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ABSTRACTS

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- *Elemental Speciation and Related Applications*

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Abstracts

KN 08

THE COMBINATION OF ICP-MS AND ESI-MS IN ELUCIDATION OF SELENIUM METABOLISM.

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Selenium is an essential trace element which is incorporated in the active center of the antioxidant enzymes glutathione peroxidases and thioredoxin reductases.

Several studies have indicated that selenium may prevent cancer. As the cancer preventive effect is not fully understood, this has triggered an increasing interest in the biochemistry of selenium and analytical techniques for the determination of various selenium-containing biomolecules.

Selenium metabolism is described by a model proposed for the first time by Ganther[1] in 1984. This model is generally accepted and often cited. This model, however, was developed before the development of hyphenated techniques for selenium speciation and the introduction of ESI-MS for identification of selenium metabolites. Hence, the model had to be changed in the new millennium, as the application of these techniques showed that the main urinary metabolite was a selenosugar and not the trimethylselenonium ion proposed in the first model.

The subject of this contribution is to review how the application of LC-ICP-MS together with ESI-MS could verify or change the selenium metabolism model.

W01

IS THE ARSENIC SPECIATION IN FOOD INFLUENCED BY COOKING?

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Provided that the arsenic concentration in drinking water is below the WHO limit of 10 µg/l most of the arsenic ingested by humans comes from the food. Especially food of marine origin like fish and mussels are well known to contain high arsenic concentrations. Rice is the only food of terrestrial origin that contributes significantly to the arsenic intake. Although the total arsenic concentrations in rice are usually below the concentrations found in marine food, the speciation is dominated by the more toxic inorganic arsenic compounds and simple methylated arsenicals. From a consumer point of view it is important to know how cooking procedures may influence the arsenic speciation in food.

In the present work we investigated three brands of rice (0.11-0.27 mg As/kg), cod fish (0.47 mg As/kg), salmon (1.2 mg As/kg) and mussels (1.8-2.9 mg As/kg) for arsenic compounds before and after cooking (values are expressed as wet mass).

Arsenite, arsenate, and dimethylarsinic were detected before and after cooking the rice. Additionally thio-dimethylarsinic acid was found in some samples after cooking. Arsenobetaine, oxo- and thio-arsenosugar-glycerol as well as the oxo- and thio-arsenosugar-phosphate were found in mussels before and after cooking. Arsenobetaine and traces of arsenocholine were detected in raw and roasted fish samples. Surprisingly arsenobetaine decarboxylated to the tetramethylarsonium ion upon roasting.

W02

SIMULTANEOUS DETERMINATION OF MERCURY AND SELENIUM SPECIES IN URINE FROM LONG-TERM MERCURY EXPOSED POPULATION BY ONLINE HPLC-ICP-MS

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Mercury and selenium in human urine has previously been studied using different analytical techniques for each species. In this study a single method, allowing the separation and determination of mercury and selenium species in human urine, is developed using reversed-phase ion-pairing high performance liquid chromatography -inductively coupled plasma-mass spectrometry (RP-IP-HPLC-ICP-MS). Selenocystine, selenomethionine, selenourea, selenocystamine, inorganic selenium, inorganic mercury(II) and methylmercury(I) were individually detected. The detection limits are 0.1-1.5 μg/L and the linear calibration range for se concentrations is between 1 and 100μg/L. The detection limits of the method for inorganic and methyl mercury are 1 μg/L and 0.6 μg/L, respectively. The method was applied to analyze urine samples from long-term mercury exposed populations. The results showed that selenocystine is the major selenium compound while both inorganic and methylmercury are detected in urine. Selenium and mercury was not found at the same elution time, which suggests that there is no Se-Hg complex in human urine.

W03

CHROMUIM SPECIATION ANALYSIS IN PROFESSIONAL EXPOSED PERSONS: OPTIMIZATION AND VALIDATION OF THE METHOD

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A method was developed for simultaneous determination of CrIII and CrVI for professional exposure evaluation. The presentation describes the optimization and validation according with the UNI CEI EN ISO/IEC 17025:2005 of the chromium speciation analysis using an HPLC-ICP-MS method with the DRC.
We used a Dionex HPLC connected with a Perkin Elmer ELAN DRC II in gas mode (NH_3) to prevent interferences. The calibration curve was built between 5-50 ng/ml for both species of chromium .
The first step was to prove different filters to avoid the chromium presence in the blank and to prevent oxidation/reduction processes after sampling, and PTFE 37 mm filter was chosen.
The evaluation of the performance of the method started with the determination of LOD, LOQ, the study of the calibration curve, precision, accuracy of the mean, using reference materials (RM). The calculated uncertainty of the measurement for the method was about 26% for both components.
The results of the validation were applied to chromium levels measured in samples (filters and hand washing) from galvanic industry by this method and showed to fit well for our purposes.

W04

ANALYSIS OF INORGANIC SELENIUM SPECIES IN ALGAL MEDIUM OVER TIME DURING EXPOSURE TO *CHLORELLA VULGARIS*

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Phosphate and sulfate are known to affect the uptake of selenium in algae and plants. Previous uptake studies have always assumed that the initial species of selenium added in an

experiment remained stable throughout. In our study, batch cultures of *Chlorella vulgaris* were grown under 15 and 1.5 mg/L phosphate and 30 and 3.0 mg/L sulfate conditions. Within these four treatments, selenate and selenite were added individually to each culture at concentrations of 10 µg/L. The total concentration and speciation of selenium in the medium for each batch culture were quantified and identified daily over a period of 9 days using anion exchange chromatography-inductively-coupled plasma-dynamic reaction cell-mass spectrometry (AEC-ICP-DRC-MS). Media sample preparation consisted of 2-fold dilution with 0.159 mol/L nitric acid in ultrapure water. The method detection limit was at least 0.1 µg/L for each species and the precision for each species was less than 1.7% RSD. Changes in selenium speciation and concentration over time in the media will be discussed in terms of possible biogeochemical implications and uptake mechanisms in *Chlorella vulgaris.*

KN 09

A TALE FROM THE BIOINORGANIC TEXTBOOK AND HOW ICP-MS CAN ASSIST TO GIVE THE ARSENIC STORY AN UNEXPECTED TWIST

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According to the HSAB principal only soft elements can bind to soft ligands. Elements such as arsenic have been classified as soft elements, however different forms of arsenic exist which actually change the softness of the arsenic. Arsenate is hard, while arsenite is soft. The common believe is when arsenic is taken up by biota and interacting with biomolecules, arsenic is always in its trivalent state. This form is soft and can interact with soft thiol groups of cysteine in peptides and proteins. This is thought to be the process by which arsenic accumulates in sulphur-rich tissues such as skin, hair and horn.

Here in this lecture it will demonstrated which information one could gain from the use of ICP-MS in speciation studies and which ambiguities still exists, even when ICP-MS and ES-MS are used simultaneously for RP-HPLC. Other methods such as electronic structure calculations, NMR and XANES become useful complimentary tools for strengthening the weakest link in the series of sample preparation and analysis steps during element analysis.

It will be shown for the first time that even hard pentavalent arsenic can bind to soft thiols of peptides and that additional sulphur may play the role as a mediator between the different pentavalent arsenic and the thiol group[1]. The lecture will give some insight into the arsenic phytochelatin complexation in plants in particular in *Brassica* spp and the difficulties of the analysis.

KN 10

SELENIUM ACCESSIBILITY AND EXPRESSION IN HUMAN BIOMARKERS FOLLOWING LONG-TERM SUPRA-NUTRITIONAL SUPPLEMENTATION

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Introduction and scope. A group of 96 elderly Danes (60-74 y) volunteered for a 5-year Se-yeast supplementation pilot study of the planned PRECISE trial. The participants were randomised to supplementation with 100, 200 or 300 ug Se/day as selenised yeast or placebo. Following the termination of the supplementation period, the Se contents in toenails, whole blood and in blood plasma were analysed. The scope of the study was to investigate whether the concentration of selenium in toenails was useful as a biomarker of exposure to

supplemented selenium. Furthermore, the scope was to understand if toenail selenium ranked the volunteers in the same way, as did plasma or whole blood selenium. Finally, the scope was to conduct selenium speciation in toenails and in blood plasma.

Methods. The selenium content was determined as ^{78}Se by ICP-MS in toenails, blood plasma and whole blood. The high sulphur content of nails hampered the accurate analysis when detecting ^{80}Se and ^{82}Se. Certified reference materials controlled the analytical accuracy and the uncertainty was estimated at 6-8 % RSD. Selenium in nails was extracted using a range of chemicals or enzymes prior to speciation by HPLC-ICP-MS. Selenium-containing plasma proteins were separated using a heparin affinity column in tandem with SEC.

Discussion. The selenium concentrations in plasma, whole blood and in toenails (biomarkers) were significantly different ($p<0,001$) between the three dosages used and placebo. This means that all biomarkers ranked the volunteers in the same way. The three biomarkers were compared as pairs. The linear relationship between whole blood-Se and toenail-Se showed a high correlation factor ($R^2=0,88$), whereas the fit between plasma and toenail selenium was slightly poorer ($R^2=0.80$). The high correlations between three biomarkers, which reflect the selenium status within days (plasma), within weeks (whole blood) and within ca. one year (toenails), demonstrate good long-term compliance among the study participants. Interestingly, the plot of Se in whole blood against plasma Se for all participants showed two different slopes. The data from the placebo group indicated that Se was incorporated primarily into blood plasma, which possibly shows that all plasma proteins are not saturated with the natural dietary selenium intake (approximately 40-50 µg/day). In contrast, for the three supplementations groups Se was predominantly incorporated into red blood cells.

The extraction efficiency of Se species from nails ranged from a few per cent when using enzymatic degradation (keratinase), to 1/3 when using alkaline extraction and up to ca. 3/4 when using 6 N HCl at 105 ^{o}C. The chromatograms obtained for the latter harsh extraction method indicated instability of the selenium species. Finally, the results from on-going efforts towards selenium speciation in plasma will be commented.

Conclusion. Selenium in toenails is a useful biomarker of exposure to selenium as selenised yeast in a human intervention study using a dose-response design. Furthermore, the PRECISE pilot trial has demonstrated good compliance, which is encouraging for conduction of a future large-scale human intervention study. The non-intrusive nature of nail sampling is practical for control of compliance in human intervention trials conducted via the internet.

W05

A COMBINATION OF ICP - MASS SPECTROMETRY AND SYNCHRONTRON X-RAY TECHNIQUES FOR STUDYING ZN UPTAKE BY *DAPHNIA MAGNA*

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Water quality criteria and environmental risk assessments of metals usually only consider exposure of the aquatic organism through the water-phase, while the potential effect of dietborne-metal is ignored. We have studied the chronic toxicity of dietary Zn to *Daphnia magna* – a small crustacean, commonly referred to as the waterflea – by using uni-cellular algae (*Pseudokirchneriella subcapitata)* enriched with Zn as a food source. The combination of ICPMS Zn data and evaluation of *Daphnia* growth and reproduction indicated that while the growth was not significantly affected by dietary Zn exposure, the reproduction rate was substantially reduced. To evaluate the relative importance of both exposure routes, a stable

isotopic tracer experiment was designed, whereby the Zn present in the algae was enriched in ^{67}Zn and that in the water in ^{68}Zn. Isotopic analysis of the three media – *Daphnia magna,* algae and water – as a function of time allows the exchange of Zn between the media and the associated kinetics to be monitored. Additionally, synchrontron XRF was used to visualise the distribution of ingested Zn over the various body compartments of the daphnids. This presentation will mainly focus on the role of ICPMS in this research and the possible pitfalls – e.g., contamination and occurrence of spectral overlap – and the way in which these were handled, will receive proper attention.

W06

APPLICATIONS WITH INDUCTIVELY COUPLED PLAMSA MASS SPECTROMETRY (ICPMS) IN HUMAN EXPOSURE STUDIES

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Human exposure studies are getting great interest for study-specific and general reasons. Three cases regarding to different matrices of interest will be presented. In all cases inductively coupled plasma mass spectrometry (ICPMS) was applied for the measurements.

- Acute and chronic exposures of soldiers, which might be in contact with depleted uranium-containing ammunition, were investigated. Chronic exposure is routinely controlled via the analysis of urine. After an incident acute exposure is based on inhalation. Related procedures of sampling and analysis were examined more closely.
- In human exposure studies blood is often the matrix of choice. Regarding to ultra-trace concentration levels and interferences high resolution (HR-)ICPMS was applied for the determination of the rather unusual element germanium (Ge) in blood of workers from special circumstances ("high-tech production"). Matrix-based interferences will be presented and obtained results will be compared with literature.
- In the field of speciation analysis a first pilot study about methyl mercury ($MeHg^+$) in finger nails was carried out by gas chromatography (GC) hyphenated to ICPMS. $MeHg^+$, which is one of the most toxic compounds at all, and inorganic Hg were investigated in finger nails from persons from different origins (Brazil and the Netherlands) and with different food intakes.

W07

FRACTIONATION, SPECIATION AND DETERMINATION OF ANTIMONY IN ATMOSPHERIC AEROSOLS BY PLASMA-BASED TECHNIQUES

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In the framework of a three-years project a series of studies were undertaken to determine Sb in: volcanic ashes (VA), urban particulate matter (UPM) and coal fly ashes (CFA) by ICP OES and ICP-MS. Measured concentrations span three orders of magnitude with urban UPM > CFA > VA.

VA: Ashes were size fractionated. Antimony content was quantified in the digested samples by ICP-MS with concentrations ranging from 0.30±0.01 μg g^{-1} (150-300 μm) to 1.07±0.02 μg g^{-1} (<36 μm). An enrichment factor (EF) of 6.3 over crustal abundance was observed in the smallest size fraction. Sb(III) was the predominant species in the four fractions (0.14-0.67 μg g^{-1}).

CFA: ICP OES was used to quantify Sb in acid digested samples and it ranged from 13.2±0.5 to 34.0±1.3 μg g^{-1}. In the soluble fraction Sb levels were between 0.30±0.02 and 1.38±0.09 μg g^{-1}.
UPM: Antimony was determined in filters extracts by ICP-MS. The study showed that population of Buenos Aires is exposed to levels of Sb ranging from 12.9±0.9 to 375±23 μg g^{-1} (equivalent to 0.87±0.06 to 15.3±0.8 ng m^{-3}). These values are compatible with the few reported for other cities. The statistical analysis showed significant correlations of Sb with other brake-lining constituents, namely Cu and Mo (Sb:Cu, r=0.87 and Sb:Mo, r=0.73).

W08

CARBON LOADED ICP WITH COLLISION CELL ICPMS: A POWERFUL TOOL FOR THE ACCURATE DETERMINATION OF METHYL-SELENIUM COMPOUNDS IN BIOPHARMACEUTICALS BY ISOTOPE DILUTION ANALYSIS

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An understanding of the beneficial effects of Se-enriched food and supplements requires methods to accurately measure the forms of Se present in the complex matrix samples, which are still scarce and therefore, urgently needed. The determination of minor Se compounds (at low part per billion levels) in the complex sample presents a clear need for enhancement of the detection capabilities of the existing MS.
With the introduction of collision cell ICPMS many of the polyatomic interferences (e.g. Ar_2^+) that affect the detection of the most abundant Se isotopes can be reduced. Matrix-induced interferences can be further minimised by coupling a high selective HPLC separation with collision cell ICPMS. This allows multi-isotope interference-"free" detection of Se to be performed in a transient signal, what is required to perform accurate Se speciation measurements by isotope dilution analysis.
Addition of carbon as organic solvents/compounds to the aqueous selenium solutions has been reported to enhance the sensitivity of the ICPMS detection of elements such as selenium and arsenic.[2] However, when using such methods for element speciation, the concentration of organic modifier added to the mobile phase was compromised by its effect on the chromatographic separation of the species of interest. Moreover, application of methane-mixed plasma for the determination of total metal concentrations in biological samples resulted in improved detection limits for As, Ge and Se in comparison with the conventional Ar method.
In this work, ultrasonic nebulisation and high-C load to the plasma, using different carbon sources, were used to enhance the sensitivity of collision ICP-MS detection (with Xe and He as collision gas) for target Se species including methyl-Se compounds. The results showed that, in comparison with conventional nebulisation, the degree of detection limits improvement achieved using both methods appears to be specie and method dependent. Double matched species-specific isotope dilution MS in on-line combination with HPLC was evaluated for the accurate quantification of major Se species such as selenomethionine (SeMet) and minor compounds such as gamma-glutamyl-methyl-Se-cysteine in selenised yeast pharmaceutical tablets. Comparison of the results obtained for SeMet using the method proposed here with those obtained by other nine participants in an international intercomparison study will be discussed.

W09

NATURAL BACKGROUND CONCENTRATIONS OF ANTIMONY AND LEAD IN ANCIENT ARCTIC ICE AND PRISTINE GROUNDWATERS USING ULTRA CLEAN ROOM PROCEDURES AND SECTOR FIELD ICP-MS

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Natural background concentrations and knowledge of their variation with time are essential to put modern values into perspective, i.e. for the calculation of enrichment factors and anthropogenic inputs into recent samples. Only ancient samples pre-dating any significant anthropogenic activities can be employed for this purpose.

