institute of Inorganic and Analytical Chemistry and Radiochemistry, Saarland University, Campus C4.1, 66123 Saarbrücken, Germany
c.moeser@mx.uni-saarland.de

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 the project europium, gadolinium and terbium as homologues of americium, curium and berkelium were used and their sorption and desorption behavior onto Opalinus clay was studied. 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 behavior could interfere the sorption of metal ions onto Opalinus clay. In addition to humic acid (HA) we used in Opalinus clay natural appear organics like lactate, formiate or propionate. Therefore, we investigated the complexation behavior of the metals with NOM.

As a selected technique, capillary electrophoresis (CE) was hyphenated with inductively coupled plasma mass spectrometry (ICP-MS). With this method, both the uncomplexed metal ions and metal organic complexes can be simultaneous detected in one analysis step.

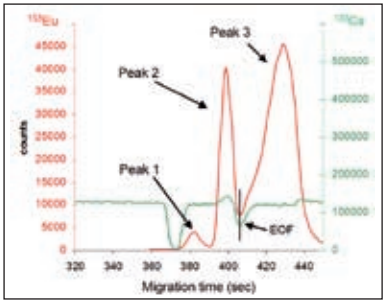


Figure 1.
Typical electropherogram of uncomplexed and HA-compexed Eu species and Cs as CE flow marker.

Figure 1 shows a typical electropherogram with three Eu species. The first signal (peak1) represents the uncomplexed metal before CE separation. The aquatic Eu^{3+} ion was complexed with the acetate in the electrolyte buffer und migrates during the separation as $EuAc^{2+}$ towards the CE cathode. Peak 2 and peak 3 pictured the HA complexed metal ions. The difference between peak 2 and peak 3 is caused by the stability of the bindings. During the separation the weak bound Eu^{3+} dissociates out of the HA complex and migrates as peak 2 towards the cathode.

The authors thank the BMWi for financial support of the project through grant no. 02 E 10196.

PO 1.8

Development of an on-line method for the determination of I2 by using time-of-flight aerosol mass spectrometry

Michael Kundel, Mathias Schott, Marco Ries and Thorsten Hoffmann

Institute for Inorganic and Analytical Chemistry, University of Mainz,
Duesbergweg 10-14, 55112 Mainz, Germany

Over the past few years, the influence of iodine species on the marine atmospheric chemistry has been investigated. Recent studies show that iodine species are involved in the tropospheric ozone depletion, the formation of new particles in the marine boundary layer (MBL) and the enrichment of iodine in the marine aerosol. In their evolution marine aerosols can act as cloud condensation nuclei. Thus aerosols have an indirect effect on the Earth´s radiative budget and consequently on the Earth´s climate.

Molecular iodine (I_2) and biogenic iodocarbons (e.g. CH_3I, CH_2I_2) that are released into marine atmosphere by algae and phytoplankton are suggested to be the most important precursors for reactive iodine in the MBL. During daylight these compounds are rapidly photolyzed to I atoms which then react with ozone to produce IO. Further reactions of IO lead to the formation of higher iodine oxides. Due to their low vapour pressure higher iodine oxides play an important role in the formation of new particles in coastal marine environments.

However, it is still an analytical challenge to identify and quantify reactive iodine containing key compounds. In the present work we describe the development of an on-line method for the determination of molecular I_2 using time of flight aerosol mass spectrometry (ToF-AMS). Aerosol mass spectrometry (AMS) provides a real-time analysis of the particle size, the particle mass and the chemical composition of non-refractory aerosols.

Due to its high vapour pressure a direct measurement of I_2 by ToF-AMS is not possible. Therefore molecular iodine has to be transferred from the gas phase to the particle phase before entering the ToF-AMS. For this purpose α-cyclodextrin was used as a derivatization agent. α-cyclodextrin molecules consist of a hydrophilic surface and a hydrophobic cavity. Due to its hollow cone structure α-cyclodextrin is capable of forming an inclusion complex with I_2.

The derivatization reaction was carried out in a 10L reaction chamber made of glass. A fine aerosol of α-cyclodextrin, which had been generated by an atomizer, was continuously introduced into the chamber. Gaseous I_2 was added into chamber by using a temperature controlled and nitrogen flushed test gas source, which was based on an open tube diffusion technique. After exiting the reaction chamber, the aerosol was analysed by ToF-AMS.

PO 1.9

A preliminary study of a DGT-labile trace metals distribution in the stratified Krka River estuary (Croatia)

Ana-Marija Blatarić[1], Cédric Garnier[2], Dario Omanović[1], Véronique Lenoble[2], Neven Cukrov[1], Stéphane Mounier[2], Jean-Louis Gonzalez[3] and Ivanka Pižeta[1]

[1] Ruđer Bošković Institute, Center for Marine and Environmental Research,
PO Box 180, 10002 Zagreb, Croatia
ablatar@irb.hr
[2] Laboratoire PROTEE, Université du Sud Toulon – Var, BP 20132, 83957 La Garde, France
[3] IFREMER, Département Biogéochimie et Ecotoxicologie,
B.P.330 Zone Portuaire de Brégaillon, 83507 La Seyne/mer cedex, France

A preliminary study of the determination of DGT-labile trace metals in Šibenik bay in the well stratified Krka River estuary (Croatia) has been performed. Six depths (down to 8 m) were selected according to previously measured salinity gradient (Fig. 1). Three to five days deployment period of diffusive DGT devices was undertaken. At each depth, three DGT replicates were used and additional three devices were used for blank estimation. Salinity, temperature and pH vertical gradients at the deployment site were regularly recorded in average every 4 hours. Each day, grab samples were taken by scuba diving in order to determine total dissolved and ASV-labile metals. Metals accumulated in DGT complexing resin were measured by ICP-MS, while differential pulse anodic stripping voltammetry (DPASV) was used for determination of ASV-labile and total dissolved metal concentrations in water samples.

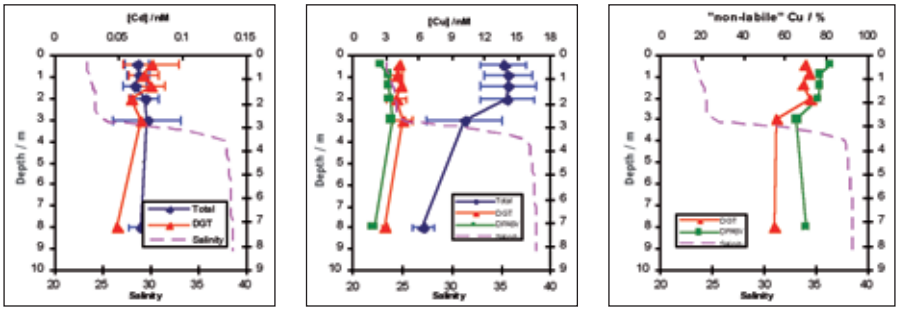


Figure 1. Vertical distribution of DGT-labile and total dissolved concentrations of cadmium and copper, and percentage of DGT and ASV non-labile copper (2008 field study).

Vertical profiles for measured DGT-labile metals (As, Cd, Co, Ni, Cu) showed relatively small variability with depth, indicating uniform distribution of DGT-labile metal species. However, an evident decrease of percentage of non-labile copper complexes in seawater layer was registered, consistent with the results obtained by anodic stripping voltammetry, even though absolute concentrations measured with both techniques were slightly different (Figure 1). This result suggests an existence of ligands forming stronger copper complexes in brackish layer. Preliminary data obtained in 2008 field-study will be supplemented by new set of data from summer 2009, on which more detailed discussion about depth/salinity profile variability will be based.

PO 1.10

Identification of volatile metal(loid) compounds formed by intestinal microorganisms by use of simultaneous EI-MS and ICP-MS detection after gas chromatographic separation

Roland A. Diaz-Bone, Markus Hollmann, Oliver Wuerfel and Dominik Pieper

Institute of Environmental Analytical Chemistry, University of Duisburg-Essen,
Universitätsstraße 3-5, 45141 Essen, Germany
roland.diaz@uni-due.de

For investigation of biotransformation processes of heteroelements in the environment, both molecular and element-sensitive detection systems are used in hyphenation to chromatographic separation. In this work, we studied the potential of our recently developed gas chromatographic system with parallel electron impact mass spectrometry and inductively coupled plasma mass spectrometry (GC/EI-MS/ICP-MS) for non-target screening and subsequent identification of volatile arsenic compounds formed by intestinal microorganisms. Therefore, either fresh fecal slurries or continuous culture sampled from the Simulator of the Human Intestinal Ecosystem (SHIME), an *in vitro* gastrointestinal model, was amended with inorganic metal(oid) salts (Ge, As, Sn, Sb, Te, Hg, Pb and Bi) as well as the nonmetal selenium.

While for Sb, Te and Bi only permethylated species were detected, a broad range of complex volatile As and Se species was observed. By combined use of molecular and elemental detection after gas chromatographic separation (GC-EI-MS/ICP-MS) as well as synthesis experiments, these compounds were identified as methylthio species (dimethyl-methylthio-arsine, $(CH_3)_2AsSCH_3$, methyl-di(methylthio)-arsine, $CH_3As(SCH_3)_2$, methyl-methylthio-selenide, CH_3SeSCH_3, di(methylthio)-selenide $(CH_3S)_2Se$), methyldithio species, (dimethyl-methyldithio-arsine, $(CH_3)_2AsSSCH_3$, methyl-methyldithio-selenide $CH_3SeSSCH_3$) as well as methylmethylthio-ethylthio-arsine, $CH_3As(SCH_3)(SC_2H_5)$, dimethylthioarsinous acid, $(CH_3)_2AsSH$ and thio-bis(dimethylarsine), $((CH_3)_2As)_2S$. Furthermore, one mixed arsenic/selenium compound, dimethyl-methylseleno-arsine, $(CH_3)_2AsSeCH_3$ was identified.

Five of these species, namely methyl-di(methylthio)-arsine, dimethyl-methyldithio-arsine, thio-bis(dimethylarsine), methyl-methylthio-ethylthio-arsine and dimethyl-methylseleno-arsine have not been described in environmental or human matrices before. Finally, the advantages of elemental and molecular detection after gaschromatographic separation are discussed.

PO 1.11

Determination of $^{13}C/^{12}C$ isotopic ratios of biogenic organometal(loid) compounds in complex matrices

Oliver Würfel[1], Roland A. Diaz-Bone[1], Manuel Stephan[2] and Maik A. Jochmann[2]

[1] Institute of Environmental Analytical Chemistry, University of Duisburg-Essen, Universitätsstraße 3-5, 45141 Essen, Germany
roland.diaz@uni-due.de
[2] Instrumental Analytical Chemistry, University of Duisburg-Essen, Lotharstraße 1, 47048 Duisburg, Germany

Methylated metal(loid) compounds are formed in the environment by abiotic as well as enzymatically catalyzed transfer of a methyl group. Due to the increased mobility and toxicity in comparison to the inorganic precursors, the investigation of the formation process is of high relevance. Though the natural abundance carbon isotope ratio can give important insights towards their origin as well as the biochemical methyl transfer process, these species have not been investigated by carbon isotope ratio mass spectrometry (IRMS) so far. This is due to the analytical challenge to precisely determine the natural isotope distribution of trace amounts of metal(loid)-bound carbon in complex organic matrices.

To overcome this problem, we tested the concept of selective derivatization of non-volatile organometal(loid)s by hydride generation (HG) followed by purge and trap (P&T) enrichment, heart-cut gaschromatography (hcGC) and subsequent analysis by GC-IRMS. Parameter optimization of HG-P&T-hcGC was conducted using online coupling to element-sensitive ICP-MS (inductively coupled plasma mass spectrometry) detection. The purity of the HG-P&T-hcGC fraction was verified by GC-MS. For the model substance trimethylarsine oxide (TMAsO), an excellent agreement of the $\delta^{13}C$-value analyzed by HG-P&T-hcGC-GC-IRMS was achieved in comparison to the bulk $\delta^{13}C$-value, which shows that no significant isotope fractionation occurred during the hydride generation and subsequent separation.

The optimized method showed good reproducibility and a satisfying absolute detection limit of 4.5 µg TMAsO (1.2 μg_{carbon}). This method was applied to the analysis of TMAsO in compost. The low $\delta^{13}C$ value of this compound (48.38±0.41‰) indicates that biomethylation leads to significant carbon fractionation. HG-P&T-hcGC-GC-IRMS is a promising tool for investigation of the biomethylation process in the environment.

PO 1.12

Towards the in vitro methylation of metals and metalloids: Capability of corrinoid-dependent methyltransferases from *Methanosarcina mazei* to volatilize metal(loid)s

Frank Thomas[1], Britta Huber[1], Roland A. Diaz-Bone[2] and Reinhard Hensel[1]

[1] Microbiology I, University of Duisburg-Essen,
Universitätsstraße 3-5, 45117 Essen, Germany
[2] Institute of Environmental Analytical Chemistry, University of Duisburg-Essen,
Universitätsstraße 3-5, 45141 Essen, Germany
roland.diaz@uni-due.de

Formation of volatile metal and metalloid-organic compounds (in general methylated or hydrated derivatives) by microorganisms are widespread in anaerobic habitats like sewage-sludge, geothermal vents as well as intestinal tracts of mammalian species including human. In most cases, these compounds represents methylated derivatives of metal(loid)s and exhibit a higher toxicity than their inorganic educts. As indicated by recent studies, methylation of metal(loid)s appears to be an inherent feature of methanoarchaea. Nevertheless, the biochemical mechanisms of the synthesis of these methylated derivatives is still poorly understood.

Here, two corrinoid-dependent methyltransferases (MtaA and MtbA) involved in the central energetic metabolism of the methanoarchaeum *Methanosarcina mazei* were heterologously expressed, purified and tested for their capability to transform inorganic metal(loid)s into volatile derivatives. We present evidence that these two methyltransferases are able to transform different inorganic metal(loid)s (As, Se, Te, Sb and Bi) into volatile derivatives including both methyl and hydride species. The spectrum of elements derivatized by these proteins is similar to the biotransformation spectrum of *M. mazei* in vivo. The enzymatic properties of the methyltransferases regarding substrate specificity are analyzed and putative reaction mechanisms discussed.

PO 1.13

Gaseous and particulate mercury in ambient air of the Upper Silesia, Poland

Halina Pyta[1], Ewa Szmyd[2] and Marianna Czaplicka[2]

[1] Institute of Environmental Engineering of the Polish Academy of Sciences,
34 Curie-Sklodowskiej St, 41-800 Zabrze, Poland
pyta@ipis.zabrze.pl
[2] Institute of Non-Ferrous Metals, 5 Sowinskiego St, 44-100 Gliwice, Poland

Mercury is a persistent, toxic and bioaccumulative heavy metal. Atmospheric mercury exists mainly in three forms: gaseous mercury (Hg_g) including elemental (Hg^0) and divalent (Hg^{2+}) mercury and particulate mercury (Hg_p). These different forms have different characteristics in terms of transport, deposition and influence on ecosystems. Hg^0 is relatively inert and has a small deposition velocity and a long atmospheric lifetime (of about 1 year), thus it constitutes the majority of atmospheric mercury (over 95%) and can be transported globally. The particulate mercury residence time is much shorter (several days to a few weeks), thus it is likely to be deposited at intermediate distances from the sources. Hg^{2+} has the shortest atmospheric lifetime (hours to several days) resulting in low concentrations in the air even though it is emitted at a significant rate.

Coal combustion in coal-fired power plants and for residential heating is the biggest anthropogenic source of mercury in Europe, contributing 52% of total emission. In Poland, which emits 20 Mg of Hg per year, coal combustion constitutes over 60% of country emission. This share is much higher (about 80%) in the Upper Silesia, the most heavily urbanised and industrialised part of Poland, populated by over 3.5 million inhabitants. The study presents the results of mercury concentration measurements carried out in four Silesian cities from June 2008 to May 2009. The measurements were conducted periodically in 24h cycles. They comprised physical mercury speciation including total gaseous mercury (TGM) and PM10-bound mercury (and additionally particulate mercury associated with PM2.5 and TSP at the reference station in Zabrze). The gold traps were used for gaseous mercury sampling. The particulate matter was collected on the glass-fibre filters with the use of a low volume sampler. MA-2 analyser (Nippon Instr. Corp.) was used to determine gaseous and particulate mercury. The determination was based on thermal decomposition of samples with gold-amalgamation of mercury vapours and detection by technique of non-dispersieve double-beam cold-vapour atomic absorption spectrometry (CVAAS). The detection limit was 0.1 ng m^{-3} for TGM and 2.5 pg m^{-3} for Hg_p.

The average TGM concentration was 3.2 ng m^{-3} (2.4 ng m^{-3} - 3.9 ng m^{-3}) and was comparable to other industrialized areas in Europe and in the world. The lowest concentrations were observed in Tychy (residential district with central heating), the highest – in Dabrowa Gornicza (in the neighbourhood of coking plant). Generally TGM concentration was higher in winter than in summer but its seasonal variability was different at the different sampling sites. The average PM10-bound mercury concentrations were from 117 pg m^{-3} in Tychy to 217 pg m^{-3} in Zabrze (sampling point by the main crossroads, high secondary emission of particulate matter). This is much higher than what is found in Europe and somewhat lower than Hg_p concentration in China. There was strong correlation between mercury and PM concentrations. Clear seasonal variations in Hg_p concentration illustrate the important contribution of mercury emission from coal burning in heating season. The highest mercury concentration was found in the finest PM2.5 fraction. It was also stated that Hg enrichment ratio for PM10 samples was similar for the sites of similar emission characteristics.

Determination of Nitro-PAHs in Total Suspended Particles of Urban Atmosphere

Hongwei Chen[1], Qun Luo[1], Kin-Fai Ho[2] and Jingqi Tao[3]

[1] School of Chemistry & Environmental Engineering, Dongguan University of Technology, Dongguan, China (523808)
[2] Department of Civil & Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
[3] School of Chemistry & Environment, South China Normal University, Guangzhou, China (510006)

Urban air pollution in many cities of the developing world in Asia, particularly in China, is increasing significantly. Atmospheric Particulate Matter (PM) pollution is dangerous to the health of millions of people and is a particular concern (1). Polycyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (nitro-PAHs) are environmental pollutants which pose a threat to human health even at low concentration levels (2), e.g. cardiovascular and respiratory morbidity and mortality due to their high carcinogenicities. Therefore, determining the contribution of specific sources to ambient PM levels is an important step toward more effective management of particulate air pollution and to reduced public health risk associated with PM exposure (3).

In this work, an efficient analytical method for the determination of Nitro-PAHs in Total Suspended Particle (TSP) of urban atmosphere, using methanol as solvent for the ultrasonic extraction of particle sample, followed by HPLC-UV/MS detection, has been developed. The efficiency of extraction was proved to be sufficient for the sample pre-treatment. HPLC operation condition is shown as following: ALLTIMA C18 5micron ST4.6×150 column, methanol: water=2:98, flow rate of 0.6 mL/min, UV wavelength for detection at 254 nm. Experimental results showed that the calibration was well founded for target compounds. 9-nitroanthracene, 2-nitrofluorene, 1-nitropyrene, 7-nitrobenz[a]anthracene were detected in the real TSP sample from the sampling sites of Hong Kong and Guangzhou, south China, with contents of 162 ng/m^3, 541 ng/m^3, 1.55 ng/m^3, 1.31 ng/m^3, respectively. These contents are relatively higher than those from previous works elsewhere.

References

(1) To Thi Hien et.al. Nitro-polycyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons in particulate matter in an urban area of a tropical region: Ho Chi Minh City, Vietnam. *Atmospheric Environment* 41: 7715-7725 (2007).
(2) Schauer, C., Niessner, R. & Poeschl, U. Analysis of nitrated polycyclic aromatic hydrocarbons by liquid chromatography with fluorescence and mass spectrometry detection: air particle matter, soot, and reaction product studies. *Analytical and Bioanlytical Chemistry* 378, 725~738 (2004).
(3) Miller-Schulze J.P. et al. Exposures to particulate air pollution and nitro-polycyclic aromatic hydrocarbons among taxi drivers in Shenyang, China. *Environ. Sci. & Technol.* (in press).

PO 1.15

Determination of arsenic species in algae by microwave-assisted extraction and high performance liquid chromatography-inductively coupled plasma-dynamic reaction cell- mass spectrometry

Syr-Song Chen, Che-Lun Hsu, Ya-Min Kao and Yang-Chih Shih

Bureau of Food and Drug Analysis, Department of Health,
161-2, Kunyang St., Nangang, 11513, Taipei, Taiwan
chen1304@nlfd.gov.tw

Arsenic is very well known that toxicity depends not only on the total concentration but also related to its chemical form: Of the inorganic forms, arsine is highly toxic, and arsenite is accepted as being more toxic than arsenate. The methylated species monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are less toxic than the inorganic forms. These compounds represent precursors of more complex organic and non-toxic forms, like arsenobetaine (AsB) and arsenocholine (AsC). Arsenic may enter the environment from industrial processes, or as inorganic arsenic pesticides and fertilizers used in agriculture. The presence of arsenic in seafood has been known for many years. Inorganic arsenic can be methylated in the environment forming organic forms. It is well known that algae have the ability to bioaccumulate the non toxic arsenic species.

The analytical procedure for analysis of arsenic species in algae was developed. It involved microwave-assisted extraction with 50% ethanol. At the power of 60 W, sample preparation time is only 6 min. An Inductively Coupled Plasma-Dynamic Reaction Cell-Mass Spectrometry (ICP-DRC-MS) was used as a High Performance Liquid Chromatography (HPLC) detector for the speciation analysis of arsenic. The six arsenic species inclusive of arsenite (AsIII), arsenate (AsV), monomethylarsonic (MMA), dimethlyarsinic (DMA), arsenobetaine (AsB) and arsenocholine (AsC) were separated by Hamilton PRP-X100 anion exchange column. Gradient elution using 3% methanol 100 mmol ammonium carbonate buffer and water at pH 8.5 allowed the chromatographic separation of all species within less than 20 min. Methane as reactive cell gas in the DRC while an Rpq value of 0.5 was used. The recoveries of arsenic species were 93.9-118.5%, 102.1-130.4%, 106.2-113.8%, 101.2-112.9%, 97.8-108.7% and 85.2-95.4% for As III, As V, MMA, DMA, AsB and AsC, respectively. The detection limits of method for six arsenic species were in the range of 0.02-0.06 ng/mL based on 3 σ of blank response (n=7). The precision was calculated to be 3.1-7.3% (CV) for all six species. It indicated that the method was well available to detect the arsenic species in algae.

Selenium isotope ratios of volatile organoselenium species as an indicator of the conditions of biomethylation

Kathrin Schilling and Wolfgang Wilcke

Geographic Institute, Johannes Gutenberg University Mainz,
J.J. Becher Weg 21 55099 Mainz, Germany
k.schilling@geo.uni-mainz.de

Selenium is a trace element which is widely distributed in the environment. The concentrations of selenium in soils range from 0.1-2 mg/kg. The anthropogenic input of selenium originating mainly from coal mines and pyrometallurgical industry cause an increase of selenium concentration in the environment.

The effect of selenium compounds range from being essential for microorganisms, plants, and humans to being highly toxic with a relatively low tolerance range. The toxicity of selenium depends on its chemical form. The inorganic selenium forms are considered to be 500 times more toxic than organoselenium compounds. Selenium is cycled by different biological pathways like reduction, oxidation and methylation which occur in soil systems. Therefore biomethylation is a natural process which offers a potential remediation strategy in Se-contaminated areas. It is well known that different kinds of organisms (fungi, bacteria and plants) can produce volatile organoselenium species, mainly dimethylselenide (DMSe) and dimethyldiselenide (DMDSe) from inorganic selenium compounds (selenate and selenite). Selenium isotope ratios ($\delta^{76}Se/^{82}Se$) could serve as indicator of biogeochemical transformations of selenium in soils. We therefore test the hypothesis that the natural abundance of Se isotopes in organoselenium compounds is indicative of the conditions of DMSe and DMDSe formation.

For our experiments we used the fungi Alternaria alternata which is widespread in the environment, especially in soils. The organism was cultivated under pH 4 and 7 at a temperature of 30°C and incubated with 5 mg Se kg^{-1} as $NaSeO_4$ or as $NaSeO_3$ for 11-15 days. The volatile selenium compounds released by the fungi culture were collected in three alkaline-peroxide gas traps. Furthermore, nutrient medium and fungi were digested with concentrated nitric acid. A higher methylation was observed by the incubation with selenite than with selenate. By the incubation with selenate only 2-10% of the supplied compounds were converted to organoselenium whereas a methylation of 20-43% was detected if selenite was supplied. The assimilation of selenium in the organism accounted for 12-25% of Se(VI) and 61% Se(IV) of total selenium. Fractionation factors of the methylation were ε = -0.18‰ to 0.30‰ (±0.20‰) for Se(IV) incubation. A greater isotopic fractionation (ε = -3.07‰) was observed for organoselenium compounds if Se(VI) was the substrate. Variations in pH did not influence ε.

PO 1.17

Solid-phase speciation and surface binding of nickel in serpentine soils from the North-east of Portugal

Sheila Alves[1], Maria de Lurdes Simões Gonçalves[1], Maria Ascensão Trancoso[2] and Margarida M. Correia dos Santos[1]

[1] Centro de Química Estrutural, Instituto Superior Técnico,
Av. Rovisco Pais, 1049-001, Lisboa, Portugal
[2] Instituto Nacional de Engenharia e Tecnologia Industrial,
DTIQ - LAACQ, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal

The aim of this work is to investigate and to compare solid-phase speciation and surface binding of Ni in serpentine (S) and nearby non-serpentine (NS) soils from the northeast of Portugal. The former commonly have high levels of trace metals like Ni, Cr and Co and low Ca/Mg ratios. In addition, serpentine soils have low concentrations of important nutrients like K and P. Low Ca concentrations combined with elevated soil concentrations of Mg and Ni are considered to be the main cause of serpentine soil toxicity (1).

Several soil samples were characterized in terms of selected physicochemical characteristics. Solid-phase speciation and surface binding of Ni were assessed through complementary wet chemical extractions. Surface bound Ni was divided into exchangeable ($CaCl_2$-extractable Ni) and both exchangeable and specifically adsorbed (EDTA-extractable Ni). Solid-phase speciation was evaluated by selective dissolutions of hydrous Mn oxides (hydroxylamine extraction - HH), amorphous Fe oxides (oxalic acid extraction – OX) and amorphous as well as crystalline Fe oxides (dithionite-citrate extraction – DC).

In non-serpentine soils surface bound Ni is mainly in an exchangeable form while in serpentine soils is mainly specifically adsorbed. The influence of soil physicochemical characteristics and of Ni bearing oxides (HH, OX, DC dissolutions) on Ni bioavailability (EDTA-extractable Ni) was examined. No relationship was found between EDTA-extractable Ni and clay content or amorphous iron oxides. A major association of Ni with hydrous Mn oxides was found. Pearson correlation analysis confirmed the influence of these oxides on Ni bioavailability (2).

Surface affinity for exogenous Ni was evaluated by adsorption studies on soils suspensions followed by voltammetric titrations at pH=7. Sorption data was fitted to a Langmuir isotherm assuming the formation of 1:1 Ni complexes with the soil surface binding sites. Although of the same order of magnitude, the concentration of surface groups of serpentine soils for Ni binding was higher than that of non-serpentine samples. Serpentine soils presented higher conditional surface formation constant, $\overline{K}^{cond}_{\equiv SNi}$, which implies the existence of surface groups with higher nickel affinity. The manganese oxides seem to be the mainly responsible factor for Ni retention in the analysed serpentine soils (2).

Acknowledgement: This work was co-financed by POCI 2010 and by the European Social Fund. Sheila Alves acknowledges FCT for PhD Grant SFRH/BD/21597/2005.

References

(1) RR Brooks. 1987. Serpentine and its Vegetation. *Dioscorides Press*, Portland, OR, USA (454 pp).
(2) S Alves, ML Simões Gonçalves, MA Trancoso, MM Correia dos Santos. 2009. Assessment of nickel availability in serpentine and non-serpentine soils from the North-east of Portugal. *Submitted for publication*.

PO 1.18

Determination of Tributyltin (TBT) at Sub-ppt Level in Whole Water Samples

Christian Piechotta, Thomas Sommerfeld, Tin Win and Irene Nehls

Federal Institute for Materials Research and Testing,
Organic Trace Analysis and Reference Materials,
Richard-Willstätter-Strasse 11, D-12489 Berlin, Germany
christian.piechotta@bam.de

Tributyltin (TBT) as a compound in antifouling agents is used to protect ship hulks. This causes an increase of its concentration in sediments and surface water, especially in harbors. The toxic tributyltin species decreases the number of males in fish populations due to their estrogenic activity to organisms. Organotin compounds were taken into consideration in new federal law concerning protection of soil and sewage sludge. In European directive related to the water contamination, the acceptable tributyltin concentration is very low and about 0.2 ng/L. So the determination of trace impurities concerning TBT in water requires a very sensitive technique like GC-ICP-MS, but basically common analytical methods do not permit the measurement of this organotin species in environmental matrices.

A preliminary step was developed for the separation of TBT from the samples mentioned above. In addition the ultra-trace amount of TBT was concentrated so that the limit of detection for common measurement techniques can be efficiently lowered. Tributyltin preconcentration procedures, like solid phase extraction (SPE) using various column packings like octyl or octadecyl reversed phase materials were established. Optimized adsorption and elution profiles for suitable recovery rates were developed and validated as well as a further concentration step using solid phase microextraction (SPME). For the accurate quantification of the preconcentrated TBT samples suitable derivatization procedures were investigated using different types of alkylation reagents. The detection of these alkylated TBT species were carried out by using a GC-AED. Standard addition procedures using triple-distilled water and tributyltin standards are elucidated as well as real samples of contaminated water.

PO 1.19

Isotopic fractionation of Cu and Zn in the soil system

Moritz Bigalke[1], Stefan Weyer[2] and Wolfgang Wilcke[1]

[1] University of Mainz, Geographic Institute, J.J. Becher-Weg 21, 55128 Mainz, Germany
Bigalke@uni-mainz.de
[2] University of Frankfurt, Institute of Geoscience, Altenhöferallee 1,
60438 Frankfurt am Main, Germany

Different isotopes of an element show distinct behaviour during chemical and physical processes because vibration frequencies of molecules of distinct isotopes differ resulting in different dissociation energies and different reactivity.

Many environmental processes cause detectable fractionation of isotope ratios. Depending on element speciation equilibrium fractionations may occur between two species but also kinetic fractionations during incomplete chemical reactions may result in measurable isotopic fractionation. For heavy elements like Cu and Zn these fractionations are in the range of a few per mil deviations from an arbitrarily defined reference value. Because of the small total variation high precision methods are necessary to detect variations of isotope ratios.

To investigate isotopic fractionation of Cu and Zn stable isotopes in soil samples the samples were measured by multicollector-ICP-MS after acid digestion and ion exchange chromatographic purification. With the used method precision were always better than 0.15‰ (2SD) for Cu and 0.11‰ (2SD) for Zn, respectively, and thus suitable for detecting isotopic fractionation in soil.

The method was applied to different soil types, which have formed under various environmental conditions. In the soils, the fate of Cu is dominated by redox reactions, organic complexation and chemical weathering. Furthermore, Cu and Zn isotopic composition was studied in contaminated soil profiles near a copper smelter to assess the potential use of stable isotope ratios as tracer of metal sources and vertical transport in the soil.

Our results showed isotopic fractionation of up to 1‰ for copper in a well developed Podzol profile. Smaller Cu isotopic variations were found in water-influenced profiles and profiles developed by oxic weathering.

In polluted soils, Zn isotopes showed lightest isotopic composition in organic layers which are most influenced by metal contamination as indicated by metal accumulation in the topsoil. These findings are consistent with Sonke et al. (2008) who described isotopic fractionation of Zn emitted from smelters (1). With increasing depth and decreasing contamination Zn isotopic composition became heavier and more similar to the isotopic composition of local bedrock the soil developed from. The use of Cu isotopes for pollution tracing was less successful because the isotopic composition of emitted Cu was very close to that of local bedrock.

Altogether stable isotope ratio measurements of metals may offer the opportunity to study long-term chemical processes during soil development and to trace pollution sources and pollutant transport in soil.

References

(1) Sonke, J.E., Y. Sivry, J. Viers, R. Freydier, L. Dejonghe, L. Andre, J.K. Aggarwal, F. Fontan, and B. Dupre. 2008. Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter. *Chemical Geology* 252:145-157.

PO 1.20

Arsenic speciation in whelks *(Buccinum undatum)*

Dagmar Urgast, Andrea Raab and Jörg Feldmann

TESLA (Trace Element Speciation Laboratory)
University of Aberdeen, College of Physical Science, Chemistry,
Meston Walk, Aberdeen AB24 3UE, Scotland ,UK

Whelks *(Buccinum undatum)* are fished on the coasts of Great Britain and are sold to Mediterranean countries and Asia for eating. As it is common knowledge that seafood can contain high amounts of arsenic, data about the arsenic distribution in the whelks had to be provided for risk evaluation purposes concerning the consumption of the whelks.

In a previous work it was found that the whelks can contain Arsenic levels up to 43.7 mg/kg (fresh weight). The various arsenic species show large differences in their toxicity. It is widely acknowledged that arsenobetaine is a non-toxic form of arsenic whereas the inorganic arsenite and arsenate are the most toxic forms of arsenic. Therefore a total arsenic concentration does not say very much about the toxicity of a food sample and speciation is needed.

In this work anion and cation exchange HPLC-ICP-MS and cation exchange HPLC-ICP-MS/ESI-MS as well as anion exchange HPLC-HG-AFS were used for speciation analyses of H_2O/H_2O_2-extracts of whelks.

During our studies it was found that the arsenic present in the whelks consists of 0,1 ± 0,1 % (n=12) inorganic arsenic, 67 ± 23 % (n=6) arsenobetaine and some other unidentified arsenic species. This means that the main arsenic species in the whelks is the non-toxic arsenobetaine.

Sorption and speciation of neptunium(V) on Opalinus Clay

D. Fröhlich, S. Amayri, J. Drebert and T. Reich

Institute of Nuclear Chemistry, Johannes Gutenberg Universität Mainz,
55099 Mainz, Germany

Several European countries including Germany, Switzerland and France explore argillaceous rock formations as potential host rock for high-level nuclear waste repositories. Detailed knowledge of the chemical and physical behaviors of the radionuclides in the near and far fields of a repository is mandatory for its safety assessment. As one of the long-lived radionuclides Neptunium (237-Np) will contribute significantly to the radiotoxicity of the nuclear waste after a period of time of more than thousand years. Opalinus Clay (OPA) was chosen as reference material to study the sorption behavior of Np(V) on natural clay in batch experiments in dependence of several factors such as pH, Np concentration, solid-to-liquid (S/L) ratio and partial pressure of CO_2 (aerobic and anaerobic conditions). Additionally, the nature of Np species sorbed onto OPA was studied at a molecular level by Np LIII-edge Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy.

Aerobic and anaerobic samples of OPA (from Mont Terri, Switzerland) were used to study the sorption behavior of Np(V) by batch experiments. Because of the high amount of calcite (~13 ± 8 %) (1) in OPA, saturated calcite solutions were used as background electrolyte to avoid partial dissolution of OPA and to keep the amount of sorbent constant during all experiments. Sorption isotherms were measured by varying the S/L ratio between 2 and 20 g/L and the Np concentration between $7 \cdot 10^{-12}$ and $8 \cdot 10^{-6}$ mol/l. Maximum sorption of 8 µM Np occurred at pH 8.5; 65 % was sorbed under aerobic conditions and 80 % under anaerobic conditions, respectively. Stronger sorption in the absence of O_2 was found to be caused by a reduction of Np(V) to Np(IV). The complexation of neptunium with carbonate in aqueous solution (2) causes a decrease in sorption at pH > 9.

Depending on the conditions during the preparation of the wet-paste samples, i.e., background electrolyte, pH and partial pressure of CO_2, EXAFS spectra indicated the formation of Np(V) carbonate complexes at the OPA surface in several cases.

This work was financially supported by the Bundesministerium für Wirtschaft und Technologie under contract No. 02E10166. Daniel Fröhlich has been supported by a fellowship of DFG-GRK 826.

References

(1) NAGRA: Projekt Opalinuston – Synthese der geowissenschaftlichen Untersuchungsergebnisse, Entsorgungsnachweis für abgebrannte Brennelemente, verglaste hochaktive sowie langlebige mittelaktive Abfälle. Technischer Bericht NTB 02-03, NAGRA Nationale Genossenschaft für die Lagerung radioaktiver Abfälle, Wettingen/Schweiz (2002).

(2) V. Neck, W. Runde, J. I. Kim, B. Kanellakopulos, Solid-liquid equlibrium reactions of neptunium(V) in carbonate solution at different ionic strength. *Radiochim. Acta*. 65, 29-37 (1994).

PO 1.22

Characterization of resin gels used for determination of different mercury fractions in natural waters by DGT technique

Pavel Diviš, Roman Szkandera and Hana Frišhansová

Brno University of Technology, Faculty of chemistry,
Purkyňova 118, Brno 61200, Czech Republic
divis79@yahoo.com

During more the last ten years, from the time when diffusive gradients in thin films technique (DGT) was introduced to scientific community for the first time, this technique has been intensively studied and developed. However, only little attention was attended to application of DGT technique for mercury measurement. In our laboratory, this issue is studied for more than five years. After solving the problems with accumulation of mercury in diffusive gel, Spheron Thiol resin gel as the best for determination of mercury by DGT was recommended. Unfortunatelly, this resin is not available on the market nowadays. From this reason, another work in this area was focused on preparation of new resin gels, capable to replace Spheron Thiol resin gel in DGT technique. During last two years, several resin gels were proposed and prepared, however, their characteristic was not tested until now.

This work summarized the results from laboratory testing of resin gels used in diffusive gradients in thin films technique for determination of different mercury fractions in natural waters. The sorbents chosen for preparation of resin gels were: Duolite GT-73, Spheron Thiol, chemically modified Iontosorb AV and Chelex 100. First of all, the preparation procedure of all resin gels was optimized. After optimalization of preparation procedure, the resin gels were tested in mercury model solutions. The recovery test and the time dependence test were performed. When the bacic tests were finished, they were followed by the tests of influence of natural ligands (humic substances, chlorides) and other parameters (above all pH and ionic strength) on mercury determination by DGT technique.

Acknowledgement: This work has been supported by grants No. GAČR 525/09/P583, MEB 080813 and SK-CZ-0044-07.

References

(1) H. Zhang and W. Davison, *Anal. Chem.*, 1995, 67, 3391.
(2) H. Dočekalová and P. Diviš, *Talanta*, 2005, 65, 1174.
(3) P. Diviš, M. Leermakers, H. Dobekalová, and Y. Gao, *Anal. Bioanal. Chem.*, 2005, 382, 1715.
(4) P. Diviš, R. Szkandera, L. Brulík, H. Dočekalová, P. Matúš and M. Bujdoš, *Anal. Sci.*, 2009, 25, 575.

PO 1.23

Copper exportation from glaciarised catchments

Damiano Monticelli, Andrea Pozzi and Carlo Dossi

Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria,
via Valleggio 11, 22100 Como, Italy
damiano.monticelli@uninsubria.it

Glacial streams are remarkable ecosystems and have been studied since the last thirty years because of their unique and interesting features. First, they are the simplest way of understanding subglacial hydrology and the chemical and physical weathering taking place beneath glaciers (1,2). Water quality studies allow assessing the contribution of these systems to global geochemical cycling of elements, their influence on aquatic environments (3) and even on global climate changes (4). Finally, it should be borne in mind that glaciers and their meltwaters are the chief water reservoirs in mountainous, temperate areas, which makes their characterisation important for both human consumption and industrial exploitation.

Regarding the characterisation of ice stream components, early studies focused their attention on major ions and tried to evaluate the extent of chemical weathering taking place below glaciers (see the review by Brown for a collection of these papers (5)). Only in the last decade (3) were the first papers published regarding trace metal concentrations and fluxes in glaciarised catchments. Apart from total metal fluxes, particular importance was given to the form in which trace metals are transported. Their fractionation between suspended matter and solution was assessed: moreover, their inorganic speciation in the latter phase was computed by a speciation software. Organic speciation has to be taken into account until recently, when the presence of strong organic ligands for copper in one Alpine ice stream was demonstrated (6), opening the possibility to better understand trace metal behaviour in glacier meltwaters. Competitive ligand equilibration with cathodic stripping determination of the labile fraction (CLE-CSV) was used as the speciation method. Aim of this poster presentation is to portray the results obtained from the analysis of four more Alpine glaciated catchments, with a four year record of one catchment. This study highlighted the presence of very strong natural ligands for copper in all of the investigated glaciarised basins. The presence of these ligands in ice streams completely changes the copper speciation and suggests that this metal is completely complexed in these ecosystems. This feature is common to other remote ecosystems, like open ocean waters and high altitude and latitude lakes. The origin of these complexants could be due to the biological activity at the ice-bedrock interface. If this hypothesis is correct, biota plays a major role in favouring exporting copper ions (and possibly other trace metals) from glaciarised catchments, preventing the scavenging of copper ions. In the absence of such ligands, copper ions could be adsorbed onto suspended particles and removed by sedimentation.

References

(1) Anderson S. P., Drever J. I., Humphrey N. F., *Geology* 25: 399-402, 1997.
(2) Hallet B., Hunter L., Bogen J., *Glob. Planet.* Change 12: 213-235, 1996.
(3) Mitchell A., Brown G. H., Fuge R., *Hydrol. Process.* 15: 3499-3524, 2001.
(4) Sharp M., Tranter M., Brown G. H., Skidmore M., *Geology* 23: 61-64, 1995.
(5) Brown G. H., *Applied Geochemistry* 17: 855-883, 2002.
(6) D. Monticelli, A. Pozzi, C. M. G. van den Berg, C. Dossi, *Aust. J. Chem.* 57: 945-949, 2004.

Assessment of accuracy and precision in speciation analysis by CLE–CSV: application to Antarctic samples

Alessio Castelletti, Carlo Dossi and Damiano Monticelli

Dipartimento di Scienze Chimiche e Ambientali, Università dell'Insubria,
via Valleggio 11, 22100 Como, Italy
alessio.castelletti@uninsubria.it

Speciation analysis by Competitive Ligand Equilibration – Cathodic Stripping Voltammetry (CLE – CSV) has been widely used in the last three decades for determining the species of trace elements in natural waters.

This kind of selective detection of the labile metal has the advantage to combine simple sample treatment, very high sensitivity and to rely on relatively few assumptions (mainly that equilibrium is reached after allowing for a long enough equilibration time). In general, the advantages of the CLE-CSV speciation scheme over other CLE methods derive from the added ligand being both the competitor and the direct detection mean. Moreover, this procedure requires a limited time, taking less than two hours to analyse a sample, after allowing a twelve hour, operator free, equilibration time. Two data are obtained by this analysis: the concentration of the natural ligand(s) (usually referred to as complexing capacity) and the conditional constant for the formation of the complex between the natural ligand(s) and the metal under investigation.

Aim of the present research is to assess the analytical performances of the CLE-CSV procedure and to estimate the accuracy and precision that can be attained for the determination of strong ligands at the ultra trace level. A thorough validation procedure may be difficultly applied; reference materials are not available in this field, as complexes of metal at trace levels in natural waters are not sufficiently stable. The assessment of analytical figures was consequently performed by analysing synthetic solution containing trace level of ligands showing known complexing characteristics. The whole protocol was evaluated. The side reaction coefficient alpha for the formation of the complex between the added ligand and the investigated metal was initially determined as usually done in the CLE-CSV protocol. The method was subsequently applied to the analysis of solution with known complexing characteristics and ligand concentrations ranging from 5 to 50 nM. Copper was used as model metal ion and ethylenediaminetretraacetic acid (EDTA) as a model ligand.

Results evidenced that the CLE-CSV protocol is not affected by systematic errors in the determination of both ligand concentration and the side reaction coefficient alpha. Good precision is obtained for ligand concentrations, with relative standard deviations (RSD%) in the range 3 – 15% (four replicates for each ligand level). Random errors associated with alpha coefficients showed higher figures with RSD% in the range 30 – 40%. The possibility to detect different classes of ligands is clearly strongly limited by the precision in the alpha coefficient values.

The CLE-CSV protocol was subsequently applied to the detection of strong ligands in water samples collected in Antarctica. The figures of merit of the protocol were demonstrated not to degrade for the analysis of real samples and the procedure was confirmed to be able to detect strong ligands at ultratrace level.

PO 1.25

Speciation of Hg on three mining districts by XANES techniques

José María Esbrí[1], Anna Bernaus[2], Eva MªGarcía-Noguero[1], Marta Avila[2], David Kocman[3], Beatriz Guerrero[2], Xavi Gaona[2], Rodrigo Alvarez[4], Gustavo Perez-Gónzalez[2], Pablo Higueras[1], Jorge Loredo[4], Milena Horvat[3] and Manuel Valiente[2]

[1] Department of Mining and Geological Engineering, University of Castilla-La Mancha, 13400 Almadén, Spain
eva.garcia@uclm.es
[2] Department of Chemistry, Autonomous University of Barcelona, 08193 Bellaterra, Spain
[3] Jozef Stefan Institute, Ljubljana SI-1001, Slovenija.
[4] Department of Mining and Mines Exploration, University of Oviedo, Oviedo 33004, Spain

The mobility, bioavailability and toxicity of mercury in the environment depend on the chemical species in which is present in soil, sediments, water or air. In this work we used synchrotron radiation to determine mercury species in soil and sediments of three mercury mining districts: Almadén (Spain), Idrija (Slovenia) and Asturias (Spain). The aim of this study was to find differences on mobility and bioavailability of mercury on three mining districts with different type of mineralization. For this porpoises we selected samples of ore, calcines, soil and sediment of the three sites, completely characterized by the School of Mines of Almadén, Josef Stefan Institute of Ljubljana and School of Mines of Oviedo.

Speciation of mercury was carried out on Synchrotron Laboratories of Hamburg (HASYLAB) by XANES techniques. Spectra of pure compounds [$HgCl_2$, $HgSO_4$, HgO, CH_3HgCl, Hg_2Cl_2 (calomel), HgS_{red} (cinnabar), HgS_{black} (metacinnabar), $Hg_2NCl_{0.5}(SO_4)_{0.3}(MoO_4)_{0.1}(CO_3)_{0.1}\bullet(H_2O)$ (mosesite), $Hg_3S_2Cl_2$ (corderoite), $Hg_3(SO_4)O_2$ (schuetteite) y Hg_2ClO (terlinguaite)] were obtained on transmittance mode, and the number and type of this compounds to reconstruct sample spectra was obtained by PCA analysis and linear fitting of minimum quadratics.

Mobility was assessed by stirring during 60 minutes with an HCl solution 0.5 M, centrifugation at 3,500 rpm during 10 minutes, and filtering the extract previously to the analyze by ICP-OES.

The results shows differences on efficiency of roasting furnaces from the three sites by the presence of metacinnabar on the less efficient (Almadén and Asturias) and absence on the most efficient (Idrija). On the three sites studied, sulfide species (cinnabar and metacinnabar) were more abundant than soluble species (chlorides and sulfates), and we found a correlation between $HgCl_2$ presence and mobility indicating that this is the most mobile species.

'Reactive' extraction of arsenosugars from brown alga Wakame *(Undaria pinnatifida)*

Jürgen Mattusch[1], Peggy Landsmann[2] and Regina Walter[2]

[1] UFZ-Helmholtz – Centre for Environmental Research, Department Analytical Chemistry, Permoserstr. 15, 04318 Leipzig, Germany
juergen.mattusch@ufz.de
[2] University of Applied Sciences, Department of Engineering and Natural Sciences, 06217 Merseburg, Geusaer Strasse 88, Germany

Marine algae form an important food basis for the above all Asian population. Beyond that they are also from economic interest e.g. for the production of gelling and thickeners for food industry and for medical applications. Thus the alginate contained in the brown alga Wakame *(Undaria pinnatifida)* in particularly high concentration plays an important role. This is the reason, which makes analysis of arsenic species essential but more difficult.

The total arsenic determination in algae can supply, however, no information about their toxic status, so that quantification and an identification of the arseno-organicals must take place additionally to the inorganic arsenic species. Usually, shaking the alga sample with water or water/methanol solutions leads to the almost complete extraction of the original arsenic species, which can be analyzed then by means of suitable coupling techniques such as HPLC-ICPMS and/or HPLC-ESIMS. An exception is the alga Wakame, with which only approx. 30% of the total arsenic are extractable. A cause of these low and strongly varying extraction efficiencies could be the covalent bonding or adsorption of the arsenic species to the gel-like alginate matrices, which consist of polysaccharides with 1,4-glycosidic-connected α-L-Guluronic acid and β-D-mannuronic acid units.

In the present work we can demonstrate, how the solubility of the alginate was increased by suitable alkaline extracting agents with the result that the extraction efficiency can be improved substantially. By means of anion exchange chromatography coupled with ICPMS and ESIMS as parallel detectors some to the arising arsenic species could be identified. The pH-dependent extraction connected with the identification of the arsenosugars setting free thereby was used, in order to characterize their bonding to the alga structure. The quantitative results were verified with standard reference materials.

Microbiological alkylation and volatilization of inorganic selenium immobilized by goethite, Se-LDH, and ferroselite

Mirko Peitzsch[1,2] and Michael Kersten[1]

[1] Geosciences Institute, Johannes Gutenberg University,
Becherweg 21,55099 Mainz, Germany
kersten@uni-mainz.de
[2] Division of Medical Microbiology, Dept. of Laboratory Medicine, Lund University,
S-22363 Lund, Sweden

Selenium under reducing cement-bearing near field conditions is preferentially precipitated in the oxoanionic form of selenite with the cement mineral hydrotalcite (Se-LDH), in the more reduced selenide form with iron as ferroselite, $FeSe_2$, or in the more oxidized form of selenate with the Fe-oxide goethite. Se sorbed by these solid phases is considered as of low mobility and thus of benefit for long-term stabilization of, e.g., the fission product ^{79}Se. We will show, however, that sulfate-reducing bacteria (SRB) including the common *Desulfovibrio gigas* are capable to volatilize the Se from all these solid phases. We used a standardized nutrient broth for sulfate reducers and incubated with 10 g L^{-1} suspension under strictly anaerobic conditions. For sampling we gently purged the head space of the culture flasks with nitrogen into Tedlar bags. Volatile organic selenium (VOSe) species were measured by a cryotrapping cryofocussing gaschromatographic system with ICP-MS detection. Alkylated species found at the tens to hundreds ng m^{-3} level above the Se-LDH and goethite cultures were the common dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe) but also ethylated forms (Figure 1). Species concentrations found during the $FeSe_2$ incubation were by 1-2 orders of magnitude lower, but two more yet unknown compounds with peaks at retention times in between those of DMSe (150s) and DESe (300s) were found to occur within a few days (Figure 1). In conclusion, microbe mediated VOSe formation cannot be neglected but must be considered as a potential fission product mobilization pathway, which may lead to onsite accumulation of highly mobile 79Se through evapoconcentration.

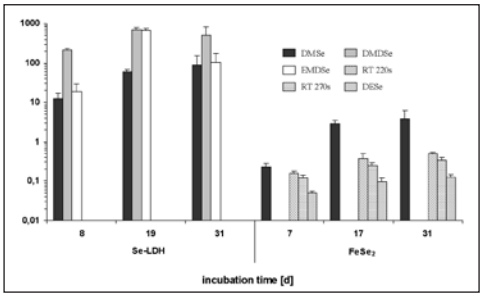


Figure 1.
Time-dependent volatilization of alkylated selenium from two different inorganic selenium sources (error bars represent standard deviation, n = 3).

Sulphur speciation in marine submicron aerosol particles using on-line thermal-desorption aerosol mass spectrometry

Sören R. Zorn[1,2], Frank Drewnick[1], Mathias Schott[3], Thorsten Hoffmann[3], and Stephan Borrmann[1,2]

[1] Particle Chemistry Department, Max-Planck-Institute for Chemistry, J.J. Becherweg 27, D-55128 Mainz, Germany
[2] Institute for Atmospheric Physics, University of Mainz, J.J. Becherweg 21, D-55128 Mainz, Germany
[3] Institute of Inorganic and Analytical Chemistry, University of Mainz, Duesbergweg 10-14, D-55128 Mainz, Germany

Atmospheric aerosol particles are known to have significant impact on both the earth's climate and human health. Therefore extended knowledge on the composition of ambient aerosol particles and on generation and transformation processes associated with such particles are imperatively needed in order to assess the effects of ambient aerosols. A modern analytical tool that is increasingly used to investigate the composition of aerosol particles with high temporal resolution is on-line aerosol mass spectrometry.

In this study the applicability of this technique to the identification and quantification of sulphur species in marine aerosol particles was investigated using an Aerodyne Research, Inc. Aerosol Mass Spectrometer (AMS) in laboratory and field experiments. The Aerodyne AMS samples ambient aerosol particles in a size range from about 60 nm up to 700 nm and focuses them onto a vaporizer, heated to 600 °C using an aerodynamic lens assembly. Non-refractory aerosol components flash-evaporate, and the generated vapour is electron impact ionized and subsequently analysed using a high resolution time-of-flight mass spectrometer. The resulting mass spectra can be used to determine mass concentrations and species-resolved particle size distributions of non-refractory aerosol components.

Since no physical separation of different species is performed prior to the mass spectrometric analysis, the identification and quantification of individual compounds within the aerosol has to be done by mathematically separating the mass spectrometric information. In order to identify and separate different sulphur-containing aerosol species known to exist in the marine atmosphere – namely sulphate, elemental sulphur, methanesulphonic acid (MSA), dimethyl sulphoxyde (DMSO), and dimethyl sulphone ($DMSO_2$) – laboratory measurements were performed to determine the standard fragmentation patterns of these species under the measurement conditions of the Aerodyne AMS.

Within the standard fragmentation patterns individual marker peaks containing a sulphur atom, but not being shared by different components, have been identified and consequently used to determine each species' contributions to the overall mass spectra. By applying a specially designed peak fitting algorithm to the high-resolution spectra and corrections for fragment intensities the quantification of the individual sulphur-containing species in ambient aerosol spectra is possible. This extraction and quantification procedure was then applied to ambient aerosol data collected during a cruise in the Southern Atlantic Ocean, determining the concentrations of these species with high temporal resolution for the first time.

In addition to these field results, a discussion on the limitations of this method for speciation of sulphur compounds and other non-refractory aerosol species using *on-line* aerosol mass spectrometry will be provided.

PO 1.29

Investigation of the source, behavior, toxicity, mobility and speciation of arsenic in soil

Mr. Ka Hei Lui and Prof. Dr.-Ing. Michael Kersten

Environmental Geochemistry Group, Institute for Earth Sciences,
Becherweg 21, 55128 Mainz, Germany
lui@uni-mainz.de

Heavy metals contamination to the terrestrial environment long exists due to the natural weathering of the parent rocks in which causing metal precipitation in the system. The widely observed increase trace element concentrations in agricultural soil due to various human activities such as liming would lead to potential harmful effects on mankind. Natural reduction in lime status for most soils would increase soil acidity and reduce soil fertility. Toxic metals and metalloids such as arsenic have the abilities to scavenge with Fe and Mn oxides present in low grade limestone and leach out from the soils under severe environmental condition. Adsorption of arsenic into the soil system depends greatly on the physicochemical behaviour in which arsenic enters the soil. Sequential extraction method was used to partition different arsenic species in associated with various metal-bearing phases. As, Fe and Mn contents in five extraction steps were determined by HG-AAS and XRF techniques. Solution matrix effect was observed throughout the HG-AAS analysis and minimized with addition of 1% cysteine as masking agent. All soil sub-samples demonstrated much higher As content than the above global average content of arsenic being found in limestone, pellet limestone for soil pH amendment and MAP/DAP phosphate fertilizers with majority of As showed strong binding with crystalline Fe phases. Direct X-ray spectroscopic analysis was deemed necessary because of possible repartitioning of As between dissolved Mn and residual Fe oxides in the first three extractions steps.

References

(1) G. T. Schmidt, K. H. Lui, M. Kersten. Speciation and mobility of arsenic in agricultural lime. *Journal of Environmental Quality.* (In press)

PO 2.1

Speciation and preconcentration of iron by cloud point extraction combined with fiber optic linear array detection spectrophotometry

Elahe Kazemi[1], Nader Shokoufi[2] and Farzaneh Shemirani[1]

[1] Department of Analytical Chemistry, Faculty of Chemistry, University College of Science, University of Tehran, P.O. Box 14155-6455, Iran
Shemiran@ut.ac.ir
[2] Faculty of Analytical Chemistry, Chemistry & Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Iran

A highly selective method for speciation and preconcentration of iron was developed using cloud point extraction (CPE) combined with fiber optic-linear array detection spectrophotometry (FO-LADS). Cloud point extraction method was based on the chromogenic reaction of Fe (II) and Fe (III) with 1-(2-pyridylazo)-2-naphthol (PAN) and then preconcentration of formed complexes using octylphenoxy polyethoxy ethanol (Triton X-114). When the system temperature is higher than the cloud point extraction temperature (CPT) of selected surfactant, the complex of Fe (II) with 1-(2-pyridylazo)-2-naphthol (PAN) could enter surfactant-rich phase, whereas the complex of Fe (III) remained in aqueous phase. Thus, an in situ separation of Fe (II) and Fe (III) could be realized. Iron complex in the surfactant-rich phase was determined by fiber optic-linear array detection spectrophotometry.

The main factors affecting the cloud point extraction, such as pH, concentration of (PAN) and Triton X-114, equilibration temperature and time, were investigated systematically. Under the optimized conditions, the enhancement factors of 167 and 158 were obtained for Fe (II) and Fe (III) respectively, the limits of detection (LOD) was 0.2 $\mu g L^{-1}$ for Fe (II) and 0.5 $\mu g L^{-1}$ for Fe (III). The relative standard deviations (n = 5, c = 40.0 µg/L) was lower than 3%. The proposed method is highly selective without any interference ions. This method was successfully applied to the speciation of iron in different samples with satisfactory results.

References

(1) D.L. Giokas, E.K. Paleologos, M.I. Karayannis, *Anal. Bioanal. Chem.* 373 (2002) 237.
(2) N. Shokoufi, F. Shemirani, F. Memarzadeh, *Anal. Chim. Acta*, 601 (2007) 204.

Traceability in elemental speciation analysis: Se and Fe species in human serum (EMRP T2J10)

Claudia Swart, Claudia Frank and Olaf Rienitz

Physikalisch-Technische Bundesanstalt,
Bundesallee 100, 38116 Braunschweig, Germany
claudia.swart@ptb.d

Selenium (Se) is an essential element found in enzymes like gluthatione peroxidase which play an important role in cancer prevention, while others like iodthyronine-5'-deiodonase are necessary in the hormone balance. However, the range between deficiency (70 µg per day for adults) and toxicity (700 µg per day for adults) is very narrow. Moreover, not only the dose but also the binding form is crucial for the uptake and effectiveness of Se in the body. Therefore, precise and traceable elemental speciation analysis is necessary to ensure a sufficient, non-toxic provision of patients with Se (1).

One goal of the project T2J10 of European Metrology Research Program (EMRP) is the development of a primary method of measurement for the determination of Se species in biological samples ensuring the traceability of Se speciation analysis. Especially in cancer therapy, Se supplements are often used to reduce negative side effects of chemotherapy and to prevent the growth of new tumours. To adjust this complementary treatment to the individual need of each patient, reliable determination of Se content and speciation in serum is important.

One approach includes the enzymatic digestion of the sample using a mixture of protease, lipase and driselase followed by separation of the species with high pressure liquid chromatography (HPLC) and detection with inductively coupled plasma mass spectrometry (ICP-MS) using species specific double ID-ICP-MS (2,3). Therefore, new species specific reference materials and isotopically enriched species are necessary and will also be developed within this project.

Another important element in clinical diagnostics is iron (Fe). In serum, especially transferrin and ferritin are named in the "Bundesärztekammerrichtlinie (RiLiBäk)" (German medical association directive) as important measurands to be determined in a range of 0.5 to 6 g/L and 10 to 600 µg/L, respectively (4). Up to now, these Fe species are mainly determined by immunoassays which can hardly meet the requirements of the RiLiBäk. Therefore, a primary analysis method comparable to the determination of Se species in serum will be developed using HPLC coupled to ICP-MS and time-of-flight mass spectrometer (TOF-MS).

References

(1) M. Navarro-Alarcon, C. Cabrera-Vique, 2008, *Sci. Tot. Environ.*, 400, 115-141.
(2) J. R. Encinar et al., 2004, *Anal. Chem.*, 76, 6635-6642.
(3) H. Goenaga-Infante et al., 2008, *Anal. Bioanal. Chem.*, 390, 629-642.
(4) Richtlinie der Bundesärztekammer zur Qualitätssicherung laboratoriumsmedizinischer Untersuchungen, 2008.

PO 2.3

Trace Metals Speciation in Water Samples by Sequential Injection Anodic Stripping Voltammetry with Monosegmented Flow and On-line UV Digestion

Watsaka Siriangkhawut[1], Kate Grudpan[1,2] and Jaroon Jakmunee[1,2]

[1] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[2] Science and Technology Research Institute, Chiang Mai University, Chiang Mai 50200, Thailand
scijjkmn@chiangmai.ac.th

A cost-effective sequential injection system incorporating with an on-line UV digestion for decomposing of organic matters before the determination of Zn(II), Cd(II), Pb(II) and Cu(II) by anodic stripping voltammetry (ASV) on a hanging mercury drop electrode (HMDE) using a small scale voltammetric cell was developed. The simplest voltammetric speciation was investigated by separation of the metal species into two groups: labile and inert. The labile species can be detected by direct ASV. The total metal was measured after destruction of dissolved organic matter by on-line UV digestion. A low-cost small scale voltammetric cell using a HMDE as a working electrode was fabricated from disposable pipet tip and microcentrifuge tube. A home-made UV digestion unit was fabricated employing a small size and low wattage UV lamps and flow reactor made from PTFE tubing coiled around the UV lamp. An on-line calibration or a standard addition procedure was developed employing a monosegmented flow technique. Performance of the proposed system was tested for on-line digestion of model water samples to release metal ions from organic complexes such as strong organic ligand (EDTA) or intermediate organic ligand (humic acid). The wet acid digestion method (USEPA 3010a) was used as a standard digestion method for comparison. Under the optimum conditions, deposition time of 180 s, linear calibration graphs in range of 10-300 µg/l Zn(II), 5-200 µg/l Cd(II), 10-200 µg/l Pb(II), 20-400 µg/l Cu(II) were obtained with detection limit of 7.4, 2.7, 5.2 and 3.8 µg/l of Zn(II), Cd(II), Pb(II) and Cu(II), respectively. Relative standard deviation were 4.2, 2.6, 3.1 and 4.7% for 7 replicate analyses of 27 µg/l Zn(II), 13 µg/l Cd(II),13 µg/l Pb(II) and 27 µg/l Cu(II), respectively. The system was validated by the analysis of certified reference material of trace metals in natural water (SRM 1640 NIST). The developed system was successfully applied for the determination of Zn(II), Cd(II) Pb(II) and Cu(II) in ground water samples collected from the nearby zinc mining area.

Comparison of some reaction media for the determination of arsenites by hydride generation atomic absorption spectrometry

Ingrid Hagarová[1], Peter Matúš[1], Jana Kubová[1], Marek Bujdoš[1] and Pavel Diviš[2]

[1] Comenius University in Bratislava, Faculty of Natural Sciences,
Mlynská dolina 1, 842 15 Bratislava, Slovakia
matus@fns.uniba.sk
[2] Brno University of Technology, Faculty of Chemistry,
Purkyňova 118, Královo Pole, 612 00 Brno, Czech Republic

In waters, arsenic is generally found in the inorganic forms of arsenite (As(III)) and arsenate (As(V)). The As(V) forms predominate in oxygenated waters while in deep well waters, where reducing conditions exist, the trivalent species may be present. Because these inorganic species show different toxicity, mobility, and behaviour in biological systems, their differentiation has generated considerable interest.

Many methodologies exist for the speciation analysis of As in water samples. Selective reduction procedure based on the highly pH-dependent reaction between arsenic species and $NaBH_4$ to generate arsine in hydride generation atomic absorption spectrometry (HG AAS) system is relatively commonly used. In this case, for As(V) strongly acidic solution is required (pH ≤ 1), while for As(III) hydride formation occurs in mildly acidic solutions (1).

The reaction between $NaBH_4$ and arsenic in solution is sensitive to pH and it appears that, for the reaction to proceed rapidly, the target species must not be present in solution as a negatively charged species. This means that arsenates must be fully protonated if they have to be converted to arsines. As pK1 for arsenic acid is 2.3, the reaction must therefore be carried out at very low pH (1-2 mol l^{-1} HCl is commonly employed). Arsenites, on the other hand, are protonated under most conditions (pK_1 = 9.2) and will react with $NaBH_4$ under conditions which are only mildly acidic. In the absence of other arsenic species, differentiation of arsenate and arsenite can therefore be simply achieved by exploiting the pH dependency of the $NaBH_4$ reaction with As.

The aim of this study was to critically evaluate the most frequently used reaction media for the speciation analysis of arsenite in the presence of arsenate. Four different reaction media has been used to achieve a selective volatilization of arsenite: 1.5 mol l^{-1} HCl (pH <1.0), 0.1 mol l-1 acetic acid (pH ~2.9), citrate buffer (pH ~3.1), acetate buffer (pH ~5.0) and phosphate buffer (pH ~7.2).

All the studied reaction media can be used for the selective volatilization of As(III) but the serious problem caused by the interference of As(V) was observed (in 0.1 M acetic acid, citrate buffer and acetate buffer) when relative content of As(III) was less than 10 % (from all the present arsenic). Natural waters usually contain less than 10 % of As(III), so speciation in the real samples should be accompanied with another speciation analysis procedure to confirm the accuracy of obtained data. This problem was not observed in phosphate buffer but in this case the sensitivity was significanly lower and the speciation analysis in this medium can be done only if relatively high contents of As(III) in the samples are present.

References

(1) I. Hagarová, *Chem. Listy* 101 (2007) 768-775.

The work was supported by Slovak Research and Development Agency under the contracts No. LPP-0038-06, LPP-0188-06, SK-CZ-0044-07 and LPP-0146-09, by Scientific Grant Agency of Ministry of Education of Slovak Republic and the Slovak Academy of Sciences under the contracts No. VEGA 1/4463/07, VEGA 1/4464/07 and VEGA 1/0272/08 and by Ministry of Education, Youth and Sports of Czech Republic under the contract No. MEB 080813

Speciation of inorganic antimony by stripping voltammetry: advantages of a gold wire electrode

P. Salaün

Earth and Ocean Sciences Department, University of Liverpool,
Brownlow Street, Liverpool L69 3GP, UK

Antimony in seawater and fresh water is mainly present as inorganic species, Sb(V) being much more predominant in oxic systems. The total concentrations are usually very low with levels around 0.2 ppb in sea water and even much lower in uncontaminated freshwater (1). Sb(III), when detected, is rarely present as more than 10% of the total concentration. However, much higher concentrations have been found in mineral water due to release of Sb present within the plastic container PET (polyethylene terephtalate) (2). This gives an indication of the potential contamination problems related to sample storage of water sample with low levels of antimony.

On-site analysis greatly reduces these problems and voltammetry is ideally suited because of its portability, miniaturisation and sensitivity. Using a gold microwire electrode previously used for Cu, Hg (3) and As (4) detection, the optimum voltammetric procedures for antimony speciation will be presented. The speciation scheme is very similar to the one developed for arsenic (4), is rapid and simple to implement. Sb(III) is first detected by anodic stripping voltammetry (ASV) either at natural pH or in acidic conditions. Sb(III) is then oxidised into Sb(V) by chlorine which is produced electrochemically at the auxiliary electrode after acidification to 0.1 M HCl. The total antimony present as Sb(V) is then directly determined and the original Sb(V) concentration retrieved by simple subtraction. This speciation scheme presents several advantages over other electrochemical methods. For instance, mild acidic conditions (0.1 M) are sufficient for the determination of Sb(V) at the sub ppb level which would usually require either a chemical reduction step to Sb(III) or a very acidic media (5 M HCl) to be achieved. In addition, Sb(III) can be measured at natural pH which not only preserves the original speciation of Sb(III) but also facilitates the analytical procedure: no acid and no stabilising agent (e.g. ascorbic acid) are required.

Particular attention will be given to the interference of arsenic. Arsenic is naturally present at much higher levels than Sb and gives an ASV signal at similar potentials. However, using an adapted deposition potential, Sb does not suffer from As. For instance, at low deposition potential (e.g. -1.8 V) and in acidic conditions (pH ≤ 1), arsenic is reduced to arsine which does not remain adsorbed at the electrode and only Sb(V) is accumulated and stripped. Under optimum conditions, low detection limits are obtained for both Sb(III) and Sb(V) (< 0.1 ppb) with short deposition times (c.a. 30s). Total Sb levels in Liverpool Bay and in fresh/mineral water favourably compare with literature values and ICP-MS analysis respectively. Relatively high levels but still lower than the European maximum contaminant level (MCL) of 5 ppb (40 nM) were detected in all tested mineral water.

References

(1) Filella, M.; Belzile, N.; Chen, Y. W., Antimony in the environment: a review focused on natural waters I. Occurrence. *Earth-Sci. Rev.* **2002**, 57, (1-2), 125-176.
(2) Shotyk, W.; Krachler, M.; Chen, B., Contamination of Canadian and European bottled waters with antimony from PET containers. *J. Environ. Monit.* **2006**, 8, (2), 288-292.
(3) Salaün, P.; van den Berg, C. M. G., Voltammetric detection of mercury and copper in seawater using a gold microwire electrode. *Anal. Chem.* **2006**, 78, (14), 5052-5060.
(4) Salaün, P.; Friedrich-Planer, B.; Van den Berg, C., Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode. *Anal. Chim. Acta* **2007**, 585, (2), 312-322.

Comparison of chemical and electrochemical hydride generation for the on-line determination of arsenic species with an atmospheric pressure glow discharge in helium

T. Fiedler, B. Gielniak, P. Wu and J. A. C. Broekaert

University of Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany
jose.broekaert@chemie.uni-hamburg.de

Most glow discharges described up to now were operated under reduced pressure. In this case it is not easy to handle glow discharges for the analysis of many samples as on-line use is difficult. Therefore atmospheric pressure glow discharges (APGD) are developed and characterized for on-line use with advanced types of sample introduction. Such plasmas can be made use of to directly analyze gaseous samples with mass spectrometry or optical emission spectrometry. A further advantage as compared to the ICP is their very low gas flow (~1% of the one of the ICP).

In this study an APGD in helium was used as radiation source to determine volatile hydride forming elements by optical emission spectrometry. The effects of different electrodes and mountings were investigated.

To produce hydrides, chemical and electrochemical (EcHG) hydride generation were used. One disadvantage of chemical hydride generation is the poor stability of sodium borohydride solutions, which therefore must be prepared daily. In electrochemical hydride generation only sulphuric acid is required and the concentration of this acid can be monitored and kept constant.

A new electrolysis cell for EcHG was developed which is divided into an anode and a cathode compartment by a Nafion® membrane. The efficiency of this cell was determined and the effectiveness compared with the one of other electrolysis cells.

The combination of EcHG and APGD has been optimized and figures of merit such as the limit of detection, the precision and sensitivity as well as the response to different species of arsenic were compared with those of chemical hydride generation APGD. The applicability to environmental and industrial samples will be shown.

Micro-XANES: A tool for the analysis of copper impurities in photovoltaic polycrystalline silicon

Günther Buzanich[1], Denise Kreßner-Kiel[2], Thomas Kaden[2], Heinrich Riesemeier[1], Martin Radtke[1] and Uwe Reinholz[1]

[1] Federal Institute for Materials Research and Testing BAM,
Richard Willstätter-Straße 11 12489 Berlin, Germany
guenther.buzanich@bam.de
[2] TU Bergakademie Freiberg, Akademiestraße 6, 09596 Freiberg, Germany

X-ray beam diameters of one micrometer can be obtained at the BAMline at the storage ring BESSY II in Berlin using compound refractive lenses (CRL). The accepted beam size for the lenses is (140 x 140) μm^2, thus the gain in the spot is about 15000. The application of such lenses in X-ray fluorescence spectroscopy (XRF) and X-ray absorption near edge spectroscopy (XANES) on grain boundaries of photovoltaic polycrystalline silicon yields information about impurities and their chemical states. It is certain, that impurities, such as metals, can dramatically decrease charge carrier lifetimes in solar cells. The efficiency of this analytical tool will be demonstrated on p-type polycrystalline silicon.

PO 2.8

Drop-on-demand aerosol generator for ICP-MS analysis

J. N. Schaper, J. Maßmann and N. H. Bings

Johannes Gutenberg University Mainz, Institute for Inorganic and Analytical Chemistry,
Duesbergweg 10-14, 55128 Mainz, Germany
bings@uni-mainz.de

Marine iodine species seem to have great influence on particle formation processes in the atmosphere (1), but only few species could yet be identified. Due to very low concentrations of these species, high efficient sample introduction systems for plasma-source mass spectrometers need to be used. However, the introduction of liquid samples into analytical plasmas is still the Achilles's heel in the field of inorganic trace and especially speciation analysis, which is commonly established through the continuous generation of aerosols via pneumatic nebulization. It is well known that this aerosol not only shows a relatively broad particle size distribution but mostly also results in a too high load for the plasma source and is thus not suitable for direct introduction into the ICP. Various spray chamber designs – optimized e.g. 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. Unfortunately, this might also result in an unfavourable loss of sensitivity.

Hyphenated techniques are an essential tool in modern elemental speciation analysis. In particular when hyphenating liquid chromatography (e.g. HPLC or IC) and capillary electrophoresis (CE) to plasma source mass spectrometry the efficient nebulization of very small liquid volumes is indispensable, because of low eluent volume flow rates, which necessitates special low-flow and micro-flow nebulizer/spray-chamber systems. Therefore, the generation of small and preferably monodisperse droplets from liquid samples for elemental trace and speciation analysis is of common interest.

In this poster we present a novel approach in generating aerosol from very small liquid sample volumes by applying a new drop-on-demand aerosol generator based on thermal-inkjet technology. The software independent design of a micro-controller allows easy regulation of droplet generation frequency as well as droplet diameter and overall flow rate. The new system may be suitable to overcome weaknesses of current hyphenating techniques like e.g. post column dilution in CE or the generation of additional noise, stemming from pumps, necessary for the delivery of the mobile phase in HPLC and the make-up liquid in CE. Also, matrix effects from organic species might be less important, because the overall solvent load of the plasma is reduced. The new aerosol generator will be characterized and its potential as a nebulizer for ICP-MS-based analysis of different marine iodine species will be outlined.

Acknowledgements: The authors kindly acknowledge the financial support within the Interdisciplinary Research Training Group GRK 826 "Trace Analysis of Elemental Species: Development of methods and applications" from the German Research Foundation DFG.

References

(1) (Gilfedder, BS; Lai, SC; Petri, M; *Atm. Chem. Phys.*, 8, 6069-6084, 2008).

PO 2.9

Fundamental characterisation of a new drop-on-demand aerosol generator: introduction of single droplets into plasma excitation and ionization sources

J. H. Petersen, J. Massmann, J. N. Schaper and N. H. Bings

Johannes Gutenberg University Mainz, Institute for Inorganic and Analytical Chemistry,
Duesbergweg 10-14, 55128 Mainz, Germany
bings@uni-mainz.de

Inductively coupled plasma mass spectrometry (ICP-MS) combined with different chromatographic or electrophoretic separation techniques is a powerful and common tool for elemental speciation analysis. However, the design of the interface used for hyphenating the separation device with the ICP influences, and thus limits, the analytical figures of merit of the developed method. Due to low eluent volume flow rates, the capability of efficient nebulisation of very small liquid volumes is one indispensable prerequisite for the selection of an appropriate tool and in many cases conventional pneumatic low-flow nebulisers are used to serve this goal. Still, the addition of make-up solvent flows is in most cases needed to meet the specifications of such nebulisers. Other drawbacks of such systems, which also limit the achievable power of detection, might be the noise and signal fluctuations generated by such nebulisers, as well as relatively broad droplet size distributions. The latter often necessitates the use of spray chambers, which additionally compromises the overall aerosol generation efficiency.

In a new approach for a micro-flow nebulizer we present a novel system, which is based on thermal inkjet printing technology. The so called “drop-on-demand aerosol generator” is micro controlled, uses a modified “stand alone” printer cartridge for aerosol generation and is capable to dose sample volumes in the pL-range. The drop diameter and the dosing frequency are adjustable, as well as the number of used dosing nozzles. This allows effective droplet generation over a wide range of flow rates.

In this poster we present a fundamental characterization of the novel drop-on-demand aerosol generator in both individual and continuous droplet generation modes. Data on the achievable precision regarding the droplets’ size, volume and size distributions will be presented.

Development and characterisation of a drop-on-demand-generator for sample introduction of very small volumes for plasma-spectrometry

J. Massmann, J. H. Petersen, J. N. Schaper and N. H. Bings

Johannes Gutenberg-Universität Mainz, Inst. für Analytische Chemie,
Duesbergweg 10-14, 55128 Mainz
email: bings@uni-mainz.de

Sample introduction in plasma spectrometry is a major bottleneck due to high losses in this step. Conventional pneumatic nebulization is the most common way of introducing liquid samples into excitation sources in inorganic analysis.

In elemental speciation hyphenated techniques, especially those based on the combination of capillary electrophoresis (CE) and plasma mass spectrometry requires additional make-up solvent flows to meet the specifications of conventional systems used for sample introduction into the plasma source. To minimize the risk of contamination and degradation of chromatographic resolution a new strategy for direct and flexible introduction of liquid samples in case of speciation analysis is desired.

Prior investigations have shown that commercially available thermal-inkjet printers can be successfully used for precise handling of small sample volumes. However, such available systems are software-dependent and limited to fixed parameter settings, which is still disadvantageous regarding e.g. flexible volume flows and adjustable droplet diameters.

In this poster we present a new approach in nebulization of liquids via stand-alone thermal-inkjet-print cartridges. This system is capable of highly efficient aerosol generation with reduced and adjustable noise-spectra.

The droplet diameter and the total volume flow rate are adjustable to match requirements of low-flow hyphenated techniques. The novel system will be characterized and the achievable analytical figures of merit of such a DOD-nebulizer combined with a quadrupole ICP-MS will be outlined.

PO 2.11

Ion chromatography-Inductively coupled plasma mass spectrometry used for the speciation analysis

ZuLiang Chen[1,2], Mallavarapu Megharaj[1,2] and Ravendra Naidu[1,2]

[1] Centre for Environmental Risk Assessment and Remediation,
University of South Australia, Mawson Lakes, SA 5095, Australia
[2] Cooperative Research Centre for Contamination Assessment and
Remediation of Environments,
Mawson Lakes Boulevard, Mawson Lakes, South Australia, 5095, Australia
Zuliang.chen@unisa.edu.au

Hyphenation of separation technologies and element-selective or molecule-selective detection systems is the general technique of speciation analyses. It has become a common practice in recent years to ion chromatography (LC) with inductively coupled plasma-mass spectrometry (ICP-MS) for ultra-sensitive detection of trace element of interest. However, conventional ICP-MS serves as an ultra-sensitive elemental detector only, and it is unable to provide inherent information about chemical species. For speciation analysis of unknown chemical species or where chemical standards not available one of the most commonly applied techniques is electrospray ionization-mass spectrometry (ESI-MS). In this presentation, we give our recently work for the speciation analysis using ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS) and electrospray mass spectrometry (ESI-MS). Various speciations, including As, Cr, Se, V, Br, I, Sn, Zn and Pb aminocarboxylic complexes, metal-EDTA complexes were determination using both LC-ICP-MS and ESI-MS. The methods used for analysis of the real samples are also presented.

PO 2.12

Elemental imaging in thin sections of mouse aortas

Dagmar Urgast[1], Andrea Raab[1], John Beattie[2] and Jörg Feldmann[1]

[1] TESLA (Trace Element Speciation Laboratory), University of Aberdeen, College of Physical Science, Chemistry, Meston Walk, Aberdeen AB24 3UE, Scotland, UK
[2] Rowett Institute of Nutrition and Health, University of Aberdeen, Greenburn Road, Bucksburn, Aberdeen AB21 9SB, Scotland, UK

Heart disease is a major cause of death in the European population and the build up of fatty deposits in important blood vessels can eventually cause a heart attack. Oxygen and other reactive compounds cause damage to living cells and this it what often starts and promotes the deposition of fatty deposits in blood vessels. Zinc is a micronutrient which protects against the reactive compounds that cause oxidation in cells. It is therefore potentially protective against oxidative damage to blood vessel tissue and, conversely, zinc deficiency might be expected to encourage vascular cell damage.

The aim of this project is to determine whether zinc deficiency at levels relevant to the UK human population can affect the development of vascular disease. Therefore feeding experiments with ApoE knock out mice were carried out exposing the mice to low, medium and normal zinc concentrations in their diet. Thin sections (35 µm thickness) of the mice aortas were prepared and then analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to generate images showing the distribution of ^{13}C, ^{24}Mg, ^{31}P, ^{34}S, ^{44}Ca, ^{65}Cu, ^{57}Fe, ^{55}Mn, ^{66}Zn in the thin sections. The laser used was a LSX 200+ 266 nm Nd:YAG laser from CETAC with a large ablation cell. Spot size and speed of translation stage were optimised using 0.2 mm thick lines (distance 0.76 mm) printed by a laser printer on paper. Optimum conditions, considering time and resolution, were found to be 100 µm spot size coupled with 25 µm/s translational speed and a distance between lines of 200 µm. Integration time for the elements varied between 10 ms (^{13}C) and 100 ms (^{55}Mn and ^{66}Zn).

The distribution of carbon intensity followed the distribution of actual tissue in the sections and therefore allowed this element to be used as internal standard. This was used to cancel out any variability in tissue thickness, ablation efficiency and laser output in order to generate semi-quantitative element maps of the tissues. The distribution of Mg, P and S was relative homogeneous within the tissue, whereas especially Ca showed strong localisation effects indicating calcification of the aortas. This shows that semi-quantitative element maps can be used to identify element distribution and hot spots of elements in tissue thin sections.

Acknowledgement: This project is funded by the Korean Research Foundation (KRF-2008-220-F00013).

Determination of superoxide dismutase (SOD) by using species-specific isotope dilution (SS-IDMS) analysis using GE-LA-ICP-MS

Sandra Braukmann, Christian L Deitrich, Andrea Raab and Jörg Feldmann

TESLA (Trace Element Speciation Laboratory)
University of Aberdeen, College of Physical Science, Chemistry, Meston Walk
Aberdeen AB24 3UE, Scotland, UK

The quantification of proteins can as best described as semi-quantitative methods and bio-analytical chemistry has so far been satisfied. However, a direct comparison between two different sets of samples (e.g., exposed and control) are necessary. Absolute measurements can not been made. Using elemental mass spectrometry is capable to determine in absolute terms the amount of a metal-containing species when separated from other species. During separation and preparation steps the integrity of the compound cannot always been guaranteed. Hence, new techniques need to be introduced. The quantification of organometallic compounds in biological samples has made a step change when the concept of species-specific isotope dilution mass spectrometry (SS-IDMS) has been used for example for butyltin or methylmercury compounds.

Here this concept is used for the quantification of the metalloprotein superoxide dismutase (SOD), which contains one copper and one zinc in each of the two subunits. The absolute quantification of SOD is necessary to assess the redox stress from so called reactive oxygen species (ROS) in a certain tissue. A copper and zinc isotopically-enriched superoxide dismutase (SOD) which has been used to quantify SOD in liver homogenates using 2 D chromatography ICPMS has been used as spike (1,2). Here we applied SS-IDMS for the separation of protein mixtures on a non-denaturing gel electrophoresis coupled with laser ablation inductively-coupled plasma mass spectrometry (GE-LA-ICPMS) as described elsewhere (3).

The isotopically enriched SOD shows the same migration time as the native SOD in the 1 D gels. When measuring the isotope ratio of copper and zinc using LA-ICPMS from the gel it is obvious that the proteins do not only migrate horizontal to the migration paths but they show also diffusion into the gel in orthogonal direction.

Considering the orthogonal diffusion of the proteins recovery rates around 89 % can be achieved for SOD when SS-IDMS-GE-LA-ICPMS is used.

References

(1) C.L. Deitrich, A. Raab, B. Pioselli, J. Thomas-Oates, J. Feldmann, Chemical preparation of an isotopically enriched superoxide dismutase and its characterisation as a standard for species-specific isotope dilution analysis, *Analytical Chemistry* (2007) **79**, 8381-8390.

(2) B. Pioselli, C. Munro, A. Raab, K. Songsrirute, J. Feldmann, J. Thomas-Oates, Denaturing and non-denaturing microsolution isoelectric focussing to mine the metalloproteome, *Metallomics*. In press August (2009).

(3) A. Raab, B. Pioselli, C. Munro, J. Thomas-Oates, J. Feldmann, Evaluation of gel electrophoresis conditions for the separation of metal tagged proteins with subsequent laser ablation ICP-MS detection, *Electrophoresis* (2009), **30**, 303-314.

PO 3.1

Investigations of mercury interaction with human blood components by means of static high senitivity ICP (SHIP)

Sascha Nowak[1], Stefan Trümpler[1], Björn Meermann[1], Gerhard A. Wiesmüller[2], Wolfgang Buscher[1], Michael Sperling[1,3] and Uwe Karst[1]

[1] University of Münster, Institute of Inorganic and Analytical Chemistry, Corrensstraße 30, 48149 Münster, Germany
[2] Environmental Specimen Bank for Human Tissues, University Hospital Münster, Domagkstraße 11, 48149 Münster, Germany
[3] European Virtual Institute for Speciation Analysis, Mendelstraße 11, 48149 Münster, Germany

To investigate the effects of mercury species intoxication and to test the efficiency of different commonly applied antidota, human whole blood was spiked with inorganic mercury (Hg^{2+}) or methylmercury ($MeHg^{+}$, CH_3Hg_+) prior to treatment with the antidota 2,3-dimercaptopropan-1-ol (British Anti Lewisite, BAL), 2,3-dimercaptosuccinic acid (DMSA) and N-acetylcysteine (NAC). Blood was fractionated into its components blood plasma proteins, plasma liquid and red blood cells, and the distribution of mercury between these fractions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and the Static High sensitivity ICP (SHIP). While this system is well characterized in combination with ultrasonic nebulizer sample introduction and has also been investigated in view of its analytical performance with wet aerosol introduction (1,2,3), there is only limited experience regarding the application of SHIP towards samples with high matrix content. The accuracy of the method was assessed by using real samples with complex matrix composition and comparison of the results with those obtained by ICP-OES operated with a conventional Fassel-type torch.

References

(1) A. Klostermeier, C. Engelhard, S. Evers, M. Sperling, W. Buscher, *J. Anal. At. Spectrom.*, 2005, **20**, 308-314.
(2) C. Engelhard, A. Scheffer, S. Nowak, T. Vielhaber, W. Buscher, *Anal. Chim. Acta*, 2007, **583**, 319-325.
(3) A. Scheffer, C. Engelhard, M. Sperling, W. Buscher, *Anal. Bioanal. Chem.*, 2007, **388**,1605-1613.

Analytical approaches to selenium speciation in eggs

Elżbieta Lipiec[1,2], Katarzyna Bierla[1], Grzegorz Siara[1,2] and Joanna Szpunar[1]

[1] Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, CNRS UMR 5254, Hélioparc, 2, av. Pr. Angot, 64053 Pau, France
[2] Katedra Chemii Analitycznej, Wydział Chemii, Politechnika Warszawska, ul. Noakowskiego 3, 00-664 Warszawa, Poland

Eggs are an important source of protein, essential vitamins and minerals and can make a significant contribution to a healthy diet. They are the most popular foodstuff of animal origin and one of the most versatile ingredients used in domestic cooking and in many branches of the modern food industry. Eggs are consumed regularly by the majority of the population and as such can be considered a good candidate to become functional food. Due to physiological processes protecting the embryo, it is practically impossible to increase significantly the level of minerals in eggs.

However, selenium, known to protect cell membranes against oxidation, can be incorporated into egg proteins and its content in eggs can be easily manipulated. Presently, Se-enriched eggs are introduced to the market in many countries. Nevertheless, it rises many concerns regarding safety and quality issues related not only to the total selenium content but also to the identity of selenium species present and their bioavailability.

Analytical methods providing information on the selenium species present in eggs have been scarce. Most of selenium is believed to be incorporated into proteins. However, the difficulties in identifying the individual Se-containing proteins spur interest in methods allowing at least the distinction between the fraction of selenium present in the form of selenomethionine (*selenized proteins*, unspecific replacement of S by Se during supplementation), selenocysteine (corresponding to *true selenoproteins*) and non-covalently bound inorganic selenium. Recently, it was demonsrated that the optimization of the sample preparation procedure and, in particular, a selenocysteine derivatization step, allowed the quantitative recovery of seleno-aminoacids prior to their specific determination in milk and meat and samples.

This work presents the development of an analytical approach based on a similar principle allowing an insight into the incorporation of selenium into egg proteins. The results obtained indicate the preferential incorporation of selenium into selenized proteins in the egg white and into selenoproteins in the yolk.

In addition, bioavailability of selenium present supplemented eggs (white and yolk) was investigated by fractionation of selenium in simulated gastric and gastrointestinal conditions. It was demonstrated that more than 50 % of selenium present could be bioavailable.

PO 3.3

Speciation analysis of glutathionine peroxidase, selenoprotein P and selenoalbumin in human serum by tandem affinity HPLC and on-line isotope dilution ICP-MS in a healthy Greek population

Sophia Letsiou[1,2], Tzortzis Nomikos[2], Demosthenes Panagiotakos[2], Christos Pitsavos[3], Christodoulos Stefanadis[3], Smaragdi Antonopoulou[2] and Spiros A. Pergantis[1]

[1] Department of Chemistry, University of Crete, Voutes, 71003, Greece
spergantis@uoc.gr
[2] Harokopeio University, El.Venizelou 70,17671 Athens, Greece
[3] First Cardiology Clinic, School of Medicine, University of Athens, Vas.Sofias 114, 11527 Athens, Greece

A previously published method (1,2) based on affinity chromatography (AF) HPLC (Hi-Trap Heparin and Hi-Trap Blue-Sepharose columns) hyphenated to inductively coupled plasma-(quadrupole) mass spectrometry (ICP-QMS) was further improved for the speciation analysis of selenoprotein P (SelP), glutathione peroxidase (GPx) and selenoalbumin (SeAlb) in human serum. The proposed methodology was used to quantitatively determine selenium species in human serum samples taken from a group of healthy volunteers (N=400). The results obtained from this population, along with already published results obtained using a variety of analytical techniques, are compared and a table containing this data is presented. The latter, we consider important in order for comparisons between the various analytical techniques currently being used to be possible. To assist with such comparisons concentration units have been converted. This is important in order for direct comparison of the ICP-MS based techniques with immunoaffinity techniques to be readily made and potential differences revealed.
The mean concentration for the determined selenoproteins in the serum samples taken from a healthy Greek subpopulation (N=110) was GPx 16.9 ± 5.0 μg Se/mL, SelP 50.5 ± 11.5 μg Se/mL and SelAlb 10.7 ± 4.1 μg Se/mL. According to these results 15% of Se is distributed in GPx, 45% in SelP and 10% in SeAlb. The method accuracy for the determination of total protein-bound Se was assessed by analyzing numerous samples of a human serum certified reference material (BCR-637, 638, 639) certified for total Se content. Also comparisons with results from other publications conducting selenium speciation in BCR 637 were in good agreement.
Furthermore, we evaluated the obtained from the healthy Greek population serum protein results with anthropometric, biochemical and lifestyle characteristics of our population using biostatistical analysis (SPSS V.16). Multivariate analysis reveals a significant inverse association between SelP and age of the participants ($p<0.001$). On the other hand sex as well as BMI of participants does not seem to influence the levels of SelP, GPx and SelAlb in human serum.
In conclusion, this is the largest study, so far, concerning the determination of serum selenium species in an apparently healthy Greek population (This is an ongoing study with more samples continuously being analyzed). The main outcome of which was the suitability of the applied analytical method for simultaneous speciation analysis of GPx, SelP and SeAlb in a large number of serum samples. The method proposed used proved to be robust and relatively time-efficient. Moreover, our results are rather promising since they provide baseline data for potential selenium biomarkers and will further our understanding of the function of Se in human metabolism. A clearer picture should be obtained after further work investigating relationships between serum selenium species and other biochemical, anthropometric and life style factors of the healthy volunteers.

References

(1) Reyes LH, Marchante–Gayon JM, Garcia Alonso JI, Sanz–Medel A (2003), *J Anal At Spectrom*, 18:1210-1216.
(2) Jitaru P, Cozzi G, Gambaro A, Cescon P, Barbante C (2008), *Anal Bioanal Chem* 391:661-669.

PO 3.4

Arsenolipids in cod liver tissue

U. Arroyo[1], M.-P. Elizalde[1], J. Mattusch[2], S. Mothes[2], M. Möder[2], R. Wennrich[2] and F.-M. Matysik[3]

[1] Centro de Química, Universidad Autónoma de Puebla. Apdo. Postal J-55, 72571 Puebla, Pue., Mexico
[2] Helmholtz Centre for Environmental Research - UFZ, Department of Analytical Chemistry, Permoserstraβe 15, 04318 Leipzig, Germany
[3] Institute of Analytical Chemistry, Chemo- and Biosensors, University of Regensburg, Universitätsstraße 31, 93053 Regensburg, Germany

Arsenic is a metalloid well known for its toxicity varying depending on the inorganic or organic species. Beside water-soluble arsenic species lipid-soluble arsenicals (arsenolipids) are present in a wide range of biological samples mainly in marine organisms (1). Arsenolipids have recently attracted considerable interest. However, human health effects are still unexplored. In order to elucidate the role of arsenolipids in organisms new analytical approaches for reliable determination of this class of arsenic compounds in various matrices are needed.

The highest concentrations of arsenolipids were found in seafood which served as source material in this study. The investigations were focused on the three mainly occurring arsenolipids found in canned cod liver. The solid samples were extracted and purified using a silica gel column and ethyl acetate/methanol as eluent. Analytical studies were conducted by means of GC-ICPMS, GC-AED, GC-MS and TOF-MS. The results obtained by GC-ICPMS and GC-AED showed the existence of arsenic compounds in the fractions collected. Three major peaks were found within a retention time window between 10 and 25 min. Additional to these major peaks, several other arsenic containing compounds could be detected by GC-ICPMS and GC-AED as highly volatile arsenic compounds (HVAs). The occurrence of HVAs and less volatile compounds (LVAs), can be correlated with the polarity of the eluent used for fractionation. For identification of the three LVAs their molecular masses [M-16] were detected in the SIM mode of GC-MS. TOF-MS which allows highly accurate mass determination was used to gain complementary information. The results showed the presence of these arsenic containing hydrocarbons with the following molecular formulas: $C_{17}H_{37}AsO$ (calculated for $[M + H]^+$ 333.2133; found 333.2136; Δm = 0.90 ppm; $C_{19}H_{41}AsO$ (calculated for $[M + H]^+$ 361.2446; found 361.2446; Δm = 0.00 ppm; $C_{23}H_{37}AsO$ (calculated for $[M + H]^+$ 405.2133; found 405.2145; Δm = 2.96 ppm. Suggestions for corresponding structures will be discussed and compared with recent results reported by Francesconi and coworkers for samples prepared from fish capelin (2).

References

(1) E. Schmeisser, W. Goessler, N. Kienzl, K. A. Francesconi, *Analyst*, **2005**, 130, 948.
(2) M. S. Taleshi, K. B. Jensen, G. Raber, J. S. Edmonds, H. Gunnlaugsdottir, K. A. Francesconi, *Chem. Commun.*, **2008**, 4706.

PO 3.5

EC/LC/ICP-MS Analysis of Amiodarone and Its oxidation products

Björn Meermann, Wiebke Lohmann, Ines Möller and Uwe Karst

University of Münster, Institute of Inorganic and Analytical Chemistry,
Corrensstraße 30, 48149 Münster, Germany
bjoern.meermann@uni-muenster.de

The on-line combination of electrochemistry (EC), liquid chromatography (LC) and mass spectrometry (MS) allows to mimick the cytochrome P450 mediated oxidative metabolism of pharmaceuticals in the body (1). In a large volume electrochemical flow-through cell, the quantitative conversion of the target compounds under optimum conditions, drugs can be oxidized to their phase I metabolites. These metabolites can be separated under reversed-phase conditions and further characterized mass spectrometry.

The antiarhythmic agent amiodarone was chosen as model compound for the evaluation of the EC-LC-MS system with both electrospray (ESI) and inductively coupled plasma (ICP) ionization because it contains iodine atoms. Amiodarone was oxidized at a porous glassy carbon working electrode at different electrochemical potentials under formation of mainly N-dealkylated species, which were also observed under cytochrome P450 catalysis. The oxidation products were separated under isocratic RP-HPLC conditions using phase optimized liquid chromatography (2), because gradient elution leads to plasma instabilities. ESI-MS provided qualitative information on the oxidation products, while for the first time, ICP-MS was used for the quantification of the metabolites.

References

(1) Lohmann W., Karst, U. *Analytical and Bioanalytical Chemistry* 2008, 391(1), 79-96.
(2) Lamotte S., Brindler R., Bischoff K.D. *CLB Chemie in Labor und Biotechnik* 2006, 57(9-10), 349-351.

PO 4.1

Arsenic speciation in Hungarian wheat by HPLC-ICP-MS

Eva Sugar[1] and Eszter Sugar[2]

[1] Central Agricultural Office Food and Feed Safety Directorate,
Mester u. 81, H-1095 Budapest, Hungary
sugar.eva@gmail.com
2 Agricultural Research Institute of the Hungarian Academy of Sciences,
Brunszvik u. 2, H-2462 Martonvásár, Hungary

The arsenic (As) is the most toxic semi-metal element, which is dangerous for the human body and other organism. Although these days the arsenic poisonings are reduced, it occurs sometimes in the world. The individual sensitivity for toxic effect of arsenic can be very different. High tolerance level of arsenic can increase continuously in human body, which can exceed the toxic level several times.

Natural high concentration of arsenic occurs in deeper levels of groundwater. Arsenic contamination of ground water is found in many countries throughout the world, including some geography areas of Hungary as well. Arsenic and its compounds are used as pesticides, herbicides, insecticides in the agriculture cultivation.

The toxicity of arsenic compounds is different therefore necessary to determinate total arsenic and its species. Actually there is bigger calm to determination of arsenic species separately all over the world, therefore more and more laboratories, as Central Agricultural Office Food and Feed Safety Directorate, adopt the modern speciation techniques to their routine methods.
First step in our laboratory was developing the coupled HPLC-ICP-MS technique for arsenic speciation in fish, rice and wheat samples. Early results shown the total arsenic concentration is higher in the marine fish and rice than wheat. This higher arsenic concentration was in organic form which is a smaller risk than inorganic As (III) or As (V). Another part of this project to determinate any coherence between the different types of Hungarian wheat and different nitrogen treatment and up-taken arsenic levels including species too.

Experiments were carried out on a winter wheat stand grown on chernozem soil with brown forest residues in Martonvásár during 2007/2008. In the two-factor long-term experiment the effect of fertilisation and genotype was studied in a crop rotation where winter wheat was grown after pea. In the split-plot design the N treatments (0, 80, 160, 240 kg ha–1) were in the main plot and the variety (Mv Toborzó – extra early, Mv Palotás – early, Mv Verbunkos – medium early) in the subplot.

Microwave (Milestone Ethos Plus) assisted digestion was used for total arsenic determination and water and enzymatic *(α-amylase)* extractions were used for speciation as sample preparation. Surveyor HPLC system was coupled to the quadrupole ICP–MS (Thermo Elemental X Series). Hamilton PRP 100 anion exchange column was used for the separation of the arsenic species (As III, As V, AB, MMA, DMA) with 20 and 200 mM ammonium carbonate solution.

Engineered nano materials in food with LC-ICP-MS

Elly Wijma, Martijn van der Lee and Ruud Peters

RIKILT- Institute of Food Safety, Wageningen UR.,
Bornsesteeg 45, PO Box 230, 6700 AE Wageningen, The Netherlands

Engineered nano materials (ENMs, by definition particles with one dimension a diameter smaller then 100 nm) become increasingly more important in food and non-food industry. In the past decennia only silver particles were used since these improve the microbiological stability of the food material. Nowadays, ENMs based on titanium, iridium, copper, gold and silicon can already be found in food, non-food products and some food supplements. Beside these new materials the application of other elements in food and non-food products as well as in the production there of are being studied. The EU has not added ENMs to the additive list yet because at present there are no good analytical tests for the determination of ENMs in food. Because of the lack of analytical tests the European parliament may not allow the use of ENMs in food and food technology on the European market before any proper risk assessment

Several methods for chromatographic separation of ENMs are described in literature (1) mostly based on field-flow fractionation (FFF) and often combined with light scattering to detect the sizes of ENMs.

Recently we developed a method for the analysis of nano particles in food and non-food materials based on hydrodynamic chromatography (HDC) in combination with ICP-MS. The method enables the detection of ENMs, there size and size distributions, as well as the elemental composition of the ENMs in food and non-food products. At first ENMs are separated from the food or non-food matrix by several physical processes. Size separation is achieved using HDC on a PL-PSDA cartridge type 1 800*7.5 mm column packed with non-coated, non-porous silica spheres. Finally, any ENMs are detected with ICP-MS.

References

(1) Harald Prestel, Reinhard Niessner and Ulrich Panne, Increasing the sensitivity of asymmetrical flow field-flow fractionation: Slot outlet technique, *Anal.Chem.*, 2006, 78 (18), 6664-6669.

Elemental analysis and soil speciation of citrus plant of Khanpur (Pakistan)

Uzaira Rafique and Shazia Akhtar

Department of Environmental Sciences, Fatima Jinnah Women University,
Rawalpindi-46000, Pakistan

Citrus trees are demanding feeders as nutrient dense food. On the other hand, citrus are sensitive to excess of certain elements in soil. The present study is undertaken to determine uptake of eight elements by different parts of *Citrus sinensis* (orange) and *Citrus paradisi* (grapefruit) grown in Khanpur, District Haripur.

Two composite soil samples from three random spots of each citrus plant was characterized for its organic matter, phosphorus and elemental concentration by methods described by Nelson & Sommers (1996), Blakemore et. al. (1987) and flame atomic absorption spectrophotometer, respectively. Sequential extraction procedure (Tessier et. al, 1979) was used to analyze the extent of elements in exchangeable, carbonate bound, Fe-Mn oxide and organic bound fraction. The results showed that macro and micronutrients are more concentrated in fruit part of both plants. The study concludes that both citrus fruit can be safely consumed to fulfill the RDA for Ca, K, Cu, Zn & Cr. On the other hand, Ca, K and Pb is found more in carbonate bound, Cu, Zn and Ni in organic bound and Cd and Cr in exchangeable form. The study also concludes that soil of Khanpur is supportive to the agriculture of citrus plants. The exchangeable (available) Cadmium transforms into unavailable form due to excessive calcium carbonate in the soil (Chen et. al., 1997). This is a very effective way of reducing the cadmium and lead uptake by crops.

Orange and grapefruit showed higher accumulation potential for nickel showing in dry plant matter.

Keywords: citrus plant, macronutrients, micronutrients, recommended dietary allowance (RDA), soil speciation.

Arsenic-containing hydrocarbons are natural constituents of sashimi tuna

Mojtaba S. Taleshi[1], John S. Edmonds[1], Walter Goessler[1], Maria José Ruiz-Chancho[1], Georg Raber[1], Kenneth B. Jensen[2] and Kevin A. Francesconi[1]

[1] Institute of Chemistry-Analytical Chemistry Karl-Franzens University Graz, Universitaetsplatz 1, 8010 Graz (Austria)
2 Institute for Physics and Chemistry, University of Southern Denmark, 55 Campusvej, 5230 Odense, Denmark

Arsenic occurs naturally in many types of seafood as water-soluble and fat-soluble organoarsenic compounds. Although water-soluble compounds have been well characterised, the fat-soluble compounds, so-called arsenolipids, have until recently remained unknown. We report that sashimi grade tuna fish, with a total arsenic content of 5.9 µg As/g dry mass, contains approximately equal quantities of water-soluble and fat-soluble arsenic. The water-soluble arsenic was predominantly arsenobetaine. Two fat-soluble compounds were isolated and characterised. The first was identified as 1-dimethylarsinylpentadecane [$(CH_3)_2As(O)(CH_2)_{14}CH_3$] by comparison of HPLC/mass spectrometric data and accurate mass data with those of an authenticated synthesised standard. The second arsenolipid was postulated as 1-dimethylarsinyl *all-cis*-4,7,10,13,16,19-docosahexane from mass spectrometric data and analogy with non arsenic-containing lipids found in fish. These two arsenolipids constituted about 50% of the total fat-soluble arsenic; the other 50% consisted of less polar arsenolipids of currently unknown structure. This is the first identification of an arsenolipid in commonly consumed seafood.

PO 4.5

Analytical approaches to comparative metabolomics of selenized yeast

Sandra Gil Casal, Johann Far, Katarzyna Bierla, Hugues Preud'homme and Joanna Szpunar

Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, CNRS UMR 5254, Hélioparc, 2, av. Pr. Angot, 64053 Pau, France

The increased use of selenized-yeast as an efficient source of selenium for supplementation raise interest about the identity of selenium species present in preparations available on the market. The commercial products seem to vary considerably in this respect even if selenomethionine is the most frequently evoked species. Selenomethionine, incorporated into yeast selenized proteins, accounts rarely for more than 60% of total Se its content, but is often considered as a parameter confirming the "organic character" of a yeast.

The presentation is focused on the low molecular weight (less than 1000 Da) selenium species present in yeast representing usually between 10 and 20 %. The presence of more than 30 different species has been evoked so far by the literature (some of them are thought to have biological activity) and the list is by no means exhaustive. However, the difficulties in identifying the individual Se-containing species spur interest in methods allowing at least the distinction between selenometabomolomic profiles of samples of different origin. The feasibility of this approach will be discussed on the basis of a comparison of eight commercially available selenized yeast samples coming from the leading producers located in Europe, the US, Canada, Brazil, Mexico and China.

PO 4.6

Detection of Ni(II) and Co(II) in fibroblasts using CLSM

Yvonne Scheller and Heinz Duschner

Institute of Applied Structure- and Microanalysis,
University medical centre of the Johannes Gutenberg University of Mainz,
Obere Zahlbacher Str. 63, D-55131 Mainz, Germany

Metals have many different functions in human cells. As essential metals they act as cofactors in enzymes, as functional factors in different molecules like for example Fe in haemoglobin. Humans take up these metals with their food. If this food contains unnatural high concentrations of specific metals or specific metals and species, the metabolism can not bear with, toxic effects and deceases can occur.

To get information about the species and their localization in cells especially living cells is difficult using standard analytical techniques and requires optical methods with high lateral resolution like the confocal laser scanning microscopy. This technique in combination with standard fluorescent dyes for metal labelling and organelle labelling is suitable to display single living cells, their structures and the localization of specific metals. Newport Green DCF binds Ni(II) and Co(II) resulting in fluorescent enhancement. As test organism human fibroblasts from gingiva were used. The fibroblasts were incubated with different concentrations (100 µM, 300 µM and 500 µM) of the metal components $NiCl_2$, $NiSO_4$, Ni_3S_2 and $CoCl_2$ for different periods of time between 16h and 48h. The cells were then incubated with Newport Green DCF and analyzed with the CLSM with a magnification of 40.

The analysis showed that incubation with all four metal components tested result in fluorescence in the cells especially in structures around the nucleus. The fluorescence in cells incubated with Ni(II) components showed brighter fluorescence then cells treated with $CoCl_2$. Prolonging the incubation time with Ni(II) components and enhancing their concentration still result in fluorescence around the nucleus. Fluorescence is also detected inside the nucleus and the cytoplasm. In contrast to that, cells incubated with $CoCl_2$ showed no fluorescence inside the nucleus even after 48h of incubation with the highest tested concentration of 500 µM and additionally the fluorescence in $CoCl_2$ treated cells seems to be more diffuse. Parallel detection of Ni(II) or Co(II) with Newport Green DCF, the endoplasmic reticulum with ER Tracker and the golgi apparatus with Bodipy TR gave hints, that the fluorescence around the nucleus correlates with the endoplasmic reticulum.

PO 4.7

Quantitative Determination of 'Organic Germanium' in Nutritional Supplementations

Erwin Rosenberg

Vienna University of Technology, Institute of Chemical Technologies and Analytics,
Getreidemarkt 9/164 AC, A-1060 Vienna, Austria
E.Rosenberg@tuwien.ac.at

Organic germanium compounds, and in particular bis-carboxyethyl germanium sesquioxide (= commonly also named germanium sesquioxide or Ge-132), has for long been under discussion as a nutritional supplement and even a therapeutic agent cancer, immunodeficiency, and other infectious diseases (1). While its beneficial effect for human health has not been demonstrated in a convincing way yet, it continues, however, to be sold via the internet in formulations of different form, e.g. as pure compound, as solution or as tablets. While the beneficial effect of germanium supplementations to the human diet may be arguable, and at least no adverse effects could be observed with the intake of this drug even at higher dosages and for extended periods of time, this is not true for the inorganic forms of germanium, notably germanium oxide (GeO_2). Germanium oxide exhibits pronounced renal toxicity, and has been reported to have led to a number of casualties in the case of regular uptake (2). This clearly points out the need for the speciation of germanium and its (organic) compounds.

Different analytical approaches have been reported in the literature. These are based on ion chromatography (with optical emission (3) or ICP-MS detection (4)), or on the differential determination of the elemental and organic bound form after digestion (5). None of these actually confirms the presence of germanium sesquioxide rather than by the element specific response of the detector, and the agreement of the retention time with the one of authentic standards.

We present here a novel approach for the determination of inorganic germanium and germanium sesquioxide, based on liquid chromatographic separation on an ion exchange column (Phenomenex Rezex RHM) with ESI-MS detection. While elemental germanium is unretained on this particular column, Ge sesquioxide can be detected in the form of its monovalent anion, whereby the exact mass of the detected anion, as well as its fragmentation pattern confirm the identity of the Ge sesquioxide.

It appears to be important to analyse the samples containing Ge sesquioxide promptly after preparation, as the drug tends to hydrolyse to the monomeric subunit, and this can further condense to more complex systems containing two, three or more Ge atoms (6).

References

(1) Omae, *Applications of Organometallic Compounds*, John Wiley & Sons, Chichester, (1999) 165-184.
(2) S.-H. Tao, P. M. Bolger, *Regulatory Toxicol Pharmacol* **25** (1997) 211-219.
(3) A. Padró, R. Rubio, G. Rauret, *Fresenius J. Anal. Chem.* **351** (1995) 449-453.
(4) P. Krystek and R. Ritsema, *J. Trace Elem. Med. Biol.* **18** (2004) 9-16.
(5) D.-Q. Zhang Z.-M. Ni, *Anal. Chim. Acta* **330** (1996) 53-58.
(6) R. Jirasko, E. Rosenberg, M. Holcapek, *Intern. J. Mass Spectrom.* **280** (2009) 198-203.

Notes

ELEMENT 2 & ELEMENT XR HR-ICP-MS
High resolution speciation capabilities

Thermo Fisher Scientific now offers you the tools to detect and quantify the volatile compounds of elements in environmental, clinical and biological samples.

The new kit for coupling Gas Chromatography (GC) to the Thermo Scientific high resolution ICP-MS ELEMENT 2 and ELEMENT XR permits analysis of the volatile compounds of elements such as sulfur, tin, phosphorous, mercury and bromine, at significantly lower levels than traditional techniques thanks to the solution's high sensitivity and, in some cases, the ability to resolve interfering ions from the mass spectrum.

For more information, visit the Thermo Scientific booth.