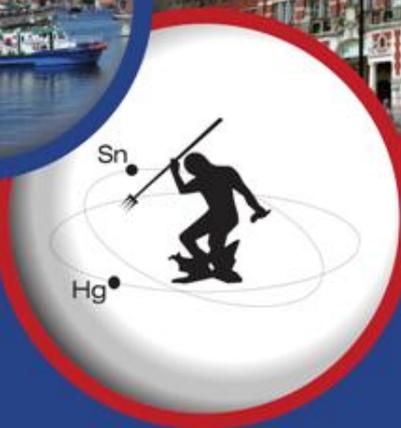




4-7 IX 2016

# TraceSpec 2016

Sn 15th Workshop  
on Progress in Trace Metal  
Speciation for Environmental  
Analytical Chemistry



Book of abstracts

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## **TraceSpec 2016**

The 15<sup>th</sup> Workshop on Progress in Trace Metal Speciation for Environmental Analytical Chemistry in September 2016 takes place at the Technical University of Gdansk (Poland). This meeting as reflected by the number 15 stands for a long tradition and is one of the well-known conferences organized by members of the International Association of Environmental Analytical Chemistry. The topic is of paramount importance as the toxicological and ecotoxicological relevance of the elements strongly depends on their compounds and their metabolization. Further, the determination of compounds is not obvious, as many methods are well element- but much less species-specific. The science of isolating the compounds and then determining them is true analytical science at the frontier level. Here, detailed knowledge on separation sciences as well as on physicochemical determination methods is asked for, which makes the field of high actuality and of high scientific value. Therefore the TraceSpec is an excellent forum for exchange of methodological knowledge and strategies followed in problem-solving at the hand of challenging tasks in real life. The conference is strongly wished to be successful in contributing to the mission stated.

**Prof. Dr. José A.C. Broekaert**

President of the  
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# **SESSION 1**

QC / QA, reference materials, spectroscopic standards and chemometric data handling

Nutrient-metal interactions

## **THE STRATEGIC IMPORTANCE OF HAVING ROBUST AND INNOVATIVE METHODS AND TECHNOLOGIES FOR ENVIRONMENTAL OBSERVATIONS TO SUPPORT THE IMPLEMENTATION OF POLICY**

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Recently, several International Programs and Conventions such as the GMOS ([www.gmos.eu](http://www.gmos.eu)) supporting the Minamata Convention, the Global Monitoring Plan (GMP) (<http://www.pops-gmp.org/>) supporting the Stockholm Convention, the World Meteorological Organization's Global Atmosphere Watch (GAW), the European Monitoring and Evaluation Programme (EMEP) supporting the CLRTAP, and various Research Infrastructure initiatives of the European Commission have made substantial efforts to establish data centres and quality control programs to enhance integration of environmental quality monitoring (i.e., atmospheric composition, water quality) from different national and regional networks, and to establish observational sites in under-sampled remote regions around the world. One of the limiting factors for the economic sustainability of long-term monitoring programmes is represented by the investment and running cost of these observational infrastructures. Specifically a number of EU programmes on air quality and cycling of persistent pollutants at different spatial and temporal scales have highlighted the need to develop more advanced monitoring systems based on nanotechnology in order to lower the management costs of these infrastructures. As part of the Group on Earth Observation (GEO)'s activities aiming to build GEOSS, a significant effort is addressed to develop global scale monitoring systems in order to support the validation of models and their use in the evaluation of effectiveness of measures undertaken by nations in the implementation of European and international conventions on environmental quality (i.e., Minamata Convention, CLRTAP, Stockholm Convention, Air Quality Directives). The aim of this lecture is to highlight selected success stories in developing advanced global observing systems for persistent pollutants and the need to develop advanced sensors and sensors platforms as well as fully integrated interoperable systems for data quality control and management.

**ARSENIC AND TIN SPECIATION IN CERTIFIED  
REFERENCE MATERIALS AT THE NIST-CHARLESTON  
HOLLINGS MARINE LABORATORY**

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In recent years, major efforts have been devoted to developing methods for arsenic and tin speciation analyses as the toxicity and biological effects of these elements are known to be species dependent. Therefore, reliable measurements pertaining to individual compounds are required to accurately determine the ecological impact and health risks associated with arsenic and tin exposure. Although sensitive and robust analytical methodologies (*i.e.* LC/GC-ICP-MS) have been developed, the lack of certified reference materials (CRMs) with certified mass fraction values for individual species has been a major limiting factor in method development and validation of routine speciation analyses. Here we detail our efforts in an attempt to certify individual arsenic and organotin species in several candidate CRMs (kelp, apple juice, seafood, etc.).

## **SHORT-TERM EFFECTS OF WOOD ASH AND NITROGEN FERTILISATION ON TRACE ELEMENT CONCENTRATIONS IN HUMUS IN A NORWAY SPRUCE FOREST**

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In a field experiment on effects of wood ash return and nitrogen fertilisation in Norway spruce forest in Norway, concentrations of trace elements in 1M NH<sub>4</sub>NO<sub>3</sub> humus extracts (M1, assumed to approximate plant-available concentrations) were compared with concentrations after HNO<sub>3</sub>/HClO<sub>4</sub> (5:1 v/v) digestion of humus samples (M2). Trace element concentrations in humus increased significantly after ash treatment for Cr, Cu, Mn and Ni with M2, and for Cr and Mn with M1. Ni, Pb and Zn decreased after ash treatment for M1. No significant effect of ash treatment was found for As, Cd, Co, Mo, Pb, V and Zn (M2) or for Co, Mo and V (M1). Nitrogen fertilisation without ash treatment had no significant effect on concentrations of trace elements with either method. Results show that evaluation of the effects of wood ash return to the forest ecosystem depend on the method used.

### **Acknowledgements:**

This work was funded by the Research Council of Norway through the Askeverdi project.

## **METAL BASED COMPLEXES IN FUNCTIONAL FOOD AS A KEY TO MORE EFFICIENT METAL BIOACCESSIBILITY**

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Functional food have a component incorporated into to give a specific medical or physiological benefit, other than a purely nutritional effect [1]. Presence of metal complexes in functional food lead to more effective pharmacological activities and better availability of minerals as well as reduces their overloading in body.

Despite large number of studies focused on extraction of bioactive compounds from plant material, still little is known about metal complexes with bioligands present in plants. Based on the lack of information, the aim of study was concerned on the optimization of extraction procedure of selected metal complexes with bioligands from various kind of functional food [2, 3]. Efficient extraction allows to get the knowledge about kind of bioligands complexing metals To obtain the information about bioavailability of these elements, *in vitro* bioavailability test was performed by application the two-step model simulating gastric (pepsin) and intestinal (pancreatin) digestion.

After the selection of the most suitable solvent, effects of several extraction parameters on the extraction efficiency of metals were studied. The determination of total and extractable amount of metals in various foodstuffs was carried out by stand-alone ICP MS. In addition, a complementary analysis of extracted metal complexes was performed using SEC-ICP MS technique. The  $\mu$ -HPLC ESI MS/MS method helps to identify bioligands responsible for the complexation of metals, thereby leading to better bioavailability of metal to the human body.

Evaluation of the extracted amount of element, not only its total concentration, is highly important due to the fact, that only a part from total content of metal is absorbed by the human body.

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## **SESSION 2**

Speciation analysis in biological tissues  
and body fluids

## ARSENIC SPECIATION IN MAMMALIAN TISSUES BECOMES MORE COMPLEX THAN EVER

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Arsenic forms more than 100 naturally occurring compounds, which alter the mobility and toxicity of arsenic. More than half of these compounds are lipophilic. Whereas most water-soluble organoarsenic compounds have been identified, show mass balance approaches on the lipophilic fraction that in tissues of marine organisms a large proportion of arsenic has not been assigned so far. Selective extraction of arsenicals with mass balance approaches shows also that a fraction of organoarsenicals are unstable during sample preparation procedures.

It becomes apparent that the identification of these complex mixtures of organoarsenicals not only needs sophisticated analytical strategies which based on the dual hyphenated techniques such as HPLC-ICP-MS/ESI-MS but also a series of chemical derivatisation methods.

In this lecture the challenges of the analysis of organoarsenicals will be illustrated by showing achievements and shortcomings of the current studies on the analysis of stranded long-finned pilot whales.

### **Acknowledgements:**

JFK is funded by the College of Physical Sciences.

## MONITORING OF TRANSFORMATIONS OF CYTOTOXIC METALLO-COMPLEXES BY ELECTROCHEMICAL REACTION CHAMBER COUPLED TO ESI MS/MS

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Metallocomplexes are increasingly important in the search for more effective anticancer remedies. As hybrids of inorganic and organic components, metal complexes tend to assemble the advantages of inorganic and organic drugs, such as treating a broad range of tumors and a selective mode of action. To explore the mechanism of the drug metabolism, its behavior in simulated physiological conditions should be examined. Studies carried out *in vivo* or even *in vitro* can be economically and time consuming; especially that oxidation or reduction can be induced by addition of specific reactive species which may interfere signals monitored by molecule specific mass spectrometers. Another method – without interfering chemical composition - is application of electrochemical reaction chamber Antec's Roxy Reactor Cell (EC) coupled to Electrospray Mass Spectrometer, which allows to obtain redox reaction at varied potentials and identification of obtained species.

The method was applied to study redox transformations of three selected metal complexes: indazolium trans-[tetrachlorobis(1H-indazole)ruthenate(III)], auranofin (2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranosato-S-(triethyl-phosphine) gold(I)) and Au(III)bipyc ([bipydmb-H]Au(OH))[PF<sub>6</sub>] (where bipydmb-H = deprotonated 6-(1,1-dimethylbenzyl)-2,2'-bipyridine)), which are now appreciably progressing in pharmacological studies.

Structures of metallo-species obtained at the varied redox potential applied in EC have been studied by ESI MS. The metallodrug analysis was performed in a buffered solution of ammonium formate at the physiological pH of blood and at pH of gastric juice (oral administration of drugs). Auranofin was found to be activated by loss of the glucose moieties, ruthenium complex by reduction of Ru(III) to Ru(II) and Au(III) complex by oxidation of pyridines. Obtained results were validated by identification of the same active forms of metallo-complexes in human serum or cancer cells cytosol and are in agreement with present state of knowledge. To sum up, electrochemical chamber is an interesting technique for preliminary studies of metallocomplexes metabolism.

### **Acknowledgements:**

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## HYDRIDE GENERATION AND ATOMIC FLUORESCENCE SPECTROMETRY AS A SENSITIVE TOOL FOR SPECIATION ANALYSIS OF ARSENIC

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Atomic fluorescence spectrometry (AFS) coupled to hydride generation (HG) can provide analytical performance comparable to that of inductively coupled plasma mass spectrometry at substantially lower costs and can be assembled from commercially available parts. These parts include just an element specific light source with high radiation intensity, a detector - photomultiplier, lenses and an atomizer. Such a simple but extremely sensitive instrument was developed in our laboratory recently [1].

The recent achievements in the field of speciation analysis of toxicologically relevant As species using this AFS instrument will be the topic of this contribution. Various approaches to HG were investigated. Firstly, the selective HG from TRIS buffer medium coupled to cryotrapping (HG-CT) will be presented. This extremely sensitive method enabled determination of toxicologically relevant arsenic species even at ppt level in microsamples of exfoliated bladder epithelial cells isolated from human urine [1]. Secondly, we dealt with postcolumn HG, *i.e.* after high performance liquid chromatography (HPLC). The optimum conditions of HG were found and the efficiency of formation of individual arsanes reached 100%. The accuracy of the HPLC-HG-AFS method was demonstrated by the comparative analyses of human urine samples with HG-CT-AFS [2]. Finally, the serious demethylation of individual As species in the course of HG from mineral acids medium will be noted. The demethylation was investigated in detail [3]. This artefact can substantially impair the results of speciation analysis based on CT or gas chromatography. Suggestions to avoid this artefact will be made.

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### Acknowledgements:

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## **KEY ISSUES OF SAMPLE PRETREATMENT FOR TRACE SPECIATION ANALYSIS**

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Speciation analysis is already a challenge, and speciation analysis at trace levels is even more difficult. Procedures applied for speciation analysis must ensure low limits of detection as well as high selectivity, especially when the concentration of other sample compounds, potentially interfering, is much higher than the concentration of the analyte. Very often, there is no other choice but to use separation and/or preconcentration techniques. Methods applied for speciation studies should ensure isolation of the analyte from sample matrix without any changes of the original speciation and with highest possible efficiency. The lower is the concentration of the analyte, the higher is the uncertainty of the results, because some additional steps have to be included in the analytical procedure. Deep interference in sample composition results in changes of the oxidation states and chemical compounds formed by the element of interest. In case of water, soil or tissues the risk of changes in chemical speciation is created even by the sampling, not to mention chemical modifications or sample storage. Most published studies regarding speciation analysis were focused mainly on methods of separation and detection of the analytes. Considering how fragile are the equilibria between speciation forms, the best solution would be to determine speciation directly in the analyzed object, using techniques which can differentiate between oxidation states. In general, only a few techniques allow performing nondestructive speciation analysis of solids or water samples. However, even the results obtained with the most reliable methods and procedures mean nothing if the sample does not represent the investigated object or the speciation has changed during the sampling step. Any chemical or physical changes have an influence on the speciation. For this reason all steps of analytical procedures (sampling, transport, storage, conservation), especially in case of procedures meant for trace speciation analysis, have to be very carefully studied for potential changes they may cause in sample's properties. It seems impossible that the speciation does not change during these critical stages of every trace analysis, but we have to try and create procedures that would prevent the changes as much as possible.

## **ON-LINE ISOTOPIC DILUTION ANALYSIS AS A POWERFUL TOOL IN SPECIATION ANALYSIS AND BIOIMAGING OF PLATINUM**

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Platinum-based anti-cancer drugs play an important role in modern chemotherapy. Cisplatin [cis-diamminedichloroplatinum(II)] is the most commonly applied compound due to its unmatched curing chances for certain types of cancer like testicular, ovarian, bladder and lung cancer. However, patients treated with Cisplatin during chemotherapy often suffer from severe side effects as neurotoxicity, ototoxicity, hair loss, infertility and nephrotoxicity which is the dose-limiting factor. The visualization of elemental distributions in biological tissues may provide valuable information about biological and medical correlations, thus the need for spatially resolved and quantitative information is increasing.

Often, trace concentrations are encountered and therefore, sensitive and reliable quantification methods for laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) are required.

Quantification via external calibration is the most common quantification strategy, which includes matrix matching of the standards. However, the preparation of matrix-matched standards is laborious and a homogeneous distribution of the spiked element is not generally accessible. Furthermore a similar behaviour of the standard tissue and the specimen is difficult to achieve.

An alternative powerful quantification approach is isotopic dilution analysis (IDA). IDA is an absolute quantification method, which is generally traceable to SI units and less affected by drift effects and statistical errors compared to external calibration. Generally, the analyte and the corresponding isotopically enriched spike can be mixed *off-line* or *on-line*, where the achievement of the isotopic equilibrium is essential.

Today, the species-specific and species-unspecific spiking modes are important methodologies in modern speciation analysis. However, the use of IDA is not limited to just high performance liquid chromatography (HPLC)-based systems and can be expanded to an *on-line* approach for LA-ICP-MS imaging. Critical parameters are e.g. the achievement of the isotopic equilibrium, measurement of the mass flows of the sample and the isotopically enriched spike and the amount of introduced material. Within this work, the combination of *on-line* IDA and bioimaging based on LA-ICP-MS is presented.

Therefore, the method was applied to rat kidney samples from Cisplatin perfusion experiments. The results show a high accordance with the conventional external calibration approach and demonstrate the applicability of the developed *on-line* IDA method for elemental bioimaging.

## **ELEMENT BIOIMAGING AND SPECIATION ANALYSIS FOR THE INVESTIGATION OF WILSON'S DISEASE**

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Wilson's disease (WD) is a rare genetic disorder of the copper metabolism, causing the accumulation of copper in different organs, including the liver, the central nervous system and cornea. This way, WD initiates manifold hepatic, neurological or psychiatric symptoms. To learn about the elemental distribution and present species in WD, liver samples were analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), micro X-ray fluorescence ( $\mu$ XRF) and X-ray absorption near edge structure spectroscopy (XANES).

Within this work, LA-ICP-MS was applied to study the distribution of copper and iron in human liver samples, which were collected by a liver biopsy of WD and control patients within a medical investigation. The analysis by LA-ICP-MS was performed with a 213 nm Nd:YAG laser using a spatial resolution of 10  $\mu$ m and a scan rate of 20  $\mu$ m/s. In a next step, copper and iron were quantified by LA-ICP-MS using homemade matrix-matched standards made of gelatin. Results showed an inhomogeneous copper and iron distribution in human liver with hotspots up to several thousand micrograms per gram liver within the hepatocytes.

Additionally, results for the elemental distribution in WD were validated by means of synchrotron radiation-based  $\mu$ XRF with a beam size of 4  $\mu$ m at the BAMline at BESSYII (Helmholtz-Zentrum Berlin). Furthermore, XANES was performed to identify the present oxidation states of copper in WD, indicating a mixture of copper(I) and copper(II) within the liver tissue.

In the contemporary medicine, rhodanine staining is routinely used to determine the copper distribution in liver tissues. Nevertheless, this method does not provide results with a high sensitivity in comparison to LA-ICP-MS. Therefore, the presented LA-ICP-MS method offers a new possible diagnostic tool. These results may also contribute to a better understanding of Wilson's disease and its development.

## ARSENIC SPECIES IN HUMAN MILK

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The toxicity of arsenic depends on its chemical form. Inorganic arsenic is highly toxic to humans whereas organic arsenic compounds are generally considered as much less toxic. Risk assessment of arsenic exposure must therefore consider the type of arsenic compound, but few studies exist so far. Furthermore, risk assessments must include studies on the most vulnerable within a population such as newborns and infants, thus estimation of these species in human milk is needed. Such assessments require sensitive and robust methods for the determination of arsenic species. Herein we report a method for the determination of arsenic species at low concentrations in human milk by high performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICPMS). The method incorporates a protein precipitation step with trifluoroacetic acid followed by addition of an organic solvent for phase separation and fractionation of arsenic species. The aqueous phase was subjected to cation-exchange and anion-exchange chromatography with aqueous pyridine and ammonium bicarbonate buffer solutions as mobile phases, respectively. For method validation, human milk and an infant milk formula were spiked with defined amounts of dimethylarsinate, methylarsonate, arsenate and arsenobetaine. The proposed method was applied to human milk samples from the NoMIC study conducted by the Norwegian Institute of Public Health. We report total arsenic and arsenic speciation data obtained in this study.

## **SESSION 3**

Total element measurements, down to ultra-trace levels in all sample types using element-specific techniques

**THE BIOLOGICAL SYSTEM OF ELEMENTS  
SPECIATION AND ULTRATRACE ANALYSIS OF CHEMICAL  
ELEMENTS ARE A STRONG MUST FOR THE FUTURE.  
BENEFICIAL, ESSENTIAL AND TOXICOLOGICAL EFFECTS  
OF CHEMICAL ELEMENTS REVISITED**

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For essentiality patterns (of specific plant species) via the Biological System of the Elements (BSE) three parameters are especially important:

1. The interelement relationships of single elements within an individual organism expressed as a linear correlation coefficient,
2. the physiological function paying attention to evolutionary development during the emergence of organic life from the inorganic environment, and
3. the uptake form of individual elements and their compounds by the living organism.

To fulfil above given requirements speciation and ultratrace analysis of chemical elements are a strong must for the future.

From the resulting configuration of the elements in the Biological System of the Elements it can be expected that in the future elements as Ba, Ge, Li, Sr, Te, and others will be classified as physiologically essential or beneficial at least, whereas elements as Tl, Pb, and Hg will continue to exercise exclusively toxicological functions on living systems in elevated concentrations and certain forms of bonding.

Stoichiometric Network Analysis (SNA) explicitly deals with which principal modes of dynamics may be open to such autocatalytic systems in various circumstances. This allows to us consider and analyze aspects of bioinorganic chemistry of metalloproteins including essentiality versus toxicity of element (speciation forms), testifying their roles as building blocks or controlling entities within or connected to autocatalytic feedback loops. The SNA theorems are used to produce a system of non-equations describing the possible or unlikely autocatalytic behaviour of certain metals within the framework of biology. This is meant to enable detailed statements and even predictions whether a certain element may be essential or beneficial to physiology, and, if so, whether there are certain ranges of redox potential or binding forms such as complexes or biomethylation products which might enable such behaviour.

Some „exotic“ element behaviour in living organisms as for Li (and others) will be presented here and a further research proposal for the future developed.

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## INTRODUCING ‘NOTICE’ (COST ACTION TD1407): NETWORK ON TECHNOLOGY-CRITICAL ELEMENTS

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Critical elements are those which are expected to play an important role in high-technology, energy supply, green and defence applications, but their supply and demand is unbalanced. Some elements with promising technology applications have been denominated as Technology-Critical Elements (TECs), and usually include Ga, Ge, In, Nb, Ta, Te, Tl, Pt group elements and most of the rare earth elements.

The European Cooperation in Science and Technology programme (COST) is the longest EU programme for cooperation in science and technology. This talk introduces a new COST action focused on the study of TCEs, which was launched last year (NOTICE, COST action TD1407). The specific aim of the action is to create a network of scientists working and interested on Technology-Critical Elements from an environmental perspective to potential human health threats, with the aim of defining the current state of knowledge and gaps, proposing priority research lines/activities, and acting as a platform for new collaborations and joint research projects.

The action will run until April 2019, counts with the participation of 22 countries and is organized in four working groups: WG1 Analysis and inter-calibration, WG2 Environmental impact and cycling, WG3 Human exposure and (eco)toxicology and WG4 Training and capacity building. Update information of the action can be followed at [www.costnotice.net](http://www.costnotice.net).

## **SOLID-PHASE EXTRACTION BASED ON MAGNETIC CORE-SHELL SILICA NANOPARTICLES COUPLED WITH AAS FOR THE DETERMINATION OF TRACE METALS IN AQUEOUS SOLUTION**

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In recent years, the number of research groups involved in magnetic nanoparticles has increased exponentially. These particles have many important applications especially in engineering nanodevices, in the biomedical industry, and also useful for environmental processes, analyses, catalysis, etc. Among the new explored magnetic particles magnetite( $\text{Fe}_3\text{O}_4$ ) has one of the most potential. In this work, a novel magnetic nanocomposites with immobilized N-ethylenediaminetriacetate groups was developed for solid phase extraction heavy metals from aqueous solution. The magnetite nanoparticles were prepared by two techniques: co-precipitation iron(II) and iron(III) salts and hydrothermal treatment. The superparamagnetic nanoparticles were coated with a thin silica oxide layer was synthesized by means sol-gel methods.

The morphology and structure of obtained solids were investigated by TEM. The TEM image of  $\text{Fe}_3\text{O}_4$  nanoparticles prepared in aqueous medium reveals a size distribution in the range of  $6.0 \pm 2.0$  nm and silica shell about 2 nm. The XPS spectrum of as-synthesized  $\text{Fe}_3\text{O}_4$  nanoparticles shows strong bands due to iron at 724,4 eV ( $\text{Fe}2p_{1/2}$ ), 709,9 eV ( $\text{Fe}2p_{3/2}$ ). The Fe/O atomic ratio for particles prepared by co-precipitation methods is 0,73, for hydrothermal – 0,74 (for reference  $\text{Fe}_3\text{O}_4$  is 0,75). The FTIR spectra of samples has sharp absorption band at 1080, 960 and 803  $\text{cm}^{-1}$  were assigned to the characteristic vibration of  $\text{SiO}_2$ , which indicates that the silica has successfully coated surface of nanocrystallites. For these nanocomposites saturated magnetization value was  $\sim 82$  emu/g. The elemental analysis shows the presence of nitrogen after the reaction with N-ethylenediaminetriacetate-silanes which corroborates the attachment of the chelating moieties to the surface of the nanocomposites. The concentration of chelating groups was found as 0,32 mmol/g.

The potential in adsorbent properties of these nanocomposites for Fe(III), Cu(II), Pb(II), Cd(II), Zn(II) in batch approach was used. The adsorption capacity was evaluated using AAS. It was observed that magnetic chelating nanocomposites retained all the studied metals with efficiency (90-99 %).

### **Acknowledgements:**

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**CONCENTRATION OF TRACE ELEMENTS IN THE MUD  
SPILLED BY SAMARCO'S DAM BURST  
AT THE SUB-DISTRICT OF BENTO RODRIGUES  
(MARIANA, MG, BRAZIL)**

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Bento Rodrigues is a sub-district from Mariana which belongs to the “ferriferous quadrangle” located in Minas Gerais, where minerals such as gold, manganese and iron have been exploited by the mining companies for decades. On November 5<sup>th</sup>, 2015, the dam called Fundão from Samarco mining company burst, causing one of the biggest world’s environmental disasters ever registered. Between 50-60 million m<sup>3</sup> of mud (mining waste) were quickly released causing numerous immediate impacts such as deaths; destruction of agricultural areas; mortality of aquatic biota and terrestrial fauna; interruption of water supply, among other problems. On November 28<sup>th</sup>, 2015, samples of mud, soil and water were collected in the impacted area and surroundings. 40 samples (mud, soil, and water) were investigated regarding trace elements determination, SEM/EDS microscopy, and extraction procedures. Water samples, tap and river surface water, were analyzed by ICP-MS showing elemental concentration in compliance with Brazilian and WHO standards for water quality. In addition, water mud-containing presented Fe and Mn concentrations approximately 4-fold higher than the Maximum Limits for water bodies, according to Brazilian laws. Mud samples were analyzed by SEM/EDS microscopy, Field-portable X-ray Fluorescence providing some semi-quantitative data from major constituents (O, Fe, Si, Al, C, P, Br, Cd, Co, Ni, Cu, Zn, and Hf) and particle characterization (size 1-200 µm). An accurate analysis of mud and soil samples was performed by ICP-MS after acid extraction and analysis. The soil samples were divided into two groups to compare natural soils and mud. Some samples were subjected to Single Extraction Procedures which suggested Ba, Pb, As, Sr, Fe, Mn and Al have high potential mobilization from mud to water. The present study provides preliminary information in order to collaborate in the development of future work which aimed at the affected area project monitoring and risk assessment.

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## SHIMADZU INNOVATIVE SOLUTIONS IN ELEMENTAL ANALYSIS

### Sebastian Szopa

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Shimadzu throughout past several years actively developed a number of analytical techniques, among them ICP-OES and ICP-MS. The result of these works is a new generation of spectrometers, ICPMS-2030 with mass detector (MS) and the ICPE-9800 with optical detection (OES).

ICPE-9800 Series of simultaneous ICP atomic emission spectrometers are next-generation systems that offer the superior accuracy necessary for simultaneous and quick analysis of multiple elements regardless of their concentration levels. The new ICP spectrometers feature Shimadzu's mini-torch system and Eco mode, which greatly reduce argon gas consumption and power consumption during measurement and under standby conditions. Furthermore, performance is ensured even with argon gas of 99.95 % purity, and not the 99.999 % purer gas generally used for ICP systems, what further reduces operating costs. In addition, a vertically-oriented torch reduces memory effects and shortens rinse time. The adoption of this torch and vacuum spectrometer enables highly stable, high-throughput analysis. The user-friendly software is supplied with spectrometers. Furthermore, the systems reduce analysis costs while providing the highest performance levels in the industry. ICPE-9800 Series systems represent the ultimate in ICP atomic emission spectrometry for environmental, pharmaceutical, food, chemical, metal, and other fields.

Shimadzu's Inductively Coupled Plasma Mass Spectrometer ICPMS-2030 supports an extensive range of analysis from trace levels to high concentrations. The optimized internal structure including the newly-developed collision cell enables analysis at sub-ppb level sensitivity by minimized spectral interference and improved transmission efficiency of atomic ions, because of these the precise quantitation results in elemental impurity analysis become more reliable. The ICPMS-2030 is the first ICP-MS for the industry which includes assistant functions for method developing and post-run diagnostics performing. The Development Assistant automatically selects the optimal mass and internal standard for the target elements and suggests concentration ranges for calibration curves, what allows any user for easy developing of reliable methods. The Diagnosis Assistant identifies the presence or absence of mass interference based on qualitative analysis to quickly generate reliable results.

# **SESSION 4**

Young scientists session  
(participants under 35 years old)

## **ELECTROSPRAY MS: (R)EVOLUTION IN SPECIATION ANALYSIS**

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During the last two decades ICP MS has taken a prominent place as detection technique in a number of coupled techniques making element speciation analysis possible. It became virtually a working horse of the scientific community seeking for species-specific information in a number of fields including environmental chemistry, nutrition and life-sciences.

The progress in electrospray ionisation Fourier transform mass spectrometry (FT MS) using electrostatic orbital trap (Orbitrap) and ion cyclotron resonance offers unparalleled resolution, accuracy of mass measurement, and intrascan dynamic range for the analysis of biomolecules. The combination of such systems with a linear ion trap allows additional experiments towards structural analysis. The coupling of HPLC – Orbitrap allows the detection of the heteroatom-isotopic pattern in mass spectra down to the intrascan abundance of 0.001 with the low- and sub-ppm mass accuracy regardless of the concentration. The species with intrascan abundance of at least 0.005 produced a cascade of product ion mass spectra to at least MS<sup>4</sup> with the preservation of the isotopic pattern and the sub-ppm mass accuracy, which largely facilitates the structure elucidation. There is, however, need for a careful optimisation of analytical protocols in order to eliminate (or at least to account for) the formation of artefact metal complexes during chromatography and electrospray ionisation.

The lecture discusses the position of element and molecular selective detection in speciation analysis illustrated by a number of examples relevant to the environmental, food and clinical analysis.

## CAN SURFACE FUNCTIONALIZATION OF GOLD NANORODS CHANGE THEIR SPECIATION IN HUMAN SERUM? A RESPONSE FROM CE-ICP-MS

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Nowadays, one of the main causes of human death is cancer. Success in its control greatly depends on effective diagnostics and efficiency of tumor treatment. Therefore, it is evident that special attention should be paid to approaches that allow simultaneously detecting and curing the tumor, preferably using the same chemical probe. For such purposes the gold nanorods (GNRs) can be applied due to their unique optical properties, facile synthesis, functionalization by a wide variety of molecules, and impending use as selective biomarkers in biodiagnostics or for selective targeting in photothermal therapeutics. The GNRs functionalized by polyethylene glycol with various terminal groups, such as carboxyl, methoxy or amino groups, are currently intensively tested on animals as photothermal agents. The type of surface functionalization is thought to play a crucial role in the speciation of GNRs in bloodstream and in delivery to cancer cells, especially from point of view of interactions with serum proteins. Getting the answer is the main purpose of our on-going research.

In this contribution, the influence of variable terminal groups on functionalized GNR surface on speciation changes of the nanomaterial in real serum environment conditions is investigated. As the analytical method of choice, capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry has been used. This hyphenated technique takes advantages of high resolution potential of CE and sensitivity and specificity of ICP-MS [1]. These benefits provided the possibility to investigate nano-bio interactions under mild, species-friendly separation conditions, at low analyte concentrations encountered in physiological setting, and using small sample volumes. The formation of the protein corona in dependence of the GNR type will be characterized as based on experiments where the mixtures of GNRs with individual proteins (albumin, transferrin) or their mixture were incubated at physiological temperature. The results will be compared with tests made with human serum.

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## SP-ICP-MS CHARACTERIZATION OF PLATINUM NANOPARTICLES UPTAKE BY *SINAPIS ALBA* AND *LEPIDIUM SATIVUM* PLANTS

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Recently, the use of engineered nanoparticles (ENPs) in commercial products and industrial applications has significantly increased leading to their release into the environment. Consequently, nanoparticles may have an impact on plants, which provides a potential pathway for human exposure. Despite the different sources of platinum in the environment (e.g. abrasion of automotive catalysts), there is a lack of information about impact of platinum nanoparticles (PtNPs) on plants.

The project was focused on the characterization of the uptake and possible translocation of PtNPs in two model plants – *Sinapis alba* and *Lepidium sativum*, known for their ability to accumulate platinum. A method based on an enzymatic digestion followed by single particle inductively coupled plasma mass spectrometry (SP-ICP-MS) analysis was developed in order to extract intact PtNPs from tissues of both plants and get information about nanoparticles size and concentration. Enzymatic digestion allows the extraction of PtNPs from the different plant tissues without changing their oxidation or aggregation state. To extract the largest number of nanoparticles, the enzymatic digestion method was optimized. SP-ICP-MS technique gives an opportunity for the simultaneous determination of the nanoparticles size and number concentration together with the dissolved platinum in the samples. The analytical performance of the proposed method was also evaluated in terms of reproducibility and recovery. On the other hand, the total amount of platinum in plant samples was determined by ICP MS after mineralization.

Obtained results showed that both analyzed plants are able to uptake intact PtNPs and translocate them to above ground organs. The presence of nanoparticles at higher size than the nominal one in analyzed tissues suggesting that nanoparticles undergone a process of aggregation. Lack of signal characteristic for dissolved platinum led to the conclusion that PtNPs absorbed by plants did not undergo any transformations to Pt ions. It was also demonstrated that developed method is highly sensitive and can be used for NPs analysis in complex samples at environmentally relevant concentrations.

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## **SEC-ICP MS PROBING OF AURANOFIN AND CISPLATIN AFFINITY TO PROTEINS AND OLIGONUCLEOTIDES PRESENT IN CANCER CELLS**

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Interactions of cytotoxic gold complexes with proteins are attracting growing attention for their relevant biological implications. Cytochrome c is small protein with several potential binding sites for metallodrugs including cysteine, histidine and methionine. Gold(I) compounds help to release cytochrome c from its binding sites in the inner membrane, which is responsible for activation of cell's apoptosis.

Changes in composition of cytosol were monitored by means of size exclusion chromatography coupled with ICP MS. Superdex column TM 200 10/300GL with mobile phase was 30 mM Tris- H<sub>3</sub>PO<sub>4</sub> o pH= 7,4 (flow rate 0,5 ml/min) was used to distinguish proteins and oligonucleotides from low molecular weight compounds. Ni-sampling cone was applied for Pt and Au determination and 0.1-0.2 ng ml<sup>-1</sup> detection limits for both Pt and Au in aspiration mode were achieved. The identity of chromatographic peaks was established by comparison of elution times for adducts obtained by incubation (37 °C) of standard mixtures of selected bioligands (cytochrome c, glutathione and oligonucleotides) with metal complexes. Additionally, internal standard addition of standard mixture to cells' lysate was applied.

Chromatograms of auranofin (complex of Au(I)) and cisplatin differed significantly by number of peaks and reaction speed. Cisplatin was found to interact with different bioligands creating unstable adducts which composition depended on bioligands ratio and incubation time. Gold complex was found to react faster with bioligands but the number of peaks/created adducts was lower. After 12 h of incubation only one peak was observed in different types of samples: lysate of cancer cell and different mixtures of standard compounds, which was corresponding to cytochrom c.

Auranofin, in contrast to cisplatin, was found to react selectively with cytochrom c involved in activation of mitochondrial apoptosis. Such a high selectivity can be responsible for higher cytotoxicity of auranofin (IC<sub>50</sub> 0.5 μM) in contrast to non-selective cisplatin (IC<sub>50</sub> 22 μM).

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## **GAS CHROMATOGRAPHIC APPROACH TO EVALUATE THE REMEDIATION OF TRIBUTYLTIN CHLORIDE THROUGH SEQUENTIAL DEBUTYLATION BY IRISH BACTERIAL STRAINS**

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Tributyltin (TBT) is a synthetic organotin compound and has a broad range of applications with an annual world production of 50,000 tons a year. Organotin compounds are widely used in marine antifouling paints on commercial, recreational and military marine vessels. TBT compounds are organic derivatives of tin ( $\text{Sn}^{4+}$ ) characterised by the presence of covalent bonds between three carbon (C) atoms and a tin (Sn) atom. They have the general formula  $(n\text{-C}_4\text{H}_9)_3\text{Sn-X}$ , where X is an anion, normally a halogen ion such as  $\text{Cl}^-$  or a group linked covalently through a heteroatom. In the aquatic environment, TBT is quickly removed from the water column where TBT molecules bond to suspended material and is deposited in benthic sediments because of its high specific gravity  $1.2\text{kg}^{-1}$  at 20 degrees, where it can last unaltered for decades, predominantly in anoxic conditions. Due to the negative impact of TBT a global ban has been enforced since January 2008 however impacted organisms have not recovered and levels in water still exceed the environmental quality target of  $2\text{ngl}^{-1}$ .

In this study an organotin method was developed to determine the ability of six isolated resistant bacterial strains ability to degrade tributyltin chloride (TBTCl) through a sequential debutylation. In which the three butyl chains are removed one by one with dibutyltin dichloride ( $\text{DBTCl}_2$ ) and monobutyltin trichloride ( $\text{MBTCl}_3$ ) as intermediate forms in liquid media and spiked sediments. The chemical analyses consists of the following: extraction, derivatisation, clean up, separation, identification and quantification. The challenges posed and the main critical steps in organotin analysis are the extraction and derivatisation of MBT and DBT since low yields can occur at this stage leading to an underestimation of their content in the samples due to their more ionic nature.

Optimum GC and detector conditions were established and the analysis of TBTCl,  $\text{DBTCl}_2$  and  $\text{MBTCl}_3$  was carried out using a Varian 450GC, 220-MS system. Separation was carried out on a capillary column coated with 5% biphenyl and 95% dimethylpolysiloxane with a splitless injection mode employed. Peak areas and height were used for quantitative calculation using the external standard method, peaks in the chromatograms were assigned to individual organotin compounds on the basis of retention time and identified using the comparison of their ion trap mass spectra with the standard MS spectra from the NIST library (National Institute of Standards and Technology Mass Spectrometry Library, Edition 1998). The GC-MS method shows reproducible separation of the organotin compounds which confirmed degradation of toxic TBTCl into its less toxic derivatives by the presence of specific peaks for  $\text{MBTCl}_3$  and  $\text{DBTCl}_2$ .

## **ACTIVE BIOMONITORING OF HEAVY METALS CONTAMINATION IN BESKIDY AND KARKONOSZE MOUNTAINS (SOUTHERN POLAND)**

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During several decades, biomonitoring researches become an effective supplementation of the technical monitoring of the environment quality. One of the ways of their implementation is an active biomonitoring, consisting of exposure of plant material, collected in less contaminated areas, on areas with higher contamination, followed by the analysis of the changes that occur during exposure. One of the most popular methods is moss bag technique, which involves exposure of a plant in nylon nets. After the exposure time increases in analytes concentration in moss, particularly heavy metals, are determined. This technique was used to assess contamination with heavy metals of forest areas in the Beskidy and Karkonosze mountains (southern Poland). In the study moss *Pleurozium schreberi* was used. The plants were collected from ecologically clean areas of Knyszynska Forest (north-eastern Poland). After the exposure, in moss samples concentrations of heavy metals: Zn, Cd and Pb, were determined, using atomic absorption spectrometry. An increase in heavy metals concentrations was observed. The results were interpreted on the base of the calculated Relative Accumulation Factors (*RAF*), which indicates the differences in analyte concentration before and after the period of exposure, relatively to the concentration of the analyte prior to the exposure. For comparison, a study in the center of Opole city (PL) was also carried out, and the largest increases in metals concentrations were observed.

In comparison to Karkonosze Mountains, considerable increases in metal concentrations were observed in samples exposed in the area of Beskidy Mountains. The biggest *RAF* values were calculated for Zn (2.81), Cd (16.1), and Pb (0.21). An important element of the study was comparison of these results with those carried out using passive method (samples collected in the growing sites) using mosses and lichens.

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## HEAVY METAL CONTAMINATION OF MOSSES AND SOIL IN FORESTS OF THE SOUTH AND NORTH- EASTERN POLAND

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In this work comparison of contamination with heavy metals in areas of north-eastern Poland is described. The study was conducted in the Białowieża Forest, Borecka Forest and Knyszynska Forest. In selected areas samples of moss *Pleurozium schreberi* and soil (stripping caries layer) were collected. The material samples were collected six times in the years 2014 and 2015, at the beginning, in the middle and at the end of the growing season. Using atomic absorption spectrometry concentrations of Mn, Fe, Cu, Zn, Cd, Ni and Pb in samples were determined.

No significant differences in mean concentrations of the metals accumulated in moss and soil samples, collected in selected areas, were observed. It could be a result of comparable matter deposition from distant sources. Though, the study has also shown local increases in concentrations, which may be caused by uncontrolled low emissions.

Comparison of the current research results with the literature ones clearly indicates reduction of heavy metals deposition in recent decades. For example, as compared to 1975, the average copper concentration accumulated in mosses collected in 2014 decreased by approx. 55%, zinc by approx. 54%, cadmium approx. 67% and lead of more than 23%. The studies, which are part of a project carried out also in the area of the Beskidy and Karkonosze Mountains (southern Poland), indicate that the north-eastern Poland areas are much less contaminated with heavy metals than the forest areas of southern Poland.

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## **SEASONAL CHANGES OF HEAVY METAL CONCENTRATION LEVELS IN MOSSES AND LICHENS GATHERED IN SOUTH AND NORTH-EASTERN POLISH FOREST AREAS**

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Climatic changes and environmental pollution have an increasing influence on the condition of ecosystems. An example of a research carried out in this field is WICLAP project, which aim is assessment of the climate change and environment pollution impact on condition of forest ecosystems, and in particular the use of remote sensing to identify changes in ecosystems under the influence of these factors. The research are conducted in the following areas: Karkonosze and Beskidy Mountains in south Poland, Borecka, Knyszyńska and Białowieska Forests in the north-eastern Poland and in Svalbard. One of the tasks of the project are biomonitoring studies, and in particular evaluation of heavy metals accumulation in the biota elements: moss, lichens and in the leaves and needles from the trees. The biota samples were collected regularly in the area of Poland since 2014, at the beginning, in the middle and at the end of the growing season.

An information about the pollutants deposition is provided by heavy metals concentration in mosses and lichens. Evaluation method is verified by calculating the *Comparison Factor (CF)*, which describes differences in concentration of the analyte accumulated in lichens and mosses, referenced to the average content of the analyte in both biosorbents. It has been found that the *CF* value over 0.62 may indicate the current deposition of the selected metals. The results indicate that in the period from April to October, in the studied areas the biggest load of heavy metals deposition (Zn, Cd and Pb) appear at the beginning of the growing season. It is probably the result of low emission sources appearing during the heating season. Such trends haven't been observed in the Knyszyńska Forest, which may indicate the full-year impact of emission from the Białystok city.

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The study was performed within the framework of the project: Ecosystem stress from the combined effects of winter climate change and air pollution - how do the impacts differ between biomes? (WICLAP) Polish Norwegian Research Programme (NCRD) POL-NOR / 198571/83/2013.

## **INFLUENCE OF APPLIED VOLTAGE ON ELECTRODIALYSIS' EFFICIENCY IN CASE OF ARTIFICIAL AND REAL HEAVY METAL CONTAINING PROCESS WATERS**

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For the treatment of heavy metal containing process waters several different technologies can be applied for the elimination of heavy metal residues and to minimize the total salinity, such as membrane separation processes. Among the membrane technologies the most widely used ones are pressure driven processes, like reverse osmosis (RO) and nanofiltration (NF), but the electro dialysis (ED) could be also a low energy consuming solution for many industrial applications. The ED's driving force is the electric potential, which provides the ion transport through the ion-exchange membranes.

In this study the effect of applied voltage on electro dialysis' efficiency was investigated in case of artificial test solution and real process water. Experiments were performed on a laboratory scale ED-R unit (Membrain P EDR-Z/10-0.8) with 10 pairs of RALEX AM(H)-PP / CM(H)-PP ion-exchange membranes. We carried out experiments at 2 – 4 – 6 – 8 – 10 V using both solutions as feed for 1 hour period length. The applied conditions (e.g. temperature, pH, flow rate) were in the applicable range of parameters.

The key parameters of the membrane were determined in both cases; demineralisation rate, percentage extraction and separation coefficient of the followed ions ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ). The effect of applied voltage on conductivity was studied as well.

We determined the limiting voltage both for artificial and real process waters. An increase in the applied voltage increased the extraction rate of all analysed ions, as expected. In case of real process water sodium and sulphate removal were three-times higher than in case of the artificial one. The heavy metal removals were higher than 85% in both cases, however it was over 99% in case of the real process water.

Higher differences between the separation coefficients related to the limiting component (sodium or sulphate) were observed at low applied voltage. With increasing voltage this difference was reduced, moreover at 10 V it could be neglected.

We successfully demonstrated that ED is an efficient method for the simultaneous removal of heavy metal ions and salts from industrial process waters.

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## **OPTIMIZATION OF COLORIMETRIC METHODS FOR ARSENIC DETECTION IN WATER**

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Arsenic in drinking water poses a great risk to human health. Arsenic is introduced into drinking water through the dissolution of naturally occurring minerals and ores. There are a number of regions in the world where arsenic may be present in drinking water sources, particularly ground water. One of the most arsenic contaminated regions in the world is Bangladesh where arsenic concentrations exceed 0.05 mg/L. The EU has set a standard limit of 10 ppb for arsenic in drinking water. In order to monitor arsenic in water at these levels highly sensitive and selective monitoring methods are required. Atomic absorption spectroscopy and mass spectroscopy are the most commonly used to methods for water quality assessments. Although these standard techniques are sensitive and reliable, they are very expensive and require trained personnel on site.

An alternative method for heavy metal analysis in water is microfluidic detection. Microfluidic detection systems such as microfluidic chip can detect multiple heavy metals on site. It is also capable of continuous measurements and does not require extensive training to be used. Integration of colorimetric methods into a microfluidic chip may prove to be an effective heavy metal monitoring and measuring strategy. The ideal candidate colorimetric method would have a low detection limit, high sensitivity, fast response time and low cost.

An extensive literature review was carried out in order to determine the most suitable colorimetric methods for arsenic detection that could be incorporated into microfluidic chip. Two ultra violet visible spectrometry methods were selected for the analysis and microcuvettes with 1 mm path length were used to test the suitability of the method for microfluidic chip incorporation.

The first method was based on leucomalachite green dye. The effect of various experimental conditions on absorbance was studied. Absorption maximum of the method was 618 nm with an optimum pH of pH 5. The method yielded the maximum absorbance at room temperature. There was not a significant difference between measurements in quartz and plastic cuvettes. The absorbance of the reaction was stable and could be measured over 2 hour period. Limit of detection was 3.7 ppm. The time taken for the maximum and constant absorbance was 5 minutes.

The second method is based on variamine blue dye and has been chosen for future studies. In this method arsenic reacts with acidified potassium iodate to liberate iodine. The liberated iodine oxidises variamine blue to a violet colored species having an absorption maximum of 556 nm.

The methods developed in this research project will help to improve the range of techniques available for water quality analysis for arsenic.

## **SEPARATING THE OPERATIONALLY-DEFINED FRACTION: DISCRETE ORGANIC SELENIUM SPECIATION IN HIGH IONIC STRENGTH ENVIRONMENTAL SAMPLES**

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Organic selenium in aqueous environmental samples is often measured as an operationally defined fraction, providing no information about the discrete speciation and making predictions about bioavailability and toxicity difficult to establish. Here, we optimized an anion exchange chromatographic method for the simultaneous analysis of organic and inorganic selenium species, for quantification with inductively coupled plasma mass spectrometry and structural identification with electrospray tandem mass spectrometry. The high ionic strength of many environmental samples, combined with the low concentrations of organic selenium species, makes direct analysis impossible in most scenarios. Therefore, we have developed an extensive preconcentration and cleanup procedure allowing selenomethionine to be analyzed with a method detection limit of 1.5 ng/L; a method which can also be applied to other organic selenium species. Following these procedures, we noted the first observance of free selenomethionine in the environment outside of a biological entity. We also demonstrated that both the fractions and absolute concentrations of discrete organic selenium species increased over the course of various biological treatment processes.

## **DEVELOPMENT OF ANALYTICAL APPROACHES TO LINK IRON SPECIATION AND BIOAVAILABILITY IN MAIZE**

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Iron (Fe) deficiency resulting from inadequate intake of bioavailable iron is a serious problem worldwide. The appropriate enhancement of the iron bioavailability from staple foods including, among others, maize, has been reported as a cost-effective and sustainable approach to address the issue of iron deficiency in man. Recent reports on tropical maize with enhanced nutritional quality showed significant differences in the concentrations of iron in maize kernels due to variations in both genetic and environmental factors. The bioavailability of iron strongly depends on its chemical form. Hence, the interest in the description of the bioavailability on the molecular level and consequently the need for the development of analytical chemistry approaches aimed at identification and quantification of individual iron species.

The total concentration of iron in maize is about 20 µg/g. The contribution discusses the development and comparison of different sequential extraction schemes to fractionate the different classes of iron species: (i) water soluble iron; (ii) starch-bound and (iii) protein bound. The typical distribution of the iron found was 10 %, 5 % and 65%.

The custom designed extraction/fractionation sample preparation was followed by the analysis by coupling of hydrophilic interaction chromatography (HILIC) with inductively coupled plasma mass spectrometry (ICP MS) and high resolution electrospray mass spectrometry (HR ESI MS) allowed the detection and quantification of more metal complexes. Species observed by this methodology convey considerable information for metal transport understanding [1,2]. Four genetic varieties of maize were systematically studied in this way. The approaches used involved: (1) the fractionation of iron species bound to different matrix constituents and (2) evaluation of iron speciation in simulated gastro-intestinal digests. The species already detected include iron citrate, mugineate and phytate accounting together for up to 10% of the total Fe. The Fe-containing proteins constitute the principal iron fraction of ca. 60 %.

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**SILICA-BASED IONOGELE FIBERS FOR ISOLATION OF VOLATILE ORGANIC POLLUTANTS FROM WATER SAMPLES BY HEADSPACE SOLID-PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY**

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Solid-phase microextraction (SPME) is a miniaturized sample preparation technique widely used in a variety of fields that integrates sampling, extraction, preconcentration, clean-up and sample introduction. A number of SPME fiber coatings are nowadays commercially available. Unfortunately, they are not free from drawbacks, where limited lifetime, batch-to-batch variation and limited sorption capacity are the major concerns. Most of the coatings provided to isolate polar analytes are solids, so the extraction mechanism is based on adsorption of analyte on the surface of the coating material. This fact results in a reduced linearity range and decreasing extraction efficiency. Moreover, competitive adsorption might occur when dealing with complex samples, thus leading to calibration problems. A solution for this problem can be the application of ionic liquids (ILs) as extraction media. Due to their unique physicochemical properties, ILs can be treated as green solvents and they can be successfully applied as SPME fibers stationary phases. The key issue is obtaining a stable film of IL on the fiber surface with simultaneous preservation of its liquid state. One of the promising solutions consists in covering fused silica fibers with stable films of ILs confined into a three dimensional sol-gel network commonly named as ionogel. In this work, several bis(trifluoromethylsulfonyl)imide anion-based ILs were studied to prepare ionogel fibers by sol-gel technology. The obtained ionogel materials were characterized by scanning electron microscopy and energy dispersive X-ray spectrometry, and subsequently evaluated as extraction phase (medium) for the headspace solid-phase microextraction (HS-SPME) of volatile organic compounds in combination with gas chromatography and barrier ionization discharge detection. The experimental parameters that affect the extraction process were optimized by means of a central composite design. Under optimal conditions, the proposed method has been validated and subsequently applied for real sample analysis.

# **SESSION 5 & 6**

Speciation studies combining several techniques

Part I & II

## **SPECIATION OF ARSENIC, MERCURY AND OTHERS: “GREEN” AND INDUSTRIAL SOURCES OF METHYLATED SPECIES AND HUMAN EXPOSURE**

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Both, Arsenic as well as Mercury are ubiquitous in the environment and exist in a variety of species with a great influence on their transport, bioaccumulation and toxicity. Furthermore they can cause serious health problems also in very low concentration or by chronic exposure. Volcanic activities, geological erosion, mining activities, and burning of fossil fuels are the major processes that contribute to contamination of air, water and soil.

In times of decreasing sources of conventional fuels, renewable energy is a more and more upcoming resource. Beneath wind, photovoltaic and hydro energy, biogas is one of the most important green energy sources and can be used as a natural gas substitute. Like natural gas, biogas is a gaseous mixture that is primarily made up of methane. It originates by anaerobic decomposition of all kind of organic matter like energy plants (grass, maize, grain, rice), excrements, agricultural residues (harvest residues, leaves) and organic waste (vegetables, old fats, brewery grains, food residues, grease). Many of these input materials can contain more or less metal(oid) compounds. For example, waste from food production may contain fish or rice which are well known to contain high amounts of arsenic (As) or mercury (Hg) but also other metal(oid)s like antimony (Sb) or tin (Sn) may occur in biogas plants. The processes to convert biomass under anaerobic conditions into biogas using micro-organisms will also result in the formation of volatile metal(oid)organic compounds. Such bio methylation was already found in gases released from natural and anthropogenic environments, e.g. geothermal gases, sewage treatment plants, marine sediments and landfill deposits. Are these results comparable?

For separation and determination of metal(oid)s in gaseous samples GC-ICP/MS should be chosen because of its high separation efficiency and low achievable detection limits. For non-volatile species HPLC-ICP/MS techniques are the usual choice because of the ease of online coupling, the variety of separation mechanisms and mobile phase allowing the preservation of the species identity. But is the use of such hyphenated, expensive systems always necessary? And how does the species contribution look like for different anthropogenic sources, natural sources and hot spots? Can species be reduced, changed or accumulated?

## **METAL MOBILITY IN CLAY - FROM ICP-MS BATCH AND CE-ICP-MS SPECIATION TO MINIATURISED CLAY COLUMN EXPERIMENTS (MCCE) USING LC-ICP-MS**

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The development of a high level nuclear waste (HLW) disposal in deep geological formations is a very important task for the future. The long term safety assessment for more than hundred thousand years needs a full knowledge of all processes of interaction between the radioactive waste and the surrounding formations. Nowadays, there is a broad scientific consensus on the technical merits of a HLW disposal in deep and stable clay formations as host rock. A wide set of geochemical parameters can influence the mobility of radionuclides originated from a leakage in a waste disposal for example competing ions released from the clay by infiltration of percolating water, natural organic matter (NOM) as complex forming ligands, changes in temperature or pH-milieu of the aquifer.

In this study trivalent europium (as chemical analogue of the actinide americium) and uranium (VI) as principal component of the waste were used and their retention onto Opalinus clay as possible host rock in the presence or absence of NOM was studied. As methods, capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry (CE-ICP-MS) as well as ultrafiltration (UF) in combination with ICP-MS was used to study the complexation behaviour of Eu(III) and U(VI) with NOM like humic acid. The influence of metal concentration, presence of competing cations from clay dissolution as well as cations from clay porewater on the complexation behaviour was analysed. For the sorption/desorption studies common batch experiments with the metal ions and clay mineral suspensions are performed. Additionally, miniaturised clay column experiments (MCCE) with online ICP-MS coupling allow for the visualization of sorption and desorption processes of europium and uranium on clay dynamically. MCCE with compacted clay was used to study the influence of NOM on the metal mobility in clay like Kaolinite or Opalinus clay. LC hyphenation with ICP-MS leads to quantitative information on the elemental composition of the eluent from the clay column directly after determination of the UV/Vis-active compounds in the diode array detector of the LC.

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## **ISOBARIC DILUTION ANALYSIS AS A NEW TOOL FOR SPECIATION AND ULTRA TRACE ANALYSIS OF <sup>99</sup>Tc**

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Isotope dilution analysis (IDA) has become a powerful internal calibration technique for ICP-MS for the highly precise and accurate determination of elements with at least two stable isotopes. However, monoisotopic elements are excluded from IDA and the calibration of many radioactive isotopes is cumbersome and expensive, since often neither elemental standards nor enriched standards are available. Technetium (Tc) is one of these monoisotopic elements inaccessible by conventional calibration methods.

<sup>99</sup>Tc is a nuclide, which is generated in high amounts in nuclear waste as a result of the neutron induced fission of <sup>235</sup>U in nuclear power plants. The present abundance of <sup>99</sup>Tc in nature is almost exclusively the result of anthropogenic contamination resulting from processes like nuclear weapon testing, reprocessing of spent nuclear fuel and waste disposal. Due to a long half-life, a high mobility and a high fission yield, <sup>99</sup>Tc is considered to be the most important radionuclide in risk assessment of radioactivity in the environment, as well as in decommissioning nuclear facilities and in the management of nuclear waste. Moreover, it is considered to be an important contributor to the future collective dose to the population. Yet, appropriate methods for the determination in environmental samples are not available. Furthermore, <sup>99m</sup>Tc is widely used as in the field of medical diagnostic. Due to low concentrations and a lack of standards, a quality control and tracer accreditation in terms of quantification, and determination of the species specific activity is impossible with current methods.

In this work, a new quantification method called isobaric dilution analysis (IBDA) is introduced and evaluated as a new calibration tool for Tc. It uses the fact that conventional mass analysers for ICP-MS cannot distinguish between two isobaric isotopes of different elements. Therefore, Tc samples were spiked with a Ru solution, exhibiting an isobaric isotope with *m/z* 99. However, element-specific responses were considered in order to obtain accurate concentrations. A crucial advantage of this method is its capability to access the calibration of transient signals when used in a post column approach. First, this approach was applied to conduct speciation analysis in Tc-based contrast agents. <sup>99</sup>Tc species were separated and quantified by means of IBDA-LC-ICP-MS and could subsequently assigned to specific structures by means of LC-ESI-HRMS. This allows an on-side quality control as well as a crucial improvement in the accreditation of novel tracer. Secondly, the approach enabled the determination of <sup>99</sup>Tc in water samples by means of online extraction chromatography with post column IBDA, revealing a measureable input of <sup>99</sup>Tc into the environment due to nuclear diagnostic facilities.

## A NEW METHOD FOR GE SPECIATION USING HPLC-ICP-MS

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Metal speciation is not only of importance for their environmental behavior but might also play an important role in technical processes. One example is germanium speciation in the technical process of bioleaching and subsequent metal recovery processes [1]. In contrast to environmental samples, such samples contain higher concentrations of germanium as well as many by-elements and may also contain high salt contents. The present study demonstrates the separation of inorganic germanate ( $\text{Ge}(\text{OH})_4$ ) and the methylated species monomethyl (MMGe) and dimethyl germanium (DMGe) and its use for the investigation of bioleaching processes of germanium.

For the separation of the three Ge-species in aqueous solution anion exchange chromatography (Hamilton PRP-X100 column (150 mm x 2.1 mm, 10  $\mu\text{m}$ )) was used and coupled to an ICP-MS (Agilent 7700,  $m/z = 72$ ) for element-specific detection. Tartrate had to be added as complexing agent into the samples to enable the chromatographic separation.

Addition of 80 mM tartrate resulted in a baseline separation of  $\text{Ge}(\text{OH})_4$ , MMGe and DMGe. DMGe elutes first, followed by MMGe and  $\text{Ge}(\text{OH})_4$ . Sulfate, which is a component of the bioleaching samples, might compete for the functional groups at the stationary phase and thus might affect the separation. Therefore, the influence of sulfate on the separation was investigated. Furthermore, the retention behavior of sulfate at the anion exchange column was studied by HPLC coupled to a triple quad ICP-MS (Agilent 8800) to analyze the sulfur as  $\text{SO}^+$  ( $m/z = 48$ ). The increasing sulfate concentration went along with a change of the peak shape of the  $\text{Ge}(\text{OH})_4$  peak and a shorter retention time of MMGe. The addition of 1 mM tartrate to the mobile phase compensates for this influence at least to a sulfate concentration of 150 mM (14 g  $\text{L}^{-1}$ ). Application of the Ge-species analysis to bioleaching solutions showed that after leaching all germanium occurred as  $\text{Ge}(\text{OH})_4$ .

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## **FAST MINIATURISED COLUMN EXPERIMENTS FOR HOST ROCK CHARACTERISATION OF FINAL DISPOSAL SITES IN CLAY**

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According to a decision of the Council of the European Union (EU), all EU member states that operate nuclear power reactors are to establish a national framework including arrangements on the final disposal of their spent fuel and high level radioactive waste (HLW) by no later than August 2015. Among the possible host rock materials, such as salt, granite, and clay, the latter is a very promising candidate due to a very low hydraulic conductivity, a high sorption capability, an efficient filtration ability for interacting molecules, small solubility of the clay components in water, and a high chemical buffer capacity.

As linker between widely used but unnatural batch experiments and the more realistic but lengthy diffusion experiments we have developed fast miniaturised column experiments. Our setup, derived from HPLC-ICP-MS (high performance liquid chromatography hyphenated with inductively coupled plasma mass spectrometry), allows the online investigation of metal adsorption on and desorption from clay dynamically. In order to do this, self-packed columns are made of homogenised natural Opalinus clay or pure clay minerals such as Kaolinite. The geochemical parameters relevant for final disposal e. g. pH, pressure or liquid flow, (column) temperature, nature and concentration of metal ions, and presence of possible ligands can be easily varied owing to the HPLC system.

The described method allows data evaluation in terms of metal sorption capacity, (de)sorption isotherms and retardation factors ( $R_f$ ). It also allows to deduce distribution coefficients ( $K_d$ ) as necessary for long term safety assessment of a possible HLW repository in clay.

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## **SPECIATION USING X-RAY METHODS – POSSIBILITIES AND LIMITATIONS**

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Nearly all methods of X-ray spectroscopy with one or two exceptions used in instrumental analytical chemistry are not well suited to perform speciation analyses. Nevertheless, there are possibilities to use these methods to obtain results in terms of element speciation with sometime multi-element capability. We may distinguish the direct analysis and the analysis after an off-line coupling of e.g. chromatography (separation step) and the sensitive quantitative multi-element detection by X-ray fluorescence spectrometry.

The principles of the direct speciation using electron and photon excitation, as well as wavelength and energy dispersive detection will be presented. Some examples will give an insight into the sensitivity and applicability of the methods. The importance of high resolution X-ray fluorescence and of X-ray emission spectra will be discussed. Several examples will support the theory illustrating the power of micro-methods when looking absolute amounts of material. Typically, the detection limits of these methods are of the order of atto-grams ( $10^{-18}$ g) in volumes of some  $\mu\text{m}^3$ .

A second aspect is the instrumental development combined with the access to powerful X-ray sources like those offered at synchrotron facilities. Today, high brilliance narrow X-ray probes are available for excitation to X-ray fluorescence. And precisely working goniometers with resolution below one second of arc are promising tools for local direct speciation analyses. Analyses are performed in reasonable time elapses. However, the time structure of synchrotron radiation has not been used until now. Fast detectors are not available to perform time resolved experiments illuminated with nanosecond pulses and with frequencies of the order of microseconds.

## **SPECIATION OF TRACE ELEMENTS IN SOIL, WATER, AND FAUNA IN TWO BLACK SHALE AREAS IN SWEDEN**

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Trace element speciation in soil, water and fauna in black shale areas was studied in a Precambrian and a Cambrian area in Sweden. The main issue in the Precambrian area was possible mobilization of As into groundwater and surface water. In the Cambrian area As, but also Mo, U, Ni, Zn and Cd were elevated. Trace elements in soil were speciated by a BCR-procedure (Zemberyova et al. 2010). Elements in water were speciated by filtering (0.2 µm), and dialysis (10 and 1 kD pore-size) (Vasyukova et al. 2012). Speciation in water was done by Visual-MINTEQ (Gustafsson 2013). In fauna As was speciated by methods described by Slejkovec et al. (2004). In the Precambrian area As and Fe were mobilized under reducing conditions in wetlands. As in groundwater was up to 100 µg/l in filtered water. After discharge into streams ferrihydrite precipitated adsorbing most of the As. However, up to 20 µg/l remained in the water. This As correlated to iron in the filtered and dialyzed water and likely to be tied to particulate humic-ferrihydrite particles and colloids (Fritzsche et al. 2011; Jacks et al 2013; Neubauer et al. 2013). Speciation of As in macrovertebrates and fish showed no elevated inorganic As and small increases of organic As indicating low bioavailability. In the Cambrian area BCR sequential extraction showed that As was associated with the reducible fraction, ferrihydrite. While U was elevated in surface water there was no uptake in plants and the Mo and U seemed to be present as anions or uncharged complexes after filtering via a cation exchanger. The results from the Cambrian area showed that U was high in surface water but largely present as Ca-complexes and thus not readily bioavailable neither to plants nor to humans. Elevated Mo in plants, notably in red clover (*Trifolium pratense*) could involve secondary Cu deficiency, molybdenosis, in cattle, possibly also in moose. Immobility of As was due to the absence of wetlands in the area, retained in the soil profiles adsorbed to ferrihydrite.

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## ANALYTICAL APPROACHES TO STUDY SELENIUM INCORPORATION INTO YEAST PROTEINS

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Selenium is an essential micronutrient which plays a vital role in most of biochemical and physiological processes including immune function, thyroid hormone metabolism and antioxidant defense systems [1]. The deficiency of selenium is a world-wide problem which is addressed by supplementation [2]. The superior availability of organic forms of selenium in comparison with its inorganic forms is well documented in the literature [3]; the most popular supplement of organic selenium for human and animal nutrition is yeast grown in Se-rich media.

In most selenized yeasts available on the market, selenium-containing proteins account for ca. 80 % of the total Se present [4]. The selenium incorporation in yeast proteins depends on the yeast strain and biotechnological process and results from the replacement of S by Se in S-containing proteins. Identification of these proteins and quantification of protein bound Se is important for the understanding of the enrichment process and the characterization of the commercial products.

A proteomics approach based on 2D gel electrophoresis – laser ablation ICP MS followed by HPLC-electrospray Orbitrap MS/MS was developed to investigate the replacement and the degree of the Se/S substitution in methionine and cysteine in Se-rich yeast. Capillary HPLC-inductively coupled plasma mass spectrometry (ICP-MS), employed in parallel to capHPLC – ESI MS, indicated the virtual independence of the ESI MS response of the peptide structure, and hence allowed the use of ESI MS data to determine the SeCys/Cys and SeMet/Met substitution ratios. However, this methodology does not allow for quantitation of individual proteins and establishing the mass balance of all the selenium species present.

The quantitative assessment of selenium incorporation into proteins can be carried out by simultaneous determination of selenoamino acids (SeMet and SeCys) upon proteolytic digestion of yeast proteins. The stability of SeCys can assured by carefully optimized derivatization.

The paper presents the development of approaches allowing both (i) the identification of Se-containing proteins and (ii) quantitative determination of proteic selenoamino acids by HPLC-ICP MS in commercial products with a focus on the selenium mass balance in samples of different provenance.

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## COMPARATIVE STUDY OF Hg SPECIATION BY GC – ICP MS, HPLC – ICP MS AND ETV – ICP AES IN DIFFERENT MATRICES

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Mercury is a persistent pollutant found in trace amounts in different compartment of the ecosystem. It is well known that the toxicity of Hg is highly dependent on its chemical form. For example, MeHg<sup>+</sup> is 10-100 times more toxic than inorganic Hg compounds.

The methods developed to perform mercury speciation involve the coupling of a powerful separation technique with a selective and sensitive detector. Among all the techniques available, the coupling GC – ICP MS has rapidly dominated the field because of its sensitivity and compatibility with isotope dilution analysis. However it requires a chemical treatment of the mercury species to make them volatile, and the efficiency of this treatment may negatively be affected by the matrix. The HPLC – ICP MS coupling analysis becomes then an interesting alternative to get rid of this chemical treatment but it requires the development of a preconcentration step to get quantification limits in the same range as the GC – ICP MS analysis.

Furthermore, these two liquid-state approaches do not allow the determination of insoluble or unstable in solution mercury species. It is then necessary to develop direct solid-state analysis. This can be achieved by ETV – ICP AES providing the adaptation of the temperature rise to separate the species.

The presentation will show the potential (in terms of sensitivity and species accessible for analysis) and the limitations of these three techniques (GC – ICP MS, HPLC – ICP MS and ETV – ICP AES) for mercury speciation in different organic and inorganic matrices, such as environmental, industrial and food matrices.

## **ADVANTAGES OF ICP-MS/MS FOR ELEMENT SPECIATION ANALYSIS**

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Elemental speciation analysis using hyphenated methods, such as liquid chromatography coupled to an ICP-MS, have become extremely popular during the last 20 years.

There is a clear need for reliable screening methods to accurately determine the levels of contaminants in many samples. For example, Arsenic and Selenium can be difficult to quantify accurately at trace levels by conventional quadrupole ICP-MS, as all the analytically useful isotopes can suffer from multiple spectral interferences.

We will explain how the MS/MS mode is able to solve these issues and give accurate results.

This presentation will provide example applications of speciation analysis using LC-ICP-QQQ-MS, with a focus on the challenges in providing routine speciation analysis.

## **SESSION 7**

Speciation of metal(loid)s in  
oceanography and freshwaters

## **SPECIATION IN THE MARINE ENVIRONMENT: FROM IONS TO MACROMOLECULES**

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Recent advances on analytical instrumentation, mainly the development of hyphenated based-mass spectrometry techniques, have allowed the accurate identification and quantification of several organometallic species. In addition, improvements on resolution and sensitivity of new analytical instruments offer nowadays the possibility of assessing new species in complex samples even when occurring at very low levels. This communication offers the recent advances/developments on organometallic speciation in the marine environment achieved in our research group. High performance liquid chromatography – inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) developments for mercury and arsenic speciation in seawater, as well as for arsenic, selenium, iodine, and bromine speciation in marine biota (fish, mollusk, and edible seaweed) are presented. Advanced sample pre-treatments, such as molecularly imprinted polymer – solid phase extraction (MIP-SPE), matrix solid phase dispersion (MSPD), and assisted pressurized liquid extraction/ultrasound extraction – enzymatic hydrolysis (PLE-EH/USE-EH), have been developed for organometallic species isolation/pre-concentration. Moreover, iodine and bromine speciation has also been performed in atmospheric particulate matter (PM10 and PM2.5) in coastal areas. In addition to the assessment