Using ultra clean room procedures and sector field ICP-MS coupled to a high efficiency sample introduction system provided detection limits of 0.006 pg/g and 0.06 pg/g for Sb and Pb, respectively, which are sufficiently low to assess reliably the natural background concentrations of both elements in ancient ice and pristine groundwaters. In the investigated ice cores from Devon Island, Arctic Canada, the lowest Pb concentrations where found during the mid-Holocene (8 to 4 k yrs BP) averaging 5.1 ± 1.4 pg/g (n=5). These values are comparable or even higher than those of Pb in pristine groundwaters from eight artesian flows sampled in triplicate in Ontario, Canada (range: 3.3 – 13 pg/g, average: 7.6 ± 5.0 pg/g). In contrast, the 18 ice samples representing the period between ca. 1.3 and 10.6 k yrs yielded an average Sb concentration of 0.08 ± 0.03 pg/g which is considerably lower than Sb in pristine groundwaters (2.2 ± 1.2 pg/g, n=34). With trace metal concentrations in groundwaters at or below the levels found in ancient arctic ice, extremely clean analytical procedures and detection power are essential to academic studies of both kinds of samples.

Poster Session Wednesday 21 Feb 2007

WedPo1. (IN)STABILITY OF $As(GS)_3$

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Phytochelatins (PCs) are cysteine rich peptides which are formed by plants in response to metal(loid) stress. The metalloid arsenic is taken up by plants as As(III) or As(V). Inside the plant As(V) is readily reduced to its trivalent form whose toxicity is based on its high affinity to sulfydryl groups. PCs are thought to reduce the toxicity of As(III) by complexing it via their –SH groups.

The quantification of As-PCs and free PCs in plant tissues by HPLC/MS-ICP/MS turned out to be tricky. The analysis of these polar compounds includes the extraction with water-based solvents. As-PCs are not stable in water and hence it is impossible to determine the initial amount of the different complexes in the plant tissues. Kinetic studies with the model compound arsenic-glutathione [$As(GS)_3$] revealed that the disintegration of that complex is a pseudo-first-order reaction in a certain pH and concentration range. If this knowledge is transferable to the As-PCs it would be possible to calculate the initial amount of the complexes by using the appropriate equation that describes their rate of degradation.

Whereas the quantification of As-PCs is achieved via the arsenic using HPLC/MS-ICP/MS the sulphur should be the key atom in the free PCs. Sulphur as analyte atom makes the use of a reaction/collision cell necessary. A comparison between two reactive cell and two collision cell gases (H_2 and O_2 versus He and Xe) should give information on the suitable ICP-MS conditions concerning the quantification of free PCs via their sulphur atoms

WedPo2. ARSENIC SPECIATION IN EDIBLE As-ACCUMULATING GASTROPODS BY LC-ICP-MS AND ESI-MS-MS

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Purple dye murex (*Murex brandaris* L.) and trunculus murex (*Hexaplex trunculus* L.) are marine gastropods used as seafood in the Mediterranean area. The determination of the total arsenic content revealed that these species bioconcentrate As, at levels of about 300-400 µg kg^{-1} dry weight.
Water-soluble arsenic species were extracted from freeze-dried samples using a 1:1 (v/v) methanol-water mixture and mechanical agitation overnight. Gradient elution cation exchange chromatography with on-line ICP-MS detection showed that arsenobetaine was the major As compound, averaging 91% and 97% of the As eluting from the column for purple dye and trunculus murex, respectively. In trunculus murex glycerol oxo-arsenosugar, arsenocholine, dimethylarsinic acid and two unknown species were identified as minor compounds based on retention time matching in spiking experiments. In purple dye murex trimethylarsoniopropionate was further detected. Gradient elution anion exchange chromatography combined with on-line ICP-MS enabled the identification of phosphate oxo-arsenosugar as the second most abundant compound. Moreover, sulfate oxo-arsenosugar and traces of arsenate were detected.
Electrospray ionisation tandem mass spectrometry (ESI-MS-MS) was used in order to confirm species identification carried out by LC-ICP-MS and to provide evidence for the structures of the unknown arsenicals, as well. Changes in speciation induced by cooking were also investigated with the aim of assessing whether the consumption of the investigated species may pose any health risks.

WedPo3. SPECIATION OF TRACE ELEMENTAL SPECIES USING GC-ICP-MS AND GC-ICP-SF-MS

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The significance of speciation for accurately understanding the true nature of trace-elements in the environment, industrial processes and biochemical pathways is currently a well acknowledged fact. Certain physiochemical information such as toxicity, bioavailability, mobility and reactivity are dependent on the specific form of an element and cannot be accessed with total element concentrations alone.

Modern speciation techniques commonly couple chromatographic techniques with ICP-MS for high selectivity and sensitivity. Capillary GC offers ultimate resolution of species, lower LODs and higher throughput. GC-ICP-MS is also a versatile technique for a wide range of applications. Most applications are prompted by the toxicity of certain trace elemental species where a threat is posed for health and/or the environment. In recent years, a number of directives have imposed maximal concentrations for various elemental species in a number of matrices. Some topical applications include the determination of methylmercury, butyl tins and brominated flame retardants in environmental samples.

This presentation highlights the remarkable features of GC-ICP-MS for the analysis of trace element species and evaluates the advantages offered by SF-ICP-MS for exceptional performance. For example, the higher sensitivity and resolution capabilities of GC-ICP-SF-MS provide an approach for the determination of ultra trace levels of elemental species outlined in recent amendments to the water framework directive.

WedPo4. CHROMIUM SPECIATION IN NATURAL WATERS USING HPLC COUPLED TO THE XSERIES^{II} ICP-MS.

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The extensive use of chromium in various industrial processes and the erosion of chromium from natural sources have resulted in its widespread occurrence in the environment. Monitoring of chromium in environmental compartments, and food and water sources is central in assessing the potential risk from exposure. The US Environmental Protection Agency (EPA) and the European
Union have specified maximum admissible concentrations of 0.1 and 0.05 mg/L for total chromium under their respective drinking water directives.
This presentation describes the use of the HPLC ICP-MS instrument package from Thermo Electron Corporation for the determination of chromium species in natural waters.
The HPLC reversed phase methodology employed complexation of Cr(III) with EDTA to improve separation. Due to the carbon containing mobile phase,
optional collision cell technology (CCT) was used for the prevention of the polyatomic interference $^{40}Ar^{12}C$ on ^{52}Cr. The use of CCT additionally suppresses interference from additional matrix in the water samples.

WedPo5. CHROMIUM SPECIATION IN SOILS AND SEDIMENTS BY HPLC-ICP-MS,

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Speciation information is critical in accurately assessing risk associated with a release of potentially toxic metals, whether by natural weathering processes or as the result of an industrial spill or catastrophic event. One of the difficulties in performing speciation analysis on soils and sediments is developing an extraction procedure that will extract the species of interest without altering their distributions. Another difficulty is developing a robust HPLC method that will tolerate the high levels of matrix elements liberated into the extraction fluid.

The current study has examined the use of several different leach methods to extract chromium followed by the determination of Cr(III) and Cr(VI) species using High Performance Liquid Chromatography (HPLC) separation followed by detection via High Resolution (HR) ICP-MS as well as Dynamic Reaction Cell (DRC) ICP-MS. Results of these leach studies will be presented and discussed in regards to their effect on the chromatographic separation method employed and which methods may be more suitable for extraction of chromium species for the purpose of studying weathering processes of soils and sediments derived from ultramafic rocks.

WedPo6. Cr SPECIATION IN YEAST USING LC SF-ICP-MS

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Interest in the speciation of Cr has increased dramatically as a result of their significantly different toxicities of Cr(III) and Cr(VI). Studies have shown that chromium supplements (Cr(III)) can help in many conditions, including reducing blood sugar levels as well as the amount of insulin needed by diabetics, lowing cholesterol levels in the blood; and improving lean body mass and reducing body fat for weight loss. As a result, consumption of Cr supplements has become popular. Because the nutritional bioavailability and toxicity of Cr

are highly dependent on its chemical forms and concentrations, speciation of Cr in such supplements is of paramount of importance for safeguarding consumer's health.
Despite the dramatically different toxicities of Cr(III) and Cr(VI) and the increasing use of Cr supplements, accurate determination of these species in such supplements is lacking. In this presentation, a method is presented for the simultaneous determination of Cr(III) and Cr(VI) in yeast using species specific double spike isotope dilution (SSDSID) with anion exchange liquid chromatography (LC) separation and sector field inductively coupled plasma mass spectrometric (SF-ICP-MS) detection. Total Cr is quantitated using ID SF-ICP-MS.

WedPo7. DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF HEXAVALENT CHROMIUM ($Cr^{(VI)}$) IN FOODS

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Chromium is a biologically-important element due to its involvement in glucose and lipid metabolism. However, when present at high concentrations and/or in its hexavalent state, the element is considered highly toxic. No methods have been developed and validated for the chemical speciation of chromium in complex foods. Hence, the UK Food Standards Agency funded a project to develop a methodology, capable of determining the presence of $Cr^{(VI)}$ in a range of foodstuffs.
The literature showed that TMAH, NaOH, and $NaOH/Na_2CO_3$ mixtures had previously been used in the analysis of $Cr^{(VI)}$ in environmental samples, and were used as the basis of this work.
Recoveries of $Cr^{(VI)}$ spiked only into the reagents ranged from between 78 and 84% (as determined using HPLC-ICP-MS). However, when food samples were added, the recoveries were significantly reduced to less than 25%. In addition to this, a matrix dependence was also observed (Cereals 0%, meat-containing ~20% and high-sugar ~15%). It is thought that the high organic content of the food-containing extract liquor resulted in either the reduction of the $Cr^{(VI)}$ to $Cr^{(III)}$, or it interacted directly with the $Cr^{(VI)}$ to produce an, as yet, unidentified species which was not amenable to being chromatographed on the ion exchange (Dionex AS-11-HC) column used in this work. The analyte exhibited a similar instability when in the presence of enzymes, used to improve the efficiency of the extraction procedures.

WedPo8. CHROMIUM SPECIATION IN PHARMACEUTICAL, NUTRACEUTICAL AND BIOLOGICAL MATRICES

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There is a renewed interest in the ability to qualitatively and quantitatively speciate the two most stable oxidation states of chromium, Cr (III) and Cr (VI). This method utilizes an integrated pumping system made of PEEK, to reduce chromium background that exists in standard stainless steel LC pumps and tubing. The LC pump is coupled to an ICPMS system equipped with a collision cell to diminish polyatomic and isobaric interferences commensurate with CAr^+, ClO^+, CrH^+, and Pd^{2+}, for $^{52}Cr/^{53}Cr$. Separation is achieved via ion chromatography in combination with the formation of a Cr (III)-EDTA complex. Identification is accomplished through monitoring ^{52}Cr and ^{53}Cr isotopes. This study optimizes incubation parameters and evaluates the resolution, reproducibility and responses of Cr (III) and Cr (VI) in pharmaceutical, nutraceutical and high salt containing biological matrices.

WedPo9. VALIDATION OF A METHOD OF COUPLED LC-ICP-MS FOR THE SPECIATION OF CHROMIUM IN DRINKING AND SURFACE WATER USED IN A DRINKING WATER COMPANY

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Antwerpse Waterwerken (AWW) is one of the largest drinking water companies in the Benelux with a yearly production of drinking water of 156 Mio. m^3 per year, nearly equally distributed over residentials, industry and other drinking water companies. Hence, production control is a main task of the Department of Water Quality of AWW. We control both surface water (which is our starting material for the production of drinking water) and drinking water for a large number of chemical and microbiological parameters. Determination of metals are demanded by the Flemish government as one of the key parameters. In this group of parameters chromium is important as the limit set by the government is 50 µg/L. Chromium is encountered in water, mainly as Cr(III), which is an essential micro-nutrient. However, also the toxic Cr(VI) has been found, mostly due to industrial pollution. Hence, determination of the toxicity of Cr in water is totally dependent on the concentration of Cr(VI) is water and not on the total amount of Cr, as stated by the Flemish decree of 2003. Speciation of Cr in water has already been worked out by a number of research groups. However, validation of these methods did give bad robustness results. Chromatographic separation was not stable either. Therefore, we established a modified method, which was statistically evaluated using a validation scheme. In our presentation we will present both this method and the different validation parameters.

WedPo10. PLATINUM SPECIATION IN THE ENVIRONMENT: EXIGENCIES OF ANALYTICAL METHODS

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Several studies have shown, that the overall amount of platinum in the environment has significantly increased within the last years. The sources of environmental platinum contamination are mainly car catalytic converters, cancerostatic platinum compounds (CPC) administrated to cancer patients as well as chemical industries.

As just a few platinum compounds pose a possible hazard, e.g. chlorinated platinum complexes and CPC, selective and highly sensitive speciation methods are necessary for assessment of the potential health risk. Liquid chromatographic methods for speciation of CPC were applied for hospital waste water, the source of CPC emission in the aquatic environment. CPC represent an important class of antineoplastic drugs, which are widely used in the chemotherapy of lung, cervical, testicular, head and neck, bladder, and ovarian cancer. The three CPC currently approved in Europe are cisplatin, carboplatin and oxaliplatin. After chemotherapy considerable portions of the drugs are excreted reaching hospital wastewater. Since nowadays cancer treatment is frequently performed out-ward, another important fraction of CPC is directly released into communal waste water.

In the present study we aimed at the development of an analytical method capable to investigate the possible formation of chloroplatinates in waste water originating from CPC excreted as metabolized and intact cis-, carbo- and oxaliplatin. Capillary electrophoresis hyphenated to ICP-MS was investigated for the speciation of chloroplatinates. Different

quantification methods comprising external calibration (with and without internal standardization) and species specific isotope dilution were evaluated according to EURACHEM guidelines.
The concentration levels of the platinum compounds in the aquatic environment are still low, accordingly enrichment methods have to be developed for this type of analysis. Different enrichment strategies for carboplatin in surface water will be presented.

WedPo11. A MOLECULAR INVESTIGATION IN THE INTERACTION OF ARSENIC UPON SELENIUM WITHIN THE *Chlorophytum Comosum* (SPIDER PLANT)
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The interaction between arsenic and selenium has been observed and studied in the mammalian system for some time. However, little effort has been put forth to investigate plausible arsenic and selenium interactions in plants at a molecular level. In this study, the *Chlorophytum Comosum* (commonly known as the spider plant) was grown in a green house from seed and supplemented with combinations of sodium selenite, sodium selenate, and sodium arsenite. The results show an antagonistic effect exerted by selenium and arsenic upon each other seen in a lower quantity of both elements uptaken by the plant if administered simultaneously rather than if supplementing with only one element. A method was employed using high performance liquid chromatography coupled to an inductively coupled mass spectrometer to simultaneously separate and speciate the selenium and arsenic compounds present within the plant's compartments.

WedPo12. CHEMICAL SPECIATION AND BIOAVAILABILITY OF MERCURY IN CONTAMINATED SOILS FROM VAL BASENTO (ITALY)
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Mercury (Hg) is a very toxic element and human activities release it in the environment in considerable quantities. It occurs in all media in a number of species, both organic and inorganic. The mercury species differ greatly in properties, but all are toxic to humans and animals. Organic forms, e.g. methylmercury, show the highest toxicity and the greatest accumulation in living organisms, in particular in aquatic ecosystems.
The aim of this study was to determine the different chemical forms of Hg and to evaluate their bioavailability in soils from an industrial area in Val Basento (Italy). Eight soil samples were collected from 4 points of the contaminated area at 0-10 cm and 40-50 cm depth. The simultaneous determination of inorganic and organic mercury extracted from the soil samples was performed by HPLC-ICP-MS. This analytical procedure allowed the identification of both its inorganic (Hg^{+} and Hg^{2+}) and organic forms ($MeHg^{+}$, $EtHg^{+}$ and $PhHg^{+}$). The accuracy (trueness and precision) of measurement method was verified for $MeHg^{+}$ by the ERM-CC580 certified sediment and by spike addition for the remaining Hg species. The total Hg concentration in soil was measured by AAS (AMA 254). The Hg bioavailability was estimated by soil solution extraction (rhizon soil samplers) followed by Hg speciation coupled with the determination of the maximum potentially bioavailable concentration. Speciation was carried out by HPLC-ICP-MS, whereas the maximum potentially bioavailability was assessed by an innovative device, the Diffusive Gradient in Thin Film (DGT), a passive sampler which mimics assimilation by diffusion in a cell cytoplasm.

Results from the present experimental study show, for all investigated soil samples, only $MeHg^{+}$ as organic form and Hg^{2+} as inorganic one. $MeHg^{+}$ concentration in soil is lower than 1% of total Hg. Less than 0,01% of the total soil mercury passes into the soil solution and it is mostly bioavailable. The highest concentration of $MeHg^{+}$ measured in soil solution is 20 µg L^{-1}.
This project is supported by the Ministry of Education, University and Research (PRIN 2005 prot. 2005077424).

WedPo13. ULTRA-SENSITIVE DIRECT DETERMINATION OF RARE EARTH ELEMENTS IN TIBET ICE CORE SAMPLES BY ICP-SFMS USING A DESOLVATION SYSTEM (ARIDUS II, CETAC).
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Rare Earth Elements (REE) have been widely adopted as excellent proxies for several geochemical processes. The successively dated snow and ice layers that are deposited in permanent glaciers have proven to be valuable archives for studying the biogeochemical cycles of trace elements in the Earth's system. So far, REE determinations have been rarely attempted in glacial paleoclimatic archives essentially because of the extremely low REE concentration and because of the limited volume of the samples. Here we present REE determination in a Tibet ice core performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Element2, Thermofinnigan) coupled to a desolvation system (ARIDUS II, Cetac). This method allows the rapid multi-element detection of REE over a wide concentration range with relatively low detection limits together with the elimination of all the spectroscopic interferences. In particular ARIDUS II allowed eliminating the interference of La oxides on Gd that were largely affecting this determination in recent studies (P. Gabrielli, et al., Anal. Chem. 78(2006) 1883-1889.). This methodology allowed thus the direct determination of all REE in a 1 ml sample of Tibet molten ice with concentration ranges between 0.04-0.7 pg/g for Tm and 3–40 pg/g for Ce.

WedPo14. SIZE FRACTIONATED CHARACTERISATION OF URBAN AEROSOLS: USE OF ELECTRIC LOW PRESSURE IMPACT COLLECTION WITH IC AND ICP-MS
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Awareness of air pollution has led to numerous studies on the chemical composition of ambient aerosols and origin of pollution sources. Atmospheric aerosols influence many atmospheric processes including cloud formation, visibility variation and solar radiation

transfer, and are believed to represent a significant health concern to human. Ambient concentrations of particulate matter (PM) are systematically monitored and air quality standards set by European Union have emphasised the need for the characterisation of PM below 10 μm (PM_{10}) by mass. Such mass based measurements are easy to measure, but are unlikely to encompass all the factors relevant to adverse health effects. Recent toxicological studies have suggested that particulate number, size and composition may all play important roles in adverse health impacts. This paper will report on a state-of-the-art particulate measurement technique, the Dekati electrical low pressure impactor (ELPI), that is used for characterisation of fine and ultrafine particulates collected in an urban environment (Sheffield) in October, 2006. Size fractionated (13 size fractions: 7nm-10 μm) airborne particles were collected (n = 7) by the ELPI over a 7-day sampling period. The water-soluble inorganic ions (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, K^+, Mg^{2+} and Na^+) were analysed by IC and the water-extractable metallic elements (Al, Ca, Cu, Fe, K, Mg, Na, Fe, Pb and Zn) were determined by ICP-MS. By assuming sodium exclusively originating from sea salt, the fractions of sea salt (ss) and non sea salt (nss) of the detected components were differentiated. The mode/modes of the particulate mass and the species mass distribution versus the stage size imply different sources of emission. Interspecies correlations give additional information on possible origin.

WedPo15. A NEW SAMPLE TREATMENT PROTOCOL FOR ORGANOTIN COMPOUNDS SPECIATION: IMPRINTED POLYMERS + FOCUSED ULTRASONICATION

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Speciation of organotin compounds has experienced a high development during the last decades due to the extremely high toxicity of these compounds, and especially, tributyltin (TBT). There are many papers dealing with this problem but sample pre-treatment still remains as the most critical step. Most of the extraction methods involve several steps and are highly time-consuming. In addition, recovery is not always satisfactory from a quantitative point of view and some methods suffer from matrix interference effect. In this context, this work proposes a new sample treatment protocol for OTC speciation: the combination of the molecularly imprinted technique with the focused ultrasonic extraction.

Sonochemistry has emerged as an interesting approach because of its potential to accelerate chemical reactions by either physical or chemical effects of cavitation clearly reducing the time of analysis. Molecular imprinting is a general protocol for creating artificial receptors with molecular recognition properties towards user-defined target molecules; one significant application has been in the field of solid phase extraction, as selective materials for clean-up and pre-concentration of analytes from complex matrices. In the last years, these polymeric materials have also been proposed and employed as chromatographic phases for separation and detection of different compounds.

This work describes the extraction method developed for OTC in several environmental samples based on the focused ultrasonic probe which allowed us to perform efficient extraction in only one minute without need to evaporate the extract. They are directly injected into a liquid chromatographic column packed with an imprinted polymer using TBT as template molecule. The skills of such a combination are presented and deeply discussed all throughout this presentation.

WedPo16. METAL DISBRIBUTION AND SPECIATION ON NATURAL COLLOIDS BY FFF-UV-MALLS-ICP-MS

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Despite colloids are recognized to play an important role in the transport and bioavailability of chemical pollutants in the environment, they were often neglected due to the lack of convenient analytical tools. Since a significant evolution of instrumentation has taken place, real possibilities are now offered to perform physicochemical works over micro-scale.
Filtration-based methods have been widely used for determining colloidal size distribution. Among these methods, Field-Flow Fractionation (FFF) is a promising technique because of its possibility of on-line fractionation and hyphenation to various detectors such as UV, Multi-Angle Laser Light Scattering (MALLS) and Inductively Coupled Plasma-Mass Spectrometer (ICP-MS).
In the present work, the FFF-UV-MALLS-ICP-MS potentiality is investigated for environmental analysis. Over the sample size characterization, the colloidal distribution of various metals and metalloids was studied. A special attention was given to the interface between FFF-UV-MALLS and ICP-MS considering qualitative and quantitative analysis. The chemical speciation associated to colloidal fractionation was examined since no information is available in this analytical field. This new approach involves combination between on-line colloidal fractionation and off-line chromatographic separation- selective and sensitive detection. Such combined method was developed on the basis of headspace-solid phase micro extraction - gas chromatography (HS-SPME-GC) and applied to organotin speciation.

WedPo17. OPTIMIZATION OF THE METHOD FOR THE DETERMINATION OF MERCURY IN ENVIRONMENTAL MATERIALS BY ICP-MS

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The present study was carried out to optimise the method for the determination of mercury by inductimely mass spectrometry (ICP-MS) in various sample matrices. Since the main problems associated with the analysis of mercury by ICP-MS arise from memory effects, the emphasis of the present work was put on finding a suitable reagent to remove these memory effects. To that end matrix effects of a range of candidate reagents were tested and potential internal standards tried for both improving the detection capabilities of the ICP-MS method and lowering the matrix effects. The study showed that the best results were obtained using dilute aqua regia solutions with concentrations between 5 and 10%. Dilute aqua regia practically eliminates the memory effects and improves the detection limits. It was found out that under optimum operating conditions and using dilute aqua regia and Gd as internal standard detection limits at ppt levels can be obtained. The method developed in this work was tested on different reference samples and the results showed that it is suitable for the determination of mercury in samples with various matrices, such as *e.g.* various environmental materials.

WedPo18. HEADSPACE SPME-GC-ICPMS COUPLING FOR SPECIATION OF VOLATILE SELENIUM.

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Selenium is today recognized as a trace element, it is thus essential to life, but in higher doses it becomes toxic for Human and animals. The concentration range between its indispensable role and its toxicity is very narrow. Selenium appears in its natural cycle in several oxidation states and as a variety of inorganic and organic compounds. Knowledge of its speciation is thus essential to assess its environmental or biological reactivity and impact.
Concerning the role of Se in humans, research studies carried on selenium metabolism, mainly based on the coupling of HPLC to mass spectrometers detectors (ICP-MS and MS) have allowed the identification of novel soluble species (selenosugars) as important urinary selenium metabolites. Further work recently published has revealed that some of these species could undergo some degradations in spiked samples stored for a long time, resulting in volatile selenium species generation. In a previous work, we showed too the presence of two volatile species containing selenium in unspiked urine samples with the help of headspace SPME-GC-MIP-AED, and quantified the natural occurrence of dimethylselenide species.
We present here the coupling of Solid Phase Microextraction to GC-ICPMS for volatile selenium species determination in liquid samples. The use of ICPMS instrument equipped with collision/reaction cell allows selenium quantification on the basis of ^{80}Se monitoring resulting in detection limits well adapted to the determination of volatile species in unspiked samples. A more complete selenium speciation analysis is achieved by the combined use of GC-ICPMS and HPLC-ICPMS methods.

WedPo19. IN-LINE PRECONCENTRATION HPLC-ICP-MS DETERMINATION OF MERCURY IN THE VENICE LAGOON.

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The city of Venice is a UNESCO world heritage site placed in a delicate lagoonal habitat that is under considerable stress due to centuries of anthropogenic pollution. From 1951 to 1988, the chlor alkali complex in Marghera on the mainland contaminated the Venetian lagoon with mercury virtually without control.
To investigate the speciation of mercury and the distribution of mercury species between the subsurface waters, the marine surface microlayer and the particulate phases present within these 2 environmental compartments, an in-line micro-column preconcentration HPLC-ICP-MS method has been developed. The sample loop commonly used in HPLC analysis was replaced with a micro-column to preconcentrate the species when the valve is in the load position, meaning that larger sample volumes can be effectively injected onto the column without saturating it. With this method a 20 fold preconcentration of the mercury species is achieved rapidly with a 2 ml injection of sample, and with little sample handling, avoiding potential contamination risks.

Preliminary results on the analysis of mercury and methyl mercury in the marine surface microlayer and sub surface waters of the lagoon, show that the concentrations of mercury in filtered waters are extremely low (< 10 ng L^{-1}) and that most of the mercury in the water column is in the inorganic form and is associated with the particulate phase.

WedPo20. SPECIATION IN NATURAL ORGANIC MATTER BY COUPLING ON-LINE COLUMN POLYACRYLAMIDE GEL ELECTROPHORESIS - ICP-MS

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Polyacrylamide Gel Electrophoresis (PAGE) is a powerful separation technique and is used extensively in various formats for separation, characterization, and analysis of proteins and biomolecules. The most important types of PAGE are isoelectric focusing, isotachophoresis, Native-PAGE or Sodium-Dodecyl Sulphate Polyacrylamide (SDS-PAGE) , and 2-D PAGE carried out either in a slab gel or in a capillar (CGE).

On-line coupling of the electrophoretic separation technique to a detector has been achieved for Capillary Gel Electrophoresis coupled to fluorescence, electroanalytical detection, and ESI-MS.

R.D.Evans and J.Y.Villeneuve (1) have described a Gel Electrophoresis Laser Ablation ICP-MS off-line hyphenated technique for characterization of humic and fulvic acids. However, beside the great potential of this coupled technique, there are some major drawbacks : (a) High blank concentration of elements can occure in gel, and (b) after destructive ablation process, either directly from the gel or after blotting, the analyte itself is not available anymore. Recently W.Bruchert and J.Bettmer (2) have described for the first time the on-line hyphenated technique PAGE-ICP-Sector Field-Mass Spectrometry for the determination of dsDNA fragments..

In this work we describe the use of the on-line Polyacrylamide Gel Electrophoresis and Inductively Coupled Plasma (Quadrupole)Mass Spectrometry hyphenated technique with a experimental setup based on Column Gel Electrophoresis Model 491 Prep Cell from Bio-Rad with several modifications due to the necessity of the analyte transport to the plasma, and to guarantee the electrical connection between the electrodes and to keep the ionic strength within the electrode chambers constant.

The performance of Column PAGE separation process of Natural Organic Matter is strongly influenced by the format of Gel Electrophoresis (NATIVE or SDS-PAGE), composition of resolving gel, composition of stacking gel, composition of sample buffer, sample/buffer ratio, running buffer, Humic and Fulvic concentration, sample loading volume, staining solution, destaining solution, maintenance solution, electric power, carrier flow, inner diameter column, column material. etc., and when the electrophoretic process is carried out in column the heating produced in the gel has to be controlled. Every factors have been thoroughly optimized

The results of metal concentrations linked to several fractions of big molecules of humic and fulvic acids from Natural Organic Matter (NOM) will be presented.

(1) R.D. Evans, J.V. Villeneuve., J. Anal. At. Spectrom, 2000, 15, 157-16.
(2) W. Brüchert, J. Bettmer., Anal. Chem. 2005, 77, 5072-5075.

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WedPo21. A STUDY OF THE INTERCONVERSION OF METHYLATED ARSENIC OXIDES TO METHYLATED ARSENIC SULFIDES IN SOLUTIONS CONTAINING FREE SULFIDE**.**

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Evidence suggests that thiolated arsenicals are urinary metabolites in both humans and rats. These thiolated species may be formed in the digestive system or as metabolites within the body. The role they may play in the overall toxicity of arsenic is an active area of research.

This research effort would benefit from an improved understanding of how the oxide and thiolated forms of arsenic can interconvert based on matrix constituents.
Data will be presented demonstrating that trimethylarsine oxide (TMAO), dimethlyarsinic acid (DMA) and monomethylarsonic acid (MMA) all produce thiolated analogs in the presence of solution phase sulfide. This conversion is shown to be pH sensitive and the conversion rate is shown to increase in the following order: MMA<DMA<TMAO. These findings will be discussed with respect to sample preparation/preservation procedures which may facilitate the oxide-sulfide inter-conversion. Finally, data pertaining to the stability of the thiolated species under acidic and basic conditions will be presented.
*Oak Ridge Postdoctoral Research Fellow
Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy

WedPo22. DETERMINATION OF ARSENOSUGARS IN MARINE ALGAE
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Marine algae contain 7.3-288 μg g^{-1} As in the samples. The amounts of arsenic in the extracts from marine algae are accounted for 21.4-94.6% of the total extracted arsenic. Found arsenic species were As^{V}, As^{III}, MMA, DMA, TeMAs and unknown arsenic. The arsenosugars in the extracts from marine algae were investigated by HPLC-ICP-MS using an anion exchange column, Hamilton PRP X-100 column. The retention times of both arsenic species using commercially available standards and arsenosugars using a *Fucus* standard sample were examined and the dependence on the pH of mobile phase was clarified. The contents of arsenosugars in the extracts from marine algae were determined using a *Fucus* sample as standards of arsenosugars. The contents of arsenosugars in the extracts were accounted for 3.4-68.0% of the total extracted arsenic. Further, electrospray mass spectrograms of the extract which was collected by a gel chromatography were measured using API 2000.

WedPo23. TOWARDS THE COMPLETE CHARACTERISATION OF THE WATER-SOLUBLE Se-FRACTION OF SELENISED YEAST
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However the water-soluble Se-fraction usually represents only 10-15% of total selenium of selenised yeast, it has always been an important target of Se-speciation. The main reasons behind this are the following: *i)* it contains most of the undiscovered Se-species synthesised by yeast cells, especially of non-peptide origin and *ii)* its chromatographic profile is characteristic to the given yeast stream and fermentation procedures.
In our presentation we describe an approach that divides the size exclusion chromatography /SEC; first LC step/ ICP-MS profile of the water-soluble Se-fraction into three regions. Each of these are further characterised by a second LC-ICP-MS step involving either HILIC /hydrophilic interaction/, SCX /strong cation exchange/ or SAX /strong anion exchange/ chromatography. The third LC step with RP /reversed phase/ or HILIC separation serves as the last clean-up process before molecular mass spectrometry-based identification through ESI-MS-MS/MS analysis. The whole procedure is backed up by continuous Se-balance monitoring for quality control and quantification purposes.
The developed sample preparation strategy helped to identify previously unknown major Se-species whose structure and possible nutritional impact will be discussed, along with the diversity found between yeast samples from different manufacturers.

WedPo24. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY HYPHENATED TO INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY FOR SPECIATION ANALYSIS OF MERCURY IN MATERNAL AND NEWBORN RATS AFTER PRENATAL AND POSTNATAL EXPOSED TO LOW DOSE OF METHYLMERCURY

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Up to now, whether the low polluted levels of mercury are harmful to pregnant women and their offspring is still debate. The precise mechanisms of mercury toxicity, including its accumulation and retention in mammals, are still not fully understood. In this study, we are interested to investigate the mercury speciation, including inorganic mercury, methylmercury, and mercury-containing proteins in maternal and infant rats after prenatal and postnatal exposure to low dose of methylmercury.

The total and methyl mercury has been firstly analysized in the liver, kidney and brain regions, including cerebrum, cerebellum, brain stem, hippocampus, inferior colliculus and the remains of the dam and pup rats by inductively coupled plasma-mass spectrometry (ICP-MS) and the hyphenated technique, reverse phase-high performance liquid chromatography (RP-HPLC)-ICP-MS. The contents of total and methyl mercury has been further determined in the subcellular fractions, such as nuclear, mitochondrion, lysosome+microsome and cytosol of dam and pup brain by RP-HPLC-ICP-MS. A full spectral scanning of mercury-containing proteins in the cytosolic fractions of some organic tissue samples (brain, liver and kidney) of rats has been screened. The mercury-containing proteins were partially purified using two dimension liquid spectrometry, first size exclusion and second reverse phase HPLC. The results could be helpful to understand the toxicity and methylmercury transportation between mothers and their infants.

WedPo25. ARSENIC ACCUMULATION AND SPECIATION IN FRESHWATER FISH LIVING IN ARSENIC-CONTAMINATED WATERS

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Striped snakehead (*Channa striata*), a carnivorous freshwater fish which serves as a popular food item in Thailand, were collected from a control site (1.4 µg As L^{-1}) and from two arsenic-contaminated ponds (Pond A 550 µg As L^{-1} and Pond B 990 µg As L^{-1}) in southern Thailand and analysed for arsenic by inductively coupled plasma mass spectrometry (ICPMS) and for arsenic species by HPLC/ICPMS performed on aqueous methanol extracts of muscle, liver and gill (n=3 fish from each site). Mean total arsenic concentration in muscle tissue of *Channa striata* collected from the control site was 1.9 µg As g^{-1} (dry mass) while fish from the contaminated sites contained 13.1 µg As g^{-1} (Pond A) and 22.2 µg As g^{-1} (Pond B); similar increased arsenic concentrations for liver and gill tissues were observed on going from control to contaminated sites. Speciation analysis on the three tissues showed that, although arsenate was the major arsenical in control fish, dimethylarsinate was by far the dominant arsenic species in fish from the two contaminated sites. The study shows for the first time a clear effect of water arsenic concentrations on natural fish tissue arsenic concentrations, and is

the first report of a freshwater fish species attaining arsenic concentrations comparable with those found in marine fish species.

WedPo26. SPECIATION OF URANYL CITRATE BY ION-EXCHANGE MONOLITHIC COLUMN CHROMATOGRAPHY COUPLED WITH ICPMS AND ISOTOPE DILUTION

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The understanding of the behaviour of radionuclides in polluted soils is necessary to evaluate the environmental risks and to develop remediation strategies. The building of a reliable and predictive model encounters two main difficulties: the analysis of radionuclides in trace or ultra-trace concentrations in environmental conditions and the understanding of the speciation of the radioelements in natural waters, which affects their toxicity and their mobility.

In this scope, it is mandatory to develop highly sensitive and specific instruments which allow to show the existence of possible highly toxic species even at ultra-trace levels. The coupling of liquid chromatography to inductively coupled plasma mass spectrometry (LC-ICPMS) has been adopted in the recent years as a prime method to answer these needs. Such couplings provide the metal chelate stability constants by the determination of the different species but with rather low precision. This precision can be improved by using the isotope dilution method.

The present study shows results from a coupling of ionic chromatography and ICPMS (IC-ICPMS) applied to the speciation of uranyle citrate. The separation of $[(UO_2)_2(Cit)_2]^{2-}$, $(UO_2)_3(Cit)_2$ and $[(UO_2)_3(Cit)_3]^{3-}$, is obtained on a weak anion exchange monolithic stationary phase with a pH gradient of the mobile phase. The contribution of the isotope dilution method on the precision of the stability constant determination is described and compared to peak area integration method.

WedPo27. CHARACTERIZATION OF METALS BOUND TO PHENOLIC COMPOUNDS IN OLIVE OIL BY REVERSED-PHASE HPLC-UV-FLD-ICPMS

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During storage, fatty acids contained in extra virgin olive oil undergo oxidative degradation with a progressive accumulation of odourless molecules, such as hydroxyperoxides and secondary products. Lipid oxidation occurs by the interaction of lipids with molecular oxygen by a self-catalyzed mechanism. However, because of the activation energy of the reaction is high, the initiation of lipid oxidation is due mostly to the decomposition of hydroperoxides using metal catalysts such as copper and iron or by the exposure to the light. The high oxidative stability of extra virgin olive oil is mainly due to its fatty acid composition, in particular to the monounsaturated-to-polyunsaturated ratio, and to the presence of minor compounds that also have an important role in preventing oxidation. As a consequence extra virgin olive oil has a longer shelf life as compared to other edible vegetable oils, with long-term preservation of its intrinsic nutritive and hedonistic properties (1). In addition to lipophilic antioxidants such as tocopherols, extra virgin olive oil also contains various polar phenolic compounds that contribute significantly to its taste (bitter and pungency) (1, 2), prolonged shelf life, and its beneficial effects on human health (anticancer, antioxidant, and antiinflammatory properties) (3).

Phenolic compounds can inhibit oxidation by a variety of mechanisms based on radical scavenging, hydrogen atom transfer, and metal-chelating attributes. The presence of metals in extra virgin olive oil is due to endogenous factors linked to plant metabolism, exogenous factors such as olive contamination by agricultural practices (fertilizers and pesticide use), or during oil extraction (by contact between olive paste and metallic surfaces in crushing and malaxation steps) or oil storage (depending on the type of container used). Endogenous and exogenous metals can be dissolved in oils as fatty acid salts. Transition metals, such as iron and copper, can catalyze the decomposition of hydroperoxides according to their oxidation-reduction potential to yield lipid peroxyl and alkoxyl radicals that initiate free radical chain oxidation (3).

The aim of the present study was to investigate the presence of copper and iron of the phenol fractions in olive oils. For this purpose, we analyzed trace elements by microemulsion preparations of olive oils with inductively coupled plasma mass spectrometry (ICP-MS). After that, an analytical methodology was performed on high-performance liquid chromatography (HPLC) with in series detection by UV, fluorescence followed by ICP-MS to characterize the individual elemental species with phenolic compounds.

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WedPo28. ARSENIC SPECIATION IN URINE AND BLOOD OF SEALS (*Phoca vitulina*) USING HPLC-ICP-MS

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Arsenic is ubiquitous in the earth´s crust and biosphere. Nevertheless, there are significant differences between terrestrial and marine organisms in the arsenic concentration and the speciation. Marine organisms are known to accumulate arsenic and to convert inorganic arsenic, present in seawater, into organic compounds.
As mammals living in the marine environment and feeding exclusively on marine organisms seals are in an exceptional position. As top predators they accumulate arsenic through their position in the food web. Common prey species include herring, flounder, and perch as well as octopus, squid, and shrimp. Invertebrates are known to contain higher level of As than marine fishes.
The concentrations of arsenic and its species in urine and blood of harbour seals were investigated. Samples were taken from seals living in different areas of the North Sea and feeding on different prey as well as from animals living permanently in the Seal Station Friedrichskoog.
The total arsenic concentrations in urine and blood were determined with ICP-MS. The urinary arsenic of the seals ranged from 174 up to 1729 µg/L. The levels in blood ranged from 66 up to 501 µg/L. Furthermore we observed significant differences in As blood level between free ranging seals and animals living permanently in the Seals Station Friedrichskoog.
The arsenic speciation in urine and blood samples was determined with HPLC-ICP-MS. First results concerning arsenic species distribution in different seal samples will be shown.

WedPo29. SILMUTANEOUS DETERMINATION OF NINE ARSENIC SPECIES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY / INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Arsenic in environmental samples has been the target of increasing research for many years. Arsenite and arsenate are the most toxic forms and are suspected to be carcinogenic. Organic species such as arsenobetaine (AsB), arsenocholine (AsC), trimethylarsine oxide (TMAO) are considered to be nontoxic. Moreover, two aromatic organoarsenic compounds 4-3-nitrobenzenearsenic acid (roxarsone, ROX) or 4-aminobenzenearsenic acid (p-arsanilic acid, p-ASA) are recently used in France as feed additives in the poultry industry for disease control and enhanced feed efficiency.
The aim of this study was to develop a speciation method using high-performance liquid chromatography / inductively coupled plasma mass spectrometry (HPLC/ICP-MS) for the determination of inorganic (As^{III} and As^{V}), organic (AsB, AsC, TMAO, MMA, DMA) and aromatic (ROX and p-ASA) arsenic species. The nine different species could be determined within 15 min on a high capacity anion-exchange column using a nitric acid gradient, an ion pairing reagent and methanol. Influence of several parameters (mobile phase concentration, gradient time, flow rate, temperature, plasma power) was studied with the assistance of experiment plan. After optimization of these parameters, some analytical figures of merit have also been estimated.

WedPo30. EVALUATION OF BIOTRANSFORMATION OF SELENIUM IN Se-ENRICHED YOGURT BY HPLC-ICP-MS

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The essentiality and antioxidant properties of some selenium species suggest that supplemented food with this element could be beneficial for humans. The use of fermented yogurt in the presence of selenium could be an interesting approach, as yogurt is a dairy product for humans. However, the biotransformation of inorganic Se should be carefully controlled. Thus, the aim of this study is to investigate the nature and amount of selenium species in yogurt obtained when fermented in presence of Se(IV) or Se(VI) (up to 5000 $\mu g\ g^{-1}$). Yogurt formation was inhibited with concentration higher that 500 $\mu g\ g^{-1}$of Se (IV) and 5000 $\mu g\ g^{-1}$ of Se(VI). However, the Se(VI), unlike Se(IV), is not biotransformed. To investigate the possible biotransformation of selenium into proteins, we carried out different sample treatments after 24 h of yogurt fermentation:
a) Dialysis to eliminate small molecules and determination of total selenium concentrations by atomic fluorescence spectroscopy (AFS), before and after dialysis. The remaining Se in the

solid is considered to be associated to macromolecules with a MW higher than 3,500 Da. The percentage of Se found was 70% when 1,2,or 5 μg g^{-1} of Se (IV) were added and 20 % for 20 μg $g^{-1}$of Se (IV). On the other hand when either 2 or 5 μg g^{-1} of Se (VI) was added, only 2% of the total selenium was incorporated.
b) Aqueous extraction of the yogurt samples followed by Se analysis using SEC-LC-ICP-MS. Results obtained showed that Se(IV) is biotransformed into proteins with molecular weight between 40-100 kDa.
c) Enzymatic hydrolysis with protease XIV in Tris–HCl at pH= 7.5 using an ultrasonic probe (USP) followed by Se speciation using ionic exchange and reversed phase ion pairing HPLC coupled to ICP-MS. Se-Cystine and Se-Methyl Se-Cysteine were the major species found in the samples. The chromatograms were cleaner, better resolved and with higher signals when samples were dialysed before enzymatic hydrolysis Interestingly Se-Methyl Se-Cysteine has been described as a precursor of active cancer chemopreventing species.
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WedPo31. PRECONCENTRATION OF TRACE ELEMENTS USING 4-PHENYLTHIOSEMICARBAZIDE FUNCTIONALIZED AMBERLITE XAD-4 AND FL-ICP-MS DETECTION

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Despite the recent improvements in instrumentation, the analysis of samples such as seawater can still provide a challenge because of the dissolved salts loading. An on-line flow injection method for the direct determination of trace elements in environmental samples is described. A mini-column packed with 4-phenylthiosemicarbazide functionalized Amberlite XAD-4 was used to preconcentrate 7 trace metals (Cd, Co, Cu, Mn, Ni, Pb and Zn), whilst simultaneously eliminating matrix interferences from natural water samples. The metals were eluted with 0.1 M HNO_3 directly to an inductively coupled plasma–mass spectrometry instrument (ICP-MS) for detection. The optimal pH for retention of the analytes was at pH 8. Limits of detection (3σ) of Cd = 0.48 μg/L, Co = 0.77 μg/L, Cu = 0.17 μg/L, Mn = 0.48 μg/L, Ni = 0.47 μg/L, Pb = 0.64 μg/L and Zn = 0.70 μg/L for the FI-ICP-MS system were obtained regardless of sample type using 0.4 ml of sample and an eluent volume of 60μl. Analysis of environmental certified reference materials using FI-ICP-MS showed good agreement with the certified values. Metal retention capacities were also calculated using a batch system and the capacities values compared very favourably with other resins reported in the literature.

WedPo32. DETERMINATION OF ARSENOSUGARS IN MARINE ALGAE

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Marine algae contain 7.3-288 □g g^{-1} As in the samples. The amounts of arsenic in the extracts from marine algae are accounted for 21.4-94.6% of the total extracted arsenic. Found arsenic species were As^{V}, As^{III}, MMA, DMA, TeMAs and unknown arsenic. The arsenosugars in the extracts from marine algae were investigated by HPLC-ICP-MS using an anion exchange column, Hamilton PRP X-100 column. The retention times of both arsenic species using commercially available standards and arsenosugars using a *Fucus* standard sample were examined and the dependence on the pH of mobile phase was clarified. The contents of

arsenosugars in the extracts from marine algae were determined using a *Fucus* sample as standards of arsenosugars. The contents of arsenosugars in the extracts were accounted for 3.4-68.0% of the total extracted arsenic. Further, electrospray mass spectrograms of the extract which was collected by a gel chromatography were measured using API 2000.

WedPo33. PRELIMINARY STUDY FOR SPECIATION OF TRACE ELEMENTS IN RICE PHLOEM SAP BY SEMI-MICRO SIZE EXCLUSION CHROMATOGRAPHY - ICPMS

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Elucidation of translocation and accumulation of trace elements into grain is one of the most interesting research targets because various kinds of grains are world wide cultivated as staple foods. Phloem sap, solution in sieve tube, plays important roles in the transfer of organic and inorganic components in to grain. However, the information for chemical speciation of trace elements in rice phloem sap has been rarely obtained, because the sampling of rice phloem sap from sieve tube (< 20 μm) is difficult and quite small amount of phloem sap can be collected at once (ca. 1 μL/hr).

Size exclusion chromatography hyphenated with ICP-MS (SEC-ICPMS) is a well-established method to get distribution patterns of trace elements along different molecular weight fractions. However, a conventional SEC-ICPMS method is not adequate for the speciation analysis for small amount of samples because a large part of the sample introduced in the conventional SEC-ICPMS system is drained. In order to modify the SEC-ICPMS for small sample amount analysis, we have improved following two points; first, a conventional gel filtration column was scaled down to semi-micro size;. second, sample introduction efficiency to the plasma was improved by using a micro-flow nebulizer and a new single path type mini-chamber (Parvus mini-chamber, Glass Expansion) as the sample introduction device. The analytical performance of the present SEC-ICPMS method was better than that of the conventional SEC-ICPMS though the sample injection volume was reduced to one-tenth □1 μL□. We applied the present method to the speciation analysis of trace elements in phloem sap of rice plant that was collected with the insect laser technique[1].

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WedPo34. SPECIATION ANALYSIS OF SELENOPROTEINS IN HUMAN BLOOD

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Selenium is an essential element for life but toxic at levels little above those required for health. In the last years it was revealed that selenium has a large number of biological functions in humans. The most important and known selenium property is the antioxidant

action (anticarcinogenic) because it forms selenocysteine, part of the active center of the glutathione peroxidase (GPx) enzyme. Therefore, knowledge regarding the speciation of selenium in the human body rather than total selenium content is necessary for better understanding of its status. In mammals, including man, about 30 selenoproteins have been reported so far but only a few of them, namely GPx, type-1 iodothyronine 5'-deiodinase and selenoprotein P (SelP), have been identified and comprehensively characterized. Hence, the search for new Se-containing proteins and the study of their characteristics and biological functions is still undergoing. The main selenoproteins in human blood (serum) are SelP, GPx and selenoalbumin (where Se is not present in active form, and hence it is considered a Se-containing protein). Speciation analysis of these selenoproteins is difficult, because of their low concentration and the high amounts of some other non-selenium proteins, which interfere in the liquid chromatographic separation (HPLC). This study aims at the development of a new analytical approach for speciation analysis of selenoproteins (SelP, GPx and albumin) at trace and ultra-trace levels and its application to the analysis of human samples, particularly blood serum. For this purpose, various separation techniques, including size-exclusion, anion exchange, reverse-phase and affinity liquid chromatography hyphenated to inductively coupled plasma-(quadrupole) mass spectrometry (ICP-MS) are investigated. Quantification of selenoprotein species is carried out by post-column (online) isotope dilution-ICP-MS, using enriched ^{77}Se. The confirmation of the species identity is carried out by electrospray ionization-mass spectrometry (ESI-MS) and Matrix-Assisted Laser Desorption/Ionization-Mass Spectrometry (MALDI-MS). Finally, information regarding the distribution of selenium in serum proteins from healthy and unhealthy subjects is addressed.

WedPo35. IN-VIVO DISTRIBUTION STUDY ABOUT GOLD NANOPARTICLES BY ICPMS

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Nowadays the development and applications of nanotechnology are of major importance in both industrial and consumer areas. These nanoparticles (< 100 nm in diameter) are not just the smaller variant of the bulk material; they seem to have quite different properties. However, the knowledge on exposure and possible toxicity of nanotechnology products is limited. Therefore a pharmacological study has been designed to investigate the distribution of nanoparticles of different sizes in-vivo in rats.

Gold nanoparticles are chosen as model substances. Rats are intravenously injected in the tail vein with different sized gold nanoparticles (smallest particle size: 10 nm in diameter) in phosphate buffered saline (PBS) solution. After 24 hours, the rats are sacrificed and the organs are collected for analysis.

Two procedures of sample pre-treatment are tested depending on the available amount of biological sample matrices. The preferred procedure consists of a microwave-assisted digestion with aqua regia followed by measurements with inductively coupled plasma mass spectrometry (ICPMS).

Next to the direct analytical results a total balance to control the recovery of the given amount of gold will be presented. Several aspects of quality control are involved in the analytical procedure and these will be presented too.

WedPo36. CE-DAD-ICP-MS AS TOOL FOR ENVIRONMENTAL SPECIATION ANALYSIS

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CE-ICP-MS became during the recent years to an important tool in the field of speciation analysis. The main disadvantage of the system is the fact, that organic ligands without a detectable element like iodine, phosphor, or sulphur cannot be detected and so no information about free or complexed metal ions can be obtained. To solve this problem and to improve the performance of this tool we adapted a diode array detector (DAD) to the CE-ICP-MS coupling. The technical solution will be presented.
The possibilities of this technique were evaluated with the element iodine and humic acid. With the iodine the time shift factor between the DAD-signal and the MS-signal were determined. The LOD of humic acid was found to be less than 20 mg/l. By the application of this technique it will be possible to determine free metal ion and metal humate complexes by the MS and free humic acid and also the metal humate complexes by the DAD. The determination of complex constants and redox investigation will be much easier than before.
The big advantage of this technique is that it is not necessary to mark the ligands by e.g. iodine. If the Ligand is a strong UV absorber like the humic acid it can be detected direct easily by the DAD. First applications will also be presented.

WedPo37. SPECIATION ANALYSIS FOR IODINE IN GROUND WATER USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (HPLC-ICPMS)

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Iodine is well known to be an essential micronutrient for human body, as it is part of the production of the thyroid hormones. Iodine deficiency leads to various disorders associated with growth and development. In order to prevent iodine deficiency disorders, usage of iodized salt has become popular worldwide. However, the excessive iodine intake can also cause high-iodine goiter, leading to retarded brain development and functional impediment. Another important fact associated with consumption of iodine is that like other elements, bioavailability and toxicity is species dependent. Inorganic forms of iodine, such as iodide and iodate , are less toxic than molecular iodine and some organically bound iodine. Likewise, the bioavailability of organically bound iodine is also less than that of mineral iodine. Therefore, total analysis and characterization of iodine species is an important pursuit.
The combination of IC as separation technique with subsequent ICP-MS detection is an effective technique for simultaneous identification of iodide and iodate. SEC-ICPMS can identify organo-iodine species. The greatest problem for iodine speciation is to resolve the stability of iodine species, and different sensitivity of iodide and iodate in HPLC-ICPMS.
Method for iodine speciation analysis was described based on high performance liquid chromatography coupled with inductively coupled plasma mass spectrometry (HPLC-ICPMS). Investigations are performed concerning preservative medium and time, influences of buffer concentration, pH on separation efficiency. The developed method allows the fast and sensitive determination of iodine species with detection limits for iodide and iodate 0.025 μg/L(as I). The linear range of iodate was more than 4 orders of magnitude, from 5 nmol L^{-1} to 50 μmol L^{-1}. Attempts were made to quantify organo-iodine using size-exclusion

chromatography (SEC) column. Then applications were performed on ground water samples, showing iodide as the main iodine species in ground water, but in a few samples high contents of organoiodine compounds were observed as well. In addition, the total iodine concentration in the samples was determined by ICP-MS and gives an idea about the actual iodine state in ground water.

WedPo38. DETERMINATION OF As, Cd, Ni AND Pb IN PM_{10} PARTICULATE MATTER.

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The CE Directive 2004/107/CE deals with the measurement of the concentration of some genotoxic carcinogenic compounds and suggest to use the European method EN 14902 to perform the analysis of As, Cd, Ni and Pb in the PM_{10} fraction of the air suspended particulate matter.
The particles were collected, according to EN 12341, by a 24 hours sampling on glass fibre filters that were digested with a mixture of HNO_3 and H_2O_2 (5 and 2 ml respectively) in a microwave oven. After digestion the undissolved filters were removed, carefully washed with ultra pure water and the solutions picked up at the final volume of 50 ml.
Analysis were performed by ICP-MS using rhodium as internal standard for all the elements choosing, when possible, at least two isotopes per element.
The calibration range for each element was optimized to fit our expected values and no matrix matching of the standard was found necessary when analyzing 1:2 dilution of the samples.
Detection limits were estimated via 10 blank analysis.
About 100 filters were analyzed covering two different climatic periods: a winter (oct-dec) and a summer one (may-jul).
The very first results show, as expected, an increase in the concentration of all the elements in the winter season and a good correlation with the total PM10 concentration.
The analytical procedure was validated via analysis of the NIES CRM n°8 (Vehicle exhaust particulate) and via parallel analysis by ETAAS of about one fifth of the samples.

WedPo39. DETERMINATION OF TRACE ELEMENTS IN ATMOSPHERIC PARTICLES PM2.5 COLLECTED IN QUARTZ AND GLASS FIBER FILTERS USING ICP-MS.

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Particulate matter in the atmosphere is generated by a variety of sources as a product of combustion and from natural and industrial processes. From this, the fine particulate matter PM2.5 is of great importance due to its impact in human health and its persistence in the environment. Trace element determinations in PM2.5 is significant as it may contain toxic elements that come in close contact with the lungs. Also, it has been used to understand chemical reactions in the atmosphere and is used in modeling studies as source-receptor.
Particulate matter 2.5 is a small portion from the overall particulate matter and the trace elements contained in the PM 2.5 represent even a smaller fraction, therefore, the determination of the trace elements in PM 2.5 needs very sensitive methodologies, such as ICP-MS. The collected atmospheric particles are digested together with the filters used for

their collection, because minute amounts of sample is trapped on the filters. Different digestion settings and acid combinations were studied in order to have a complete digestion of the sample and the filters.
Quartz and glass fiber can furnish contaminants that can interfere with the trace element determinations by ICP-MS. For interference minimization, two approaches were studied: serial dilutions of the samples and the use of collision cell.

WedPo40. DEVELOPMENT AND APPLICATION OF AN ULTRATRACE METHOD FOR THE SPECIATION OF ORGANOTIN COMPOUNDS IN NATURAL CRYOGENIC HOMOGENIZED BIOLOGICAL MATERIALS

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An accurate, ultra-sensitive and robust method for the speciation of mono, di and tributyltin (MBT, DBT and TBT) by speciated isotope dilution-gas chromatography-inductively coupled plasma-mass spectrometry (SID-GC/ICP-MS) was developed to quantify butyltins concentrations in three cryogenically homogenized natural biological materials. These materials consisted of a "simple" fresh-frozen Mussel Tissue (SRM 1974b) together with "complex' materials; a protein-rich material (Whale Liver Control Material, QC03LH03) and a lipid-rich material (Whale Blubber, SRM 1945) containing up to 72 % lipids. The degree of commutability between these cryogenic materials and a freeze dried mussel tissue reference material (ERM-CE477, IRMM) was investigated regarding spike equilibration/interaction, extraction efficiency and the absence of detectable transformations. An inter-method comparison consisting in varying extraction conditions and spiking strategies allowed the assignment of reference concentrations of butyltins in cryogenic SRMs and Control Materials for the first time. The reference concentrations of MBT, DBT and TBT in SRM 1974b are 0.92 ± 0.06, 2.7 ± 0.4 and 6.58 ± 0.19 $ng.g^{-1}$ (wet mass, 95 % CL as Sn) respectively and 0.38 ± 0.06, 1.19 ± 0.26 and 3.55 ± 0.44 $ng.g^{-1}$ (wet mass, 95 % CL as Sn) respectively in SRM 1945. In the QC03LH03 material, DBT and TBT concentrations are 30.0 ± 2.7 ng g^{-1} and 2.26 ± 0.04 $ng.g^{-1}$ (wet mass, 95 % CL as Sn). The concentration range of butyltins in these materials is one to three orders of magnitude lower compared to ERM-CE477. This study demonstrated that cryogenically processed and stored biological materials represent a promising alternative to conventional freeze-dried materials for organotin speciation analysis since they represent at present the best conditions to minimize thermolabile species degradation and long-term archival.

WedPo41. ELEMENTAL STUDY OF THE REMAINS OF AGNÈS SOREL (1422-1450) BY ICP-OES SUPPORTS THE THESIS OF A DEATH CAUSED BY MERCURY INTOXICATION

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Profiting of its reinterment, the contents of the funeral urn of Agnes Sorel (1422-1450) were subject to a multidisciplinary study under the direction of Dr. P. Charlier in order to better understand the life and death of Agnes Sorel, official mistress of french king Charles VII.

Elemental analysis was performed using the multi-waves ICP spectrometer Activa® after microwave assisted mineralisation.
Several samples taken at the different levels of the urn were analysed. The great sensitivity and the high resolution of the spectrometer allowed us to quantify directly very difficult elements such as mercury. We thus could confirm the presence of a lead sarcophagus previously described in historical texts. The elemental composition of some residues suggested their biological origin, and were attributed to the decomposition fluid. All analyzed samples contained mercury at different concentrations but, by far, the highest levels were found in hairs. Moreover, mercury concentration in samples taken on the skull (e.g. rests of skin) were moderate, indicating that mercury did not come from an external post-mortem use, for example medieval embalming method. The very high levels of mercury found in hair strongly suggest that Agnès Sorel died from an intoxication of this metal, which is supported by other findings of the multidisciplinary study.

WedPo42. NOVELTY IN SPECIES SPECIFIC - UNSPECIFIC ISOTOPIC DILUTION APPLIED HERE TO ORGANO-TINS & -MERCURY SPECIATION IN BLOOD SAMPLE AND BIOLOGICAL TISSUE BY GC-MS AND GC-ICPMS

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In the last years, it has been demonstrated that the application of Isotope Dilution Analysis to elemental speciation provides not only a higher quality of the analytical results. However, the implementation of such methodologies in a routine basis is scarce mainly due both spike's technique requirements, data mining. Moreover, the limited accessibility of the routine testing laboratories to expensive techniques (GC/ICP-MS, labelled compounds) is also not in favour of a widespread technique.
In this sense, the measurement of isotope ratios of organometallic species using a unique - simple ID method and a GC-MS allows the immediate implementation of routine analytical methodologies based on the use of IDA. In this work, the simultaneous determination of organometallic species (MeHg, MBT, DBT &TBT…) for unknown contamination samples degree with a large dynamic range by using a GC-MS / ICPMS has been developed. The novelty is due to multiple labelled calibration curve approach, universal spike technique and data mining.
The method was compared with a previously published GC/ICPMS isotope dilution procedure, developed in our laboratory, by injecting the same samples following isotopic dilution methods. A comparable analytical result in terms of precision and accuracy are demonstrated for both atomic and molecular mass spectrometric detectors (even better with the new ID method in case of blind sample).

WedPo43. ARSENIC OCCURRENCE IN PLANTS GROWING IN A MINING CONTAMINATED AREA

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Mining activities generate a large amount of waste rocks and tailings which get deposited at the surface. The degraded soils, and the waste rocks and tailings are often very unstable and can become sources of pollution. Populations of a variety of higher plant species are able to colonize these polluted environments responding by exclusion, indication or accumulation of

metals. Natural Arsenic occurrence in terrestrial plants is generally low with background contents ranging from 0.2 to 0.4 mg As kg^{-1}. To understand how terrestrial plants take up, transport and metabolise these arsenic species, it is essential to characterize arsenic species in plant tissues.
In the present study several plant samples were collected in a mining contaminated area located in the Eastern Pyrenees (Spain), where abandoned As mines can be found. Plant samples were analysed for total and arsenic species by ICP-MS and the coupled technique HPLC-ICP-MS respectively. In previous studies different arsenic pattern was obtained in plants of the same species but growing in several areas with different levels of arsenic. The aim of this study is to obtain information about the arsenic species present in different parts (roof, shoots and leaves) of plants growing in soils with very high arsenic contents. Relevant information regarding arsenic soil-to-plant uptake and plant detoxification mechanisms is obtained.

WedPo44. ON-LINE PRECONCENTRATION AND SPECIATION OF Sb(III) AND Sb(V) IN URINE USING A FULLY AUTOMATED HG-ICP OES SYSTEM

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A novel approach was studied for the on-line preconcentration and separation of inorganic Sb species using an hydride generation inductively coupled plasma optical emission spectroscopy (HG-ICP OES) system. The biopolymer L-methionine inmobilized on controlled pore glass (CPG) was used for the selective retention of Sb(III) at pH 10. A 30% HCl solution was used to elute the bound species. Prior to Sb determination, a pre-reduction step with thiourea became necessary. Conversion into hydrides was required to increase detectability of both species by ICP OES and thus match their expected levels in urine. The detection limit (LoD) for the preconcentration of 10 mL of sample was 70 ng L^{-1} with a RSD of 2%. An enrichment factor of 20 was achieved when 10 mL of sample were passed through the system, reaching a throughput of 23 samples per hour The method was successfully applied to the determination of Sb species in urine. This study demonstrated that L-methionine is an effective metal chelator. In addition, the coupled technique allowed to reach LoDs that are normally afforded by the much expensive ICP-MS methods.

WedPo45. DEVELOPMENT OF ANALYTICAL METHODS FOR IODINE SPECIATION IN FRESH WATER USING SEC-ICP-MS

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Analytical methods for physicochemical speciation of iodine in fresh water samples were developed to elucidate its behavior in the environment. An inductively coupled plasma mass spectrometer was combined with a size exclusion high performance liquid chromatograph (SEC).

Freshwater samples were collected from Lake Towada and rivers surrounding the lake. After filtration by a 0.45 μm pore size membrane filter, iodine in the water samples were pre-concentrated with an ultrafiltration filter, which has cut-off size of 10 kDa. The fraction with molecular size over 10 kDa was concentrated to 100 times in the original water, and then introduced to a SEC-ICP-MS. The SEC-ICP-MS consisted of a high performance liquid

chromatograph with a SEC column, a GL-530 (Hitachi), and an ICP-MS instrument (VG-PQ-Excel, Thermo Instrument). The buffer solution of 0.01M Tris-HNO_3 (pH 7.3) was selected as the mobile phase. Molecular size chromatograms of all river and lake water samples showed two peaks of UV absorptions and also concentrations of iodine: 30 kDa and >700 kDa peaks. Ratios of the iodine concentration in 30 kDa peak to sum of both peaks varied greatly depending on season of sample collection.

This work was supported by Aomori Prefecture

WedPo46. SPECIATION AND DISTRIBUTION OF SELENIUM IN ALLIUM CEPA L. – DIFFERENT APPROACHES OF IN-VIVO AND IN-VITRO INVESTIGATIONS

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Nowadays the investigations of selenium metabolism in plants have become an important analytical challenge. It has been found that selenium accumulating plants are very interesting material for the study of selenium metabolism. In this work the experiments were performed on selenium enriched onions (Allium cepa L.).

Usually applied approach for the investigation of the element speciation is based on the destruction of the plant by using the different extraction solutions and then the extracted compounds are identified and quantified by the hyphenated techniques (mostly coupling of the chromatographic separation method to the element-specific detector). In-vitro analysis requires performing the long procedure of sample preparation what can have a consequence on the original speciation equilibrium. In certain cases, for example when the efficiency of extraction is very low, applying more innovative approach should be considered and in-vivo investigations could be carried out.

In this work two different approaches of the investigation of selenium spectiation were used. The microscopic X-ray Absorption Near Edge Structure Spectroscopy (μ-XANES) and confocal microscopic X-ray fluorescence analysis (μ-XRF) were used for the in-vivo determination of selenium distribution and for the local speciation of selenium in roots and leaves of onion. Distinct energy differences of the XANES spectra of various selenium reference compounds having different oxidation state allow adjusting the excitation energies used for μ-XRF mapping.

For in-vitro study of selenium speciation in onion the anion exchange high performance chromatograpy (column: Hamilton PRP-X100) coupled with mass spectrometry detection was applied. Selenium speciation analysis was performed after selenium extraction by hot water from dried and row plant material.

The results obtained by AE HPLC ICP-MS were compared to the results obtained by μ-XANES and μ-XRF. We have found that both approaches in-vitro and in-vivo investigations gave similar information about selenium speciation in onion. The ratio of inorganic vs. amino acid selenium compounds differs in various subparts of the plant. Detailed in-vivo investigation of the distribution of various selenium species in virtual cross sections of root tips and green leaf shows that the selenium transport takes place via different mechanisms, depending on the nature of the selenium compounds originally taken up.

WedPo47. MEASUREMENT OF TRACE ELEMENTS IN MILK SAMPLES BY INDUCTIVELY COUPLED MASS SPECTROMETRY

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Essential trace element deficiencies and levels of toxic trace elements can be determined by measurement of elements in serum, blood or urine samples. The cause of the deficiency/toxicity, however, is not always easy to clarify. In infants, milk (either from the mother or from milk formulas) is usually the sole source of nutrition after birth and thus deficiency will often stem from an inadequate supply. Toxic elements may also be passed from mother to infant in the milk and may also be introduced into milk formulas via the manufacturing process or the use of contaminated water in preparing the feed. Here we are developing a method to measure essential trace elements(Cu, Zn, Se, Mn, Cr, Ni) and toxic elements (Pb, Cd, Hg, As, Al, Sb) in milk samples (human milk, cow's milk, milk formula and milk powder) using an Elan DRC II ICP-MS.
Dynamic reaction cell conditions (DRC) were optimised using solutions mimicking the high calcium, phosphate and protein concentrations of milk samples. Potential interferences remaining at these conditions were assessed by comparing mass spectrum scans of milk samples to theoretical isotope patterns. Optimum DRC conditions: Cd, Sb – reaction gas: O_2, gas flow: 0.6mLmin^{-1}, RPq: 0.7-0.75. Cu, Zn, Se, Mn, Cr, Ni, Al – reaction gas: NH_3, gas flow: 0.8mLmin^{-1}, RPq: 0.6-0.75. Hg, Pb – ICP-MS standard mode, RPq: 0.25. Calibration curves produced by standard addition calibration on the different types of milk samples showed good agreement. Milk formula was chosen as a calibrant matrix. Recoveries for different types of milk sample were as follows - human milk: 93.1-111.2%, cow's milk: 82.9-121.5%, milk powder: 93.8-105.6%.

WedPo48. REFERENCE VALUES FOR INORGANIC ELEMENTS AND ORGANIC COMPOUNDS IN BLOOD, PLASMA AND URINE : THE NEW S.I.V.R. LIST
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The Reference Value Italian Society (SIVR), founded in 1993, has the goal to acquire and diffuse the knowledges about environmental and occupational xenobiotics reference values.
SIVR acivities are focused onto the determination of the xenobiotics concentrations in biologic fluids collected from general population subjects. This activity has based on multidisciplinar working groups that study methodological problems like preanalytical factors, analytical methods, biological variability factors, statistical elaborations.
The reference values involved either inorganic or organic substances (or their metabolites) that are absorbed from living environment (indoor and outdoor) during non working activities.
The definition of the reference value is very important to assess the environmental exposure and acquire the instruments for a correct evaluation of the background level of the biomarkers used in the biological monitoring of professional exposure.
All that passees through the use of analytical methods suitable to determine low concentrations of the analyte (in terms of detection limit, repeatability, accuracy) and the knowledge of variability factors due to personal habits (smoking, drugs assumption etc), individual characteristics (age, sex etc), diet and specific factors depending on the analyte nature.
In general the SIVR methodology envisages four categories of reference values:
- Validation Reference Values (VRV) proposed by a laboratory with specific experience in the determination of the analyte but using a non validated analysis procedure

- Tentative Reference Values (TRV) produced as a result of specific experiments in which a small number of laboratories partecipate with different methods of analysis or produced by a single laboratory using a partly validated method
- SIVR Reference Value (VR) produced by a number of laboratories according to the complet method defined by SIVR or by a single laboratory using a completely validated method
- Metanalitic Reference Values (MRV) obtained by analysing published studies in the last five years in the scientific literature and critically analysed by SIVR methodology

These procedures has been applied in the compilation of the SIVR reference values second list, published at the end of 2005, and available in the SIVR web site www.valoridiriferimento.com.

WedPo49. DETERMINATION OF TRACE ELEMENTS IN URINE BY USN-ICP-MS : CRITICAL EVALUATION OF MEASUREMENT UNCERTAINTY

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The paper presents a method for the simple and reliable routine determination of Pb, Cd, Co, Cr, Mn, Tl, Cs, Ba, Sr, Be, V, Bi, Hg, Sb, Pt and Rh in urine by inductively coupled plasma mass spectrometry equipped with ultrasonic nebulizer (USN-ICP-MS). The complete method validation for all the elements is described, including the evaluation of detection limits, the short- and long-term stability, the precision and accuracy and the uncertainty of measurement.

The urine samples were analyzed directly after a 1/5 (v/v) dilution with 1% (v/v) nitric acid containing rodium as internal standards. Limits of detection are in the range 0,6 ng/l (for Pt), to 110 ng/l (for Cr) and 400 ng/l (for Hg) calculated to the undiluted urine. Repeatability and short-term stability were investigated by measuring the RSDs for all elements (at 0,5 µg/l) in two periods of 5 min (with 10 measurements) ad 30 min (with 10 measurements), respectively. The RSDs are in the range 2-4% for repeatability and 3-7% for short-term stability, which are completely satisfactory figures of merit for urine analysis.

Spike recoveries of 0,5 µg/l from multi element calibration solution are in the range 85-115%.

In the present method the samples are diluted and directly analyzed by ICP-MS; according to the ISO "Guide to the Espression of Uncertainty of Measurement " (GUM), the uncertainty of the measurement is therefore built by the contributions of three factors: the dilution step, the repeatability and the calibration curve.

Comparing the three factors affecting the uncertainty, it was verified that at high elements concentration the major component of uncertainty was the repeatability contribution (60-70% of combined uncertainty), while at low concentrations the calibration becomes the more important.

At 0,2 µg/l typical values of relative expanded uncertainty resulted of about 50-80%

WedPo50. PEAK EFFICIENCY COMPARISON OF MICROMIST-100 AND HEN MICRONEBULISERS ON As, Se, Cr SPECIATION BY HPLC-ICPMS

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Speciation studies are currently mostly carried out through HPLC-ICPMS coupling. One of the advantages of microbore LC versus conventional LC separation techniques is the

introduction of lower amounts of undesired organic material and salt buffers into the detector. This is caused by the lower flow-rate and small sample volume associated with microbore column. In addition, better sensitivity at a low sample uptake rate could be obtained with the use of low-flow, more efficient mass transport, nebulizers.In order to assess the capabilities of such a coupling, a method for the simultaneous analysis of As(III), As(V), DMA, Se(IV), Se(VI) and Cr(VI) has been tested. The main advantage expected was a better resolution of the peaks. Thus, reducing the dead volume of the system was mandatory. An Agilent 1100 capillary system and a micronebuliser were used. Separation was performed in a Hamilton PRP-X100 (150x1 mm, 3 μm) anion exchange column, based on a gradient step of $NH_4NO_3/(NH_4)_2HPO_4$ pH 8. (Extracolumn volume allowed, 1.88 μL). For a MicroMist-100 nebulizer wide peaks were obtained (around 60 seconds) whereas thin peaks were achieved with HEN (less than 30 seconds). The reason of this different behavior owed to the higher dead volume of the first one, which increased the axial diffusion. MicroMist-100, with a 0.25 mm id capillary, generated around 12 μL of extracolumn dead volume. However, HEN, with a 0.1 mm id capillary only contributed with 1.57 μL.
Regarding mobile phase composition, it was found that DMA and MMA peak widths narrowed with concentration of phosphate decreasing. When low concentration of phosphate was used, these species were totally retained in the column, and only eluted when concentrated mobile phase was pumped. Thus, DMA and MMA suffered less axial diffusion.
Finally, the use of HEN and a low content of phosphate in the mobile phase improved the separation efficiency. It allowed to increase the sample amount injected (15 μL) and the chromatographic flow (100 μL/min), improving the sensitivity and reducing the total analysis time of the method.

WedPo51. ANALYSIS OF PHOSPHOPEPTIDES BY LIQUID CHROMATOGRAPHY COUPLED TO INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY AND TO LC CHIP MASS SPECTROMETRY.
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A method for the detection and identification of phosphopeptides by liquid chromatography interfaced to inductively coupled plasma mass spectrometry (LC-ICP-MS) and to LC Chip Mass Spectrometry (MS) is described. LC-ICP-MS is used for ^{31}P detection and HPLC-Chip-MS provides the corresponding structural information. The method is demonstrated for the analysis of a mixture of synthetic phosphopeptides P60c-src Substrate II and Pp60 c-src, and phosphoproteins α-casein, β-casein. "Real samples" were studied to explore the potential use of phosphopeptides as biomarkers for disease. Presented is the analysis of cerebrospinal fluid from patients with vasospasm post subarachnoid hemorrhage versus cerebrospinal fluid from "normal" patients is also presented.

WedPo52. SIZE FRACTIONATED MEASUREMENTS ON ATMOSPHERIC AEROSOLS IN THE URBAN ENVIRONMENT
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Awareness of air pollution has led to numerous studies on the chemical composition of ambient aerosols and origin of pollution sources. Atmospheric aerosols influence many atmospheric processes including cloud formation, visibility variation and solar radiation transfer, and are believed to represent a significant health concern to human. Ambient concentrations of particulate matter (PM) are systematically monitored and air quality standards set by European Union have emphasised the need for the characterisation of PM

below 10 μm (PM_{10}) by mass. Such mass based measurements are easy to measure, but are unlikely to encompass all the factors relevant to adverse health effects. Recent toxicological studies have suggested that particulate number, size and composition may all play important roles in adverse health impacts. This paper will report on a state-of-the-art particulate measurement technique, the Dekati electrical low pressure impactor (ELPI), that is used for characterisation of fine and ultrafine particulates collected in an urban environment (Sheffield) in October, 2006. Size fractionated (13 size fractions: 7nm-10 μm) airborne particles were collected (n = 7) by the ELPI over a 7-day sampling period. The water-soluble inorganic ions (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, K^+, Mg^{2+} and Na^+) were analysed by IC and the water-extractable metallic elements (Al, Ca, Cu, Fe, K, Mg, Na, Fe, Pb and Zn) were determined by ICP-MS. By assuming sodium exclusively originating from sea salt, the fractions of sea salt (ss) and non sea salt (nss) of the detected components were differentiated. The mode/modes of the particulate mass and the species mass distribution versus the stage size imply different sources of emission. Interspecies correlations give additional information on possible origin.

WedPo53. THE POSSIBLE BIOAVAILABILITY OF SE SPECIES FROM DIETARY SUPPLEMENTS

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Four commercially available dietary selenium supplements were investigated from the point of view of their role in the human selenium supplementation. Both total selenium content and the species distribution were studied. An ICP-MS system was applied for total Se determination, while analyzing the species distribution an HPLC was coupled to the ICP-MS system. A traditional sample preparation method, proteolytic digestion was applied to assess the original species distribution of the dietary supplements.

Significant amount of organically bound species could be identified, as SeMet in the proteolytic extract of two samples. In the remaining supplements only inorganic species can be identified.

Simulated human digestion was also employed to estimate the bioavailability of Se and its species from the dietary supplements. As the effect of the simulated digestion different extraction efficiency of selenium from the dietary supplements can be observed. In the case of the supplement with high amount of organically bound Se species extracted by proteolytic digestion (SelenoPrecise), the SeMet content remains still high even after simulated human digestion.

The results of the enzymatic and the simulated human digestion revealed that speciation analyses applying traditional sample preparation protocols (proteolytic digestion, extraction with diluted HCl or NaOH) are not appropriate for assessing the applicability of the given food product for human Se supplementation purposes.

WedPo54. ANALYSIS OF SELENIUM INCORPORATION IN SOYBEAN PROTEINS

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The study of selenium (Se) containing proteins in plants is a growing area of research interest. Preliminary investigations of Se in selenized soybean sprouts are in progress. A protocol for analysis of selenium containing water soluble proteins in sprouts is being developed. Se was detected in high and mid-molecular weight proteins of the enriched sprouts. Distribution of Se in the globulins (storage proteins) and whey proteins was studied. Globular proteins were

isolated based on differences in isoelectric points (11S and 7S fractions). The results to date were accomplished by SEC-ICPMS studies.
Gel electrophoresis of Se-containing protein fractions showed prominent protein bands. Investigation of these bands to determine Se association, employing MALDI and nano LC-MS are under way and these results will be presented and discussed

WedPo55. DETERMINATION OF 4 PESTICIDES IN VEGETABLES AND FLOWERS BY HPLC-ESI-MS/MS

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Pesticides are widely used in the agricultural practice to protect the plants. Becouse of the different abrogates, there are several groups of pesticides: viricids, bactericids, fungicids and zoocids. The latest group is the largest and its alcategories are: acaricids, aficids, insecticides, nematicids and rodenticids. In our work we had to determine 4 pesticides becouse of industrial order.
In this study HPLC-ESI-MRM method was developed for the identification and quantification these 4 pesticides, namely: hexythiazox, bupirimate, acetamiprid and pirimicarb in vegetables and flowers. Ion source dependent (ionisation voltage, ionisation temperature) and compound dependent (curtain gas flow rate, declustering potential, collision energy, collision entrance and exit potentional) parameters were optimised for each compounds where the two most efficient transitions were selected and monitored in electrospray ionisation (ESI+) mode. Reverse phase (RP) C18 20 mm x 2,1 mm X-TERRA coloumn was used for the separation of these different polarity compounds and gradient elution was applied with methanol and deionised water. Methanol was used for the extraction, besides, a mixing, centrifuging and filtring step were parts of the sample preparation procedure. External and internal (standard addition) calibration was applied for the quantification. The aim of the separation was not only to separate the molecules from each-other, but to separate the compounds from the matrics. Total selectivity was accessed, becouse one mother ion- daughter ion transition is appertained only one molecule.

WedPo56. ELEMENTAL SPECIATION VIA HPLC-ICP-MS APPLIED THE DETECTION OF CHEMICAL WARFARE AGENT DEGRADATION PRODUCTS IN FOODS.

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As the threat of terrorist attacks looms over the US, scientific methods must be developed to assess the nature and extent of a terrorist act. One route of attack entailing great concern is contamination of the food supply. In order to assess whether food has been exposed to toxins or poisons, methods must be developed. Whenever possible, methods developed for counterterrorism should be rapid, simple, robust and easily transferable to other laboratories. They should have broad applicability to a wide variety of matrices and have adequate sensitivity to detect and identify specific toxins, poisons or degradation products of the toxins or poisons. Such methods for the detection of phosphorous containing chemical warfare agent degradation products (CWADPs) are explained here using HPLC and ^{31}P specific

detection capabilities of ICP-MS. Multiple chromatographic separation techniques are explored and evaluated in this study. Separation of >8 CWADPs was accomplished with low detection limits. The separations were applied to a variety of food types.
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WedPo57. CRITICAL EVALUATION OF INTERNAL STANDARDS AND MEASURING CONDITIONS FOR THE SIMULTANEOUS DETERMINATION OF IODINE AND COBALT IN BOVINE SERUM AND URINE
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Iodine deficiency still poses an important health risk in many regions. In the nutrition of cattle this can occur particularly if self-produced forage without additives is used predominantly and iodine supplementation does not take place to a sufficient extent. Control of the iodine status of cattle is necessary to avoid health damage and to guarantee high productivity of dairy cows as well as an unimpaired growth of beef cattle. Additionally, a sufficient iodine supply of dairy cows contributes significantly to the human iodine supply via dairy products.
Cobalt, being the central atom of vitamin B_{12}, represents an important trace element, which is taken up by cattle in inorganic form and converted by rumen bacteria into the essential vitamin. Since the forage, depending on the soil, may contain very little cobalt as well as iodine, control of the Cobalt supply is necessary, too.
The determination of cobalt by ICP-MS is usually carried out in acidic solution. In contrast, the determination of iodine is hardly possible in acidic solution, since it is disturbed by the formation of volatile hydrogen iodide in the spray chamber when iodine is present as iodide. Additionally, the oxidation of iodide by atmospheric oxygen to elemental iodine may lead to a loss during the sample storage by diffusion of iodine into the walls of plastic containers. To avoid these problems, samples can be diluted with TMAH solution, since in the strongly alkaline solution elemental iodine disproportionates to iodide and iodate, which do not form any volatile compounds under these conditions. However, to determine cobalt and iodine simultaneously, both have to be stabilized in sample solutions and in external standards.
In this work the signal characteristics of different iodine species in alkaline and acidic solution as well as the storage stability of the solutions were studied. Subsequently, an ammonia/ammonium chloride buffer was selected to guarantee the stabilization of cobalt by formation of ammine complexes and of iodine due to alkaline conditions. A series of internal standards was tested in order to enable an external calibration. It turned out that for iodine, depending on the matrix, different internal standards were necessary and another internal standard for cobalt. Using the developed method, the storage stabilities of undiluted serum and urine samples were examined at different temperatures and iodine and cobalt were determined in a series of clinical samples.

WedPo58. ANTIMONY SPECIATION IN ASH LEACHATES BY HPLC-ICP-MS
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The study of selenium (Se) containing proteins in plants is a growing area of research interest. Preliminary investigations of Se in selenized soybean sprouts are in progress. A protocol for analysis of selenium containing water soluble proteins in sprouts is being developed. Se was detected in high and mid-molecular weight proteins of the enriched sprouts. Distribution of Se in the globulins (storage proteins) and whey proteins was studied. Globular proteins were isolated based on differences in isoelectric points (11S and 7S fractions). The results to date were accomplished by SEC-ICPMS studies.
Gel electrophoresis of Se-containing protein fractions showed prominent protein bands. Investigation of these bands to determine Se association, employing MALDI and nano LC-MS are under way and these results will be presented and discussed.

WedPo59. CHIRAL SPECIATION OF THE PESTICIDE BROMOCYCLEN IN ENVIRONMENTAL SAMPLES BY SPME-ENANTIOSELECTIVE GAS CHROMATOGRAPHY WITH ECD AND ICP-MS DETECTION

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The development of analytical methods for the efficient separation of enantiomers is one of the most important tasks in several research fields, particularly in pharmaceutical and agrochemical research. This is mainly due to the different biological activity that can be exhibited by a pair of enantiomers. Most published papers have focused on the separation of chiral pharmaceutical products as a consequence of the more severe guidelines for marketing new chiral drugs. However, it should be recognized that the same chiral principles apply to pesticides containing stereogenic centers such as bromocyclen
Bromocyclen is a chiral organochlorine pesticide (OCP), which has been widely used against ectoparasites for the treatment of domestic animals in Europe. This pesticide is used as racemate despite the fact that it may undergo preferable degradation of the (+)-enantiomer in organisms of high trophic levels. Therefore, to evaluate the unwanted effects of bromocyclen as pollutant, it is important to understand their chiral discrimination in biological systems. For this purpose separation methods of high stereoselectivity are required.
Accordingly, a separation of the two enantiomers of the Bromocyclen by capillary gas chromatography (CG) has been developed, using a commercial chiral column (CP-Chirasil-Dex CB). Moreover, we also investigated the feasibility of coupling an extraction/enrichment procedure for Bromocyclen enantiomers from real samples based on solid phase microextraction (SPME) to enhance the analytical characteristics of the enantioselective gas chromatography analysis.
Finally, we compared the performance of SPME-enantioselective GC combined with both ECD and ICP-MS detection for the determination of the enantiomers of bromocyclen in real environmental samples such as fish tissue.

WedPo60. CHARACTERIZATION OF METAL-ANTHOCYANINS COMPLEXES IN WINES BY SEC AND RP-HPLC-ICP-MS

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Wine propoerties are affected by the presence of metals such us Fe, Cu, Mn, and Zn [1]. It seem to be that they are involved as catalysts in biological systems or as promoters of some enzymes. The metals also participate in some redox processes in cell metabolism and they are responsible of the stability, colour, organoleptic propeties and clarity of wines. On the other hand, anthocyanins (glycosylated anthocyanidins) are some of the main phenolic compounds in red wines that determine the purple-red colour of young red wines [1]. The levels of grape anthocyanins decrease during ageing since they react with a variety of other wine constituents that induces the formation of more stable pigments. The anthocyanins have a great complexing capacity, especially for Fe and Cu. The fractionation of wine samples by using ion exchange resins has been studied by Karadjova et al. and the speciation of Cu, Zn and Fe was measured. They concluded that the majority of polyphenols form salts and chelates with metals, mainly Fe and Cu. The usual approaches for metal speciation in wines, are based in both atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The evolution of metals throughout the ripening of grapes and vinification processes has also been studied [1] but under our knowledge, the reversed phase (RP)-HPLC on-line coupled to ICP-MS have not been yet performed.
In the present work, the metal-anthocyanins complexes characterization in wines has been carried out by on-line coupling of RP-HPLC-ICP-MS after purification using a size exclusion column (SEC-low molecular weight range) that allows a better understanding of the metal anthocyanins bindings. In addition, the use of thin layer chromatography to detect fraction containing anthocyanins was used in parallel with ICP-MS for metals to test the complexation process.
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WedPo61. MICRO-HPLC FOR PROFILING THIO- AND OXO-ARSENOSUGARS IN BROWN ALGAE
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Arsenosugars are the major arsenic compounds in marine mussels and algae. Two years ago a new group of arsenosugars, the so called thio-arsenosugars have been reported for the first time in marine mussels and one year later also in marine algae. In general arsenosugars in algae exist in two different forms, the usually dominating oxo-arsenosugars and at minor concentrations their thio-analogues. Whether the thio- or the oxo-analogue arsenosugars are first biosynthesised in marine algae is still unclear.
In the present work a method for the simultaneous determination of oxo- and thio-arsenosugars has been developed. We used a Micro-HPLC with an Atlantis® (1.0*150 mm) reversed-phase column for the separation of the arsenosugars. We investigated the retention behaviour of the arsenosugars with ammonium nitrate and ammonium citrate, propionic acid and nitric acid as mobile phases.
With the optimised method we determined the concentrations of the thio- and oxo-arsenosugars in different types of algae from Denmark. In the algal material depth profiles as well as differences of young and old parts of the plant were established.
In the poster we will present the results on the method optimization as well as the concentrations of the thio- and oxoarsenosugars in various parts of the algae.

WedPo62. SELENIUM SPEIATION IN SOILS BY HPLC-ICP-MS

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Selenium exists in several oxidation states and its behaviour is complex in both the environment and living organism. It is an essential element but can be toxic at high concentrations. The narrow interval of concentration between the two opposite effects requires accurate and precise knowledge of the selenium as well as each species present in the environment.
In general, the primary source of selenium in plants and human is attributable to soils. Therefore, studying the species of selenium in soils can help in the understanding and evaluation of its behaviour in the environment. Nevertheless analytical selenium speciation in soils is not widely reported in the literature.
In the present study various soils of interest such as seleniferous or contaminated soils were analyzed for total content and selenium species. The extractants tested for speciation were water, phosphate buffer and phosphoric acid. The "pseudototal" selenium content obtained by applying extraction with aqua regia was assessed in order to establish the mass balance and estimate the recoveries of the extraction method. All the extracts were analyzed by the coupled technique HPLC-ICP-MS. Phosphoric acid was the most efficient extractante being the inorganic species the predominant ones. The results are also discussed / compared in relation to the type of soil and extractant.

WedPo63. INVESTIGATION OF MONOMETHYLARSENOUS ACID **($MMAs^{III}$)** IN BRAZILIAN HUMAN URINE BY A COMBINED LIQUID AND GAS CHROMATOGRAPHIC APPROACH

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It has been demonstrated that trivalent methylated As acids, monomethylarsonous acid ($MMAs^{III}$) and dimethylarsinous acid ($DMAs^{III}$), exhibit significantly stronger genotoxic effects than the corresponding pentavalent ones and even inorganic arsenic. In one study it was claimed that $MMAs^{III}$ could serve as an indicator in urine to identify individuals with increased susceptibility to toxic and cancer-promoting effects of arseniasis. In respect to general analytical principles, however, in all the reports cited, identification of $MMAs^{III}$ and $DMAs^{III}$ in urine is only based on HPLC retention time comparison between sample and standard. Concerning the latter, for example when using the Reay and Asher method for $DMAs^{III}$ synthesis, instead of the desired compound, dimethyldithioarsinic and dimethylthioarsinous acid are produced leading to wrong reference species. Dimethylarsinothioic acid was identified on the base of mass fragmentograms obtained by HPLC-ESI-MS not only in the Reay and Asher standard, but also as an arsenosugar metabolite in sheep urine. In the light of these results it cannot be excluded that studies using DMPS (2,3- dimercapto-1-propane sulfonate) as arsenic-complexing agent also produced S-containing analogues of the analytes. To try to solve this puzzle further, simultaneous HPLC-ICP-MS/ESI-MS analysis will be necessary. However, in most cases the $MMAs^{III}$ and $DMAs^{III}$ concentrations in urine are too low to be detected by ESI-MS. Therefore we chose another approachs: **(i)** The retention time interval of $MMAs^{III}$ was cut from the HPLC run with urine samples from Brazilian children exposed to arsenic-rich drinking water, and then volatilized by hydride generation at pH 5. The GC separation led to clear isolation of $MMAsH_2$. This indicates that the analyte is either $MMAs^{III}$ ($MMAs^{V}$ is separated by HPLC separation and not volatilized under the applied pH conditions) or a compound, which contains a $MMAs^{III}$ group that can be cleaved under the reaction conditions applied. **(ii)** Mass

of 48 and 50 monitored as sulphur oxide (^{48}SO, ^{50}SO) during arsenic speciation. In this case, ICP-MS with reaction cell (reaction gas: O_2, 0.6 mL min^{-1}) was applied. The sulphur amount within the retention time interval of $MMAs^{III}$ in urine sample was minimum on the background of the chromatogram.

WedPo64. USE OF MICROCOLUMNS FOR SAMPLE PREPARATION PRIOR TO THE ANALYSIS OF ARSENIC SPECIES BY HPLC-ICP-MS.

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To understand the biogeochemical cycles of arsenic in the environment, it is necessary to analyse the arsenic species that are transported and mobilized in natural waters, such as rivers, lakes, aquifers, and coastal seawaters. In these types of samples, arsenic speciation is hampered by the extremely low concentrations of these species, and the interferences caused by the potentially high concentrations of group I and II metals and chloride on the chromatographic separation and the subsequent detection by ICP-MS.

To overcome these problems, the use of micro-columns prior to analysis to remove the matrix interferences and/or preconcentrate the target analytes has been investigated. Adjustment of the sample pH, and the choice of appropriate eluent solutions have enabled us to separate some arsenic species from chloride in seawater and preconcentrate other species in samples of lake water, thus reducing disturbance of the chromatography due to saturation of the column with chloride, and matrix interferences on the detection, due to the excessive presence of easily ionisable elements in seawater.

WedPo65. THE INSIGHT INTO BIOACCUMULATION OF PLATINUM BY *ARABIDOPSIS THALIANA* BY ICP AND ESI MS

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The determination and speciation of platinum in complex matrices, such as environmental or biological samples is still a difficult task due to its extremely low concentrations and significant matrix effects. Nevertheless, investigation of mobility and bioavailability of Pt is necessary, as allows to assess the phytotoxicity of the metal emitted from automobile catalysts.

The bioaccumulation of Pt by *Arabidopsis thaliana* cultivated hydroponically with nutrient solutions containing Pt(II) ions at elevated (50 µg L^{-1} and 500 µg L^{-1}) concentrations was studied by using inductively coupled plasma quadrupole mass spectrometry (ICP MS). The obtained results showed that most of the studied metal (6 mg of Pt per g of the sample) was accumulated in roots (86%), and only a small fraction was really metabolised and

transported to leaves (14%). The water soluble platinum species were extracted from roots and leaves and separated by SEC – ICP MS. It was found that in this fraction phytochelatins served as bioligands binding Pt(II) ions. The phytochelatins induction was verified using extracts of cadmium treated plant as a standard for RPLC – ESI MS method. Due to low sensitivity of ESI MS, formic acid was used instead of TFA to assure appropriate pH for phytochelatins separation, but also to increase S/N value (from 5 to 90).

WedPo66. SELENIUM-SPECIATION IN SOIL AND PLANT SAMPLES USING ANION-EXCHANGE CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Selenium (Se) plays an important role in environmental and health studies, having been reported to be both toxic and essential. In high concentrations Se is toxic to human, but its deficiency can cause many heart diseases and cancer. In proper amounts, Se gives protection from several heart diseases, prevents heavy metal toxic effects and has anti-carcinogenic activity.

The solubility of Se in most soils is rather low; therefore many agricultural areas of the world, including Hungary, produces crop plants and forage with low Se content. Our nutrition is deficient in selenium and it is a real risk for the human health. Besides, some people living in areas with high soil concentrations of selenium (e.g. western United States) might have higher exposure because of the natural selenium levels found locally, particularly if they consume crops primarily grown in that area. Metal industry workers, health service professionals, mechanics, and painters may be also exposed to higher levels of selenium.

Total selenium concentrations in soil range from 0.1 pg Se g^{-1} (parts of China and Finland) to 100 pg Se g^{-1} (Ireland and some states of the U.S.). The concentration depends on the Se content of the parent material, which often increases with depth closeness to the sea, presence of fine particles and organic matter in the soil. However, knowledge of the total selenium concentration is not sufficient to evaluate Se availability and toxicity. In soils, selenium generally seems to be present in inorganic forms, in the following oxidation states: selenides [Se(-II)], elemental Se [Se(O)], selenites [Se(IV)] and selenates [Se(VI)]. It is also possible to find organic selenium compounds.

Organic and inorganic species of Se have been separated and quantified using methods mostly based on liquid chromatography (LC) coupled with UV spectrophotometry (UV), hydride generation atomic fluorescence spectrometry (HG-AFS), ICP-AES and ICP-MS. Other methods developed for Se compound separation are based on capillary electrophoresis (CE) coupled with ICP-MS or electrospray ionization mass spectrometry (ESI-MS) and ion chromatography coupled with ICP-MS.

In this work, we studied Se compounds in plant and soil samples, which are originated from a Hungarian open-field experiment. In this experiment, the selenium was spread over the fields in the form of an inorganic salt (sodium selenite) in different and high doses (30, 90, 270, 810 kg ha^{-1}). The aim of the experiment was to study the effect of a high selenium contaminant; observe the moving and transform of contaminants in soil and plants and find a suitable method to degrade the pollution (high concentration of selenium) in soil.

The separation of Se compounds was carried out with an IC-ICP-MS system with collision cell technology (CCT). Water-extraction method was used to obtain the available selenium species from the samples.

We optimized the IC-ICP-MS system, studied the conversion of the selenium in soil and plant samples and the danger of the leaching effect in soil.

WedPo67. SPECIATION OF CELL LYSATE FOR SE AND CD SUPPLEMENTED BENIGN AND MALIGNANT PROSTATE TISSUE LINES, RWPE-1 AND RWPE-2.
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Considering the increase in incidence of prostate cancer, little effort has been given to understand the interactions of relevant elements associated with prostate cancer. Selenium has long been purported as a cancer chemopreventive agent for certain tumorous cancer types, which is supported by studies such as that of Clark et al. (J. Am. Med. Assoc. 1996, 276:1957-1963). They showed that taking a selenium supplement decreased the incidence of prostate cancer. Also it has been shown that selenium supplementation can induce apoptosis in cultured cancer cells (Bhamre et al, 2003, 54: 315-321). On the other hand, cadmium has no known physiologic functions and is suspected to be a carcinogen. This work aims to explore how selenium and cadmium are incorporated into both non-tumorigenic, RWPE-1, and tumorigenic, RWPE-2 cultured prostate cell lines with initial studies using size exclusion chromatography coupled to an inductively coupled plasma mass spectrometer. Total elemental uptakes and speciation data will be shown and discussed

WedPo68. ISOCRATIC HPLC SEPARATION OF INORGANIC, METHYL- AND DIMETHYLMERCURY WITH ICPMS AS ELEMENT SELECTIVE DETECTOR
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The toxicity, biochemical behaviour, and bioavailability of mercury are strongly dependent on the chemical form of the element. In contrast to inorganic mercury, organic mercury species are more dangerous because alkyl mercury compounds such as methyl- and dimethylmercury can rapidly pass through the placenta and blood brain barrier to irreversibly affect the central nervous system.
Inorganic and methylmercury are commonly detected in environmental samples. In contrast dimethylmercury has been found only in landfill gases and air. The high volatility of dimethylmercury could be an explanation for this.
In the present work we describe the development of a liquid chromatographic method for the determination of inorganic, methyl- and dimethylmercury with subsequent ICPMS detection. An Atlantis® (Waters, Vienna, Austria) reversed phase column with 60 mM ammonium acetate, 5% methanol, and 0.1% 2-mercaptoethanol at pH 6.8 was used for the separation of the mercury species. Depending on the sample introduction system employed, species dependent ICPMS response was observed. During the investigations we experienced decomposition of the dimethylmercury standard under certain conditions. In a systematic study the reasons for this instability were elucidated.
In the presentation the optimisation of the chromatographic conditions, the influence of the sample introduction system, as well as the reasons for the instability of dimethylmercury will be discussed.

WedPo69. SIZE FRACTIONATED CHARACTERISATION OF URBAN AEROSOLS: USE OF ELECTRIC LOW PRESSURE IMPACT COLLECTION WITH IC AND ICP-MS
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Awareness of air pollution has led to numerous studies on the chemical composition of ambient aerosols and origin of pollution sources. Atmospheric aerosols influence many atmospheric processes including cloud formation, visibility variation and solar radiation transfer, and are believed to represent a significant health concern to human. Ambient concentrations of particulate matter (PM) are systematically monitored and air quality standards set by European Union have emphasised the need for the characterisation of PM below 10 μm (PM_{10}) by mass. Such mass based measurements are easy to measure, but are unlikely to encompass all the factors relevant to adverse health effects. Recent toxicological studies have suggested that particulate number, size and composition may all play important roles in adverse health impacts. This paper will report on a state-of-the-art particulate measurement technique, the Dekati electrical low pressure impactor (ELPI), that is used for characterisation of fine and ultrafine particulates collected in an urban environment (Sheffield) in October, 2006. Size fractionated (13 size fractions: 7nm-10 μm) airborne particles were collected (n = 7) by the ELPI over a 7-day sampling period. The water-soluble inorganic ions (Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, K^+, Mg^{2+} and Na^+) were analysed by IC and the water-extractable metallic elements (Al, Ca, Cu, Fe, K, Mg, Na, Fe, Pb and Zn) were determined by ICP-MS. By assuming sodium exclusively originating from sea salt, the fractions of sea salt (ss) and non sea salt (nss) of the detected components were differentiated. The mode/modes of the particulate mass and the species mass distribution versus the stage size imply different sources of emission. Interspecies correlations give additional information on possible origin.

WedPo70. CHEMICAL SPECIATION OF NICKEL AND MANGANESE IN WELDING FUMES

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The chemical forms of the elements influence bioavailability and therefore influence uptake, toxicity and in some cases detoxification. For the discretion of welding fumes from a toxicological point of view determination of toxic metals species in welding fumes generated by different welding processes is a fundamental problem. As the carcinogen effect of hexavalent chromium has been observed early, the analytical techniques for the determination of chromium (Cr) species in welding fumes had been worked out in the 1980s, while chemical speciation of nickel (Ni) and manganese (Mn) have been less investigated.

Respirable and inhalable fractions of welding fumes were collected in welding plants, where different types of steels were welded with metal active gas (MAG) and metal inert gas (MIG) arc-welding techniques. Welding fumes were sampled with 'fixed point' and personal sampling strategies applying different sampling heads: Institute of Occupational Medicine (IOM) sampler and conical inhalable sampler (CIS) for the inhalable aerosol fraction and the Higgins-Dewell (HD) cyclone for the respirable aerosol fraction. The different species of Ni and Mn were separated with different extraction procedures, finally the "insoluble" components were digested applying microwave assisted digestion. The sample solutions were analysed by inductively coupled plasma quadrupole mass spectrometry (Q-ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES).

The findings suggest that the measurements of both the chemical composition and the size distribution of particles formed during a welding process have particular importance.

WedPo71. FOR THE DETERMINATION OF TRIHALOMETHANES IN DRINKING WATER BY GC-ICP-MS

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Compound-independent calibration (CIC) is a quantitative technique based in the theoretical advantage of some element specific detectors which provide an elemental response proportional to the concentration of an element and independent of the chemical structure of the molecules which contain this element. It means that the molecular structure does not affect the detector response and it should enable universal calibration. The main advantages of this approach are that compounds not available as standards can be quantified using readily available substances and the simplification of the calibration procedure (multi-element and multi-level calibrations can be generated from a single injection) especially when using an appropriated Internal Standard (IS). The coupling of Gas Chromatography to Inductively Coupled Plasma-Mass Spectrometry (GC-ICP-MS) provides an excellent tool for the application of CIC, due to the element specific detection of ICP-MS and the lower level of matrix interferences when the sample is introduced into the plasma as a dry aerosol.

Trihalomethanes (THMs) are the main disinfection-by-products formed during water chlorination by the reaction between natural organic matter and chlorine. New regulations have been developed for the control of those substances in drinking water due to the adverse effects they can cause on human beings, so new methodologies for the quantification of THMs are needed. In this work we demonstrate that the elemental response for chlorine and bromine is linear and independent of the molecular structure for THMs ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) and the selected IS ($CBrCl_3$) when using GC-ICP-MS. The optimum operational conditions for the GC separation and the ICP-MS detection are presented. The CIC methodology has been applied and validated for the determination of THMs in drinking water showing adequate analytical characteristics in application of the European Legislation.

WedPo72. IODINE SUPLEMENTATION IN PREGNANT AND BREAST-FEEDING WOMEN AS FOLLOWED BY ICP-MS

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Iodine is an essential trace element. The thyroid hormones, *thyrosine (T4)*) and triiodothyronine (T3) contain iodine playing a very important role in the cellular metabolism and growth and development processes of the organs, especially of the brain. The thyroid gland actively absorbs iodide ion from the blood to synthesize and release these hormones into the blood. Those actions are regulated by a second hormone secreted from the pituitary (1).

The key to good thyroid function is adequate, but not excessive, iodine intake. In adults intakes in the range 100-300 micrograms/day are desirable. However, iodine requirements are increased in pregnant and breastfeeding women. Iodine deficiency during pregnancy has been associated with irreversible mental retardation (1). So, daily prenatal supplement (e.g. providing 150 µg of iodine/day will help to ensure that pregnant and breastfeeding women consume sufficient iodine during these critical periods. The status of human iodine nutrition is reflected in urinary iodine.

Of the many methods available for determination of iodine in biological samples and foods, those most commonly used are based on kinetics, spectrophotometric measurements and

neutron activation. However, such determinations of iodine in biological samples is generally tedious and often insufficiently sensitive. Today inductively coupled plasma mass spectrometry (ICP-MS) has proved to be useful to determine iodine remplacing the clasical methods (2).
Thus, the objective of this work is to investigate KI supplementation in pregnant and breastfeeding women and its effect on the iodine deficiency symptoms in premature and full-term children. The study was carried out in the urine of born upon maturity and of premature children fed with "maternal" milk or children fed with "formula"milks. Also, analysis in milk and urine samples of the corresponding supplemented mothers. Total and speciation analysis of I vas carried out by ICP-MS and HPLC-ICP-MS, respectively. The results obtained on the speciation and total analysis of I in urine and milk samples will be discussed.

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WedPo73. EVALUATION OF ARSENIC LEVELS IN HAIR OF PEOPLE EXPOSED TO CONTAMINATED DRINKING WATER: ARSENIC LEVELS, SPECIATION AND RELATED HEALTH DISORDERS.

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Arsenic is widely distributed throughout the earth's crust. The element may be found in water, which has flowed though arsenic-rich rocks. Inorganic arsenic is considered as a toxic element and several health effects have been observed in population drinking arsenic rich water over long periods. Long term exposure to arsenic via drinking water causes different kinds of cancer (lung, kidney, skin, bladder…) as well as skin pigmentation changes and hiperkeration (1).
Human hair and nails is frequently used for monitoring the human long-time exposure to arsenic. The arsenic concentration in hair and nails is usually higher than in other tissues, which may be a result of the high content of keratin in them. Moreover, hair and nails are more advantageous than other tissues or fluids (blood, urine…) in terms of sample collection, storage, and transportation (2).
Inductively coupled plasma mass spectrometrometry (ICP-MS) seems to be the most suitable technique for the the analysis of arsenic due to its high sensitivity and selectivity and the possibility to measure in a wide range of concentrations.
With the aim of investigating the features of the ICP-MS for the analysis of arsenic, a comparative study between the analytical characteristics of a single ICP-MS, (ICP-MS(Q)) and an a collision cell ICP-MS (ICP-MS(ORC)) have been carried out for the determination of total As. The possible intoxication by As of population from an Asturian region (Spain) exposed to high levels of this element in drinking water (concentrations approximately fifty times higher than the legal levels) was evaluated as well as the level of a control population non exposed. The results observed for exposed people show that the As concentrations in the hair ranges from basal levels (0,01-0,4 ppm) to 5 ppm. This wide range of values found among the results is probably due to the difference in the intake of contaminated water by the people analyzed. Finally, As speciation and possible Se influence in hair, serum and urine from exposed and non-exposed people, as related to such disease states, was carried out.

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WedPo74. FAST AND ACCURATE DETERMINATION OF SULPHUR SPECIES IN PETROLEUM PRODUCTS BY SPECIES-SPECIFIC AND SPECIES-UNSPECIFIC GC/ICP-IDMS

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The legal limit for sulphur in gasoline and diesel fuel has been lowered constantly by the legislative during the last few years, which leads to the necessity of further improvements in the desulphurisation steps by refineries. To optimize these processes the concentration and nature of the different sulphur species as well as the whole sulphur content must be known. Routine analyses are therefore necessary which guarantee a fast and reliable determination of the total sulphur content as well as of the different sulphur species.

In the past, hyphenation of GC with ICP-MS combined with the isotope dilution analysis (ID) has demonstrated its reliability for accurate determinations of volatile elemental species. Using ^{34}S-labeled spikes of thiophene, dibenzothiophene and 4-methyldibenzothiophene species-specific isotope dilution analysis of these dominant species found in crude oil products were carried out.

A species-unspecific isotope dilution analysis, which includes the addition of a definitive gas flow of a ^{34}S-spike to the GC separated species, was also developed. Species-unspecific GC/ICP-IDMS allows the determination of all sulphur species even if the structure is unknown. As a consequence, the total sulphur concentration can be calculated from the mass flow chromatogram. Analysis of the Standard Reference Material BCR107 shows excellent agreement with the certified value as well as with the results received by the species-specific isotope dilution analysis. Other samples are also analysed and the results will be discussed.

WedPo75. ICP MS DETERMINATION OF COPPER AND ZINC IN NONFAT SOYBEAN POWDER – PARTICIPATION OF THE NATIONAL CENTER OF METROLOGY, BULGARIA IN THE CCQM P64 COMPARISON

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The Comité Consultatif pour la Quantité de Matiére (CCQM) was created by the CIPM (Comité International des Poids et Measures) in 1993 to coordinate the activities of national metrology laboratories in establishing traceability to the SI at the highest level and to stimulate understanding of the concept of uncertainty and the assignment of uncertainty statements in chemical measurements The CCQM working groups are involved in the identification, development and execution of a series of international comparisons that will establish the technical basis for the mutual recognition of measurement capabilities among the metrology organizations and some designated partners.

In most of the countries element concentration in food items are regularly measured. Important conclusions and decisions linked to the medical, health and commercial spheres derive from these measurement results that have to be of good quality. Since this is not always the case, the CCQM has launched different Pilot Studies and Key Comparisons on measurements in food matrices.

Besides toxic and harmful elements, essential elements in food are given attention because the lack of them can result in serious innutrition and potential diseases. Ca, Fe, Cu and Zn are essential micronutrients for human beings, especially for children – adequate mineral intake supports appropriate growth and development and helps to prevent diseases in future. The 64th CCQM Pilot Study was focused on the determination of Ca, Fe, Cu and Zn in soybean as it is

one kind of typical foodstuff and a raw material of many food products. Soybean is human's important source for the intake of protein and some essential elements.
In this work, the participation of the Section of Inorganic Analysis (National Center of Metrology, Bulgaria) in the 64th CCQM Pilot Study – determination of trace elements in nonfat soybean powder – will be presented. A detailed description of the microwave digestion method and the ICP MS conditions used will be provided. The results of Cu and Zn determination will be discussed. The uncertainty budget for the measurement of Cu and Zn in soybean powder by ICP MS with external calibration established following the CETAC-Eurachem Guide will be presented and discussed in details.

WedPo76. STUDIES ON THE COMPLEXATION OF LANTHANIDES WITH HUMIC ACIDS VIA CE-UV/VIS-ICP-MS

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Due to the upcoming challenge to handle and deposit highly radioactive nuclear waste, detailed knowledge about the behaviour of radiotoxic nuclides like Pu or Np isotopes under environmental conditions is absolutely necessary. Basic questions in this context are for example if these nuclides are mobilised or immobilised when getting in contact with enviromental substances, like clay minerals or humic substances (humic or fulvic acids), and following this, which species are most important for kinetic and thermodynamic reasons.
Several studies showed that one possible pathway for radiotoxic nuclides into environment is the complexation with humic acid and the resulting mobilization.
As a model system, several lanthanides have been used, as their behaviour in humic acid complexation is already known. Furthermore, their handling is much easier than the use of the radioactive actinides.
Capillary electrophoresis (CE) has been coupled to a Diode-Array-UV/Vis-detector and an ICP-MS. This system allowed to separate free and complexed lanthanides, and to detect the humic acid via its UV absorption and the lanthanides via ICP-MS, resp.. This methodology enables the estimation of the related logß-values which were finally compared to reference data.

WedPo77. A ROBUST METHOD FOR DETERMINATION OF PLATINUM GROUP ELEMENTS CONCENTRATIONS (PGE) IN VEGETATION SAMPLES.

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A robust method has been developed for analysis of platinum group elements (PGE) in vegetation samples. Microwave was applied for sample digestion. Most of the possible interferences cannot be resolved by a high-resolution mode of HR-ICPMS. A cation exchange interference removal protocol was employed to remove the elements contributing to isobaric and polyatomic interference to PGE. The quantitative analysis was carried out by standard addition calibration using a Finnigan Mat Element 2 HR-ICPMS detection system taking advantage of highly sensitive low-resolution mode. The method was validated on NIST SRM 1575a spiked with 1ng g^{-1} PGE (Ru, Rh, Pd, Ir, and Pt) standard solutions. Recovery of 80- 90% was recorded. The results obtained for different type of vegetation samples will be presented.

To increase the recovery of analysis and to reduce the sample preparation and instrumental time isotope dilution analysis was employed (ID HR-ICPMS). Samples were

spiked with isotope enriched PGE standards. Microwave digestion, matrix removal by anion exchange and quantification by HR-ICP MS were employed. The method was also validated on NIST SRM 1575a spiked with 1ng g^{-1} PGE (Ru, Pd, Ir, and Pt) standard solutions. Recovery of 90-100% was recorded.

WedPo78. SPECIFIC AND QUANTITATIVE TITANIUM SPECIATION STUDIES IN HUMAN SERUM BY HPLC-ICP-MS AND POST-COLUMN ISOTOPE DILUTION

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Due to its excellent properties, titanium is becoming increasingly used in many different fields. Among them, in medicine, this metal is frequently used in surgical and dental implants manufacture. There is also an increasing interest in the design and use of titanium complexes as anticancer drugs. However, little is known about its biological chemistry. Recently, some studies have stated Ti(IV) binds to human transferrin (Tf), even stronger than Fe(III) does.
Currently, most of the studies about the binding of Ti(IV) to Tf have been carried out by non-specific molecular techniques (UV) and only in aqueous standards. The coupling of HPLC to ICP-MS allows the specific and quantitative detection of Ti and other elements simultaneously (Fe, P, S, etc.) opening the door to carry out Ti speciation studies directly in biological fluids. This information would be invaluable to advance in the knowledge of Ti biochemistry.
In this work, experimental conditions to achieve complete Ti to Tf binding were optimised. Size Exclusion Chromatography was selected in order to maintain the weak Ti-Tf interaction during speciation analysis under physiological conditions in real human serum samples. Quantitative information was obtained by post-column isotope dilution analysis.

WedPo79. ARSENIC SPECIATION WITH NANO-HPLC-PLASMA MASS SPECTROMETRY

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A nano-high performance liquid chromatography-inductively coupled plasma mass spectrometry (nano-HPLC-ICPMS) method is developed, using a demountable direct injection high efficiency nebulizer (d-DIHEN), to reduce sample and mobile phase consumption, minimize organic waste generation, reduce analysis time, and enhance separation efficiency. A HPLC column (50 mm x 0.3 mm i.d.), packed with 3.5 µm C_{18} material, is explored for chromatographic separation of five arsenic species present in the environment naturally or introduced as a pollutant: sodium (meta) arsenite (AsIII), arsenic acid (AsV), dismethylarsenic acid (DMA), disodium methylarsenate (MA), and p-arsenilic acid (p-ASA). A fast chromatographic separation of five arsenic species is achieved in less than 12 minutes at a solution flow rate of 0.9 µL min^{-1} using a 50-nL sample injection. HPLC-ICPMS interface provides well defined flow injection profiles at various concentrations, giving a correlation coefficient of 0.999 for each individual arsenic species calibration curve. Precision values for peak height and area of five arsenic species range from 0.5 to 6.5 %RSD and absolute detection limits are within 0.4 to 5.4 pg arsenic, which are comparable to previously reported data at higher solution uptake rates (20 □L/min to 1 mL/min) and larger sample injection volumes (20 – 100 µL).

WedPo80. ROUTINE SPECIATED ARSENIC ANALYSIS IN URINE, USING HPLC-ICP-CR/C-MS

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Arsenic speciation is increasingly required in urine to evaluate the potential toxic effects and for the assessment of dietary exposure to the various forms of this element. The coupling of HPLC with ICPMS is the most suitable technique for routine monitoring of As species in urine, due to its wide availability, simplicity of operation and rapid analysis.

For routine purposes, separation should be fast (below 15 minutes), sensitive (quantification limits below 0.5ppb) and must allow the separation of all the toxic inorganic and organic forms of As in urine - AsIII, AsV, MMA, DMA - from the non toxic AsB..
Work has been performed on an Agilent 7500ce ICPMS equipped with an octopole collision/reaction cell, which may be necessary to resolve residual Cl-based overlaps on As with some separations.
Different separations and mobile phases have been tested. Using a newly developed column and a mobile phase composed of 2mM phosphate buffer solution, 10mM CH_3COONa, 3mM $NaNO_3$, 1% EtOH, adjusted to pH=11, the desired separation can be achieved in 12 min using an isocratic elution and injecting 5µl of undiluted urine. Moreover, the elimination of the main interferent of As, which is ArCl, can be achieved either by separating the elution of Cl from As species or eliminating ArCl using octopole reaction system. Detection limits vary between 0.035 and 0.1µg/L depending on the species. Repeatability of peak area and retention time on 15 urine samples ranges respectively between 0.95 and 1.8% and between 0.08 and 0.11%. The method has been validated analyzing NIES certified reference material no.18.
The developed method offers new possibilities for routine monitoring of arsenic speciation in urine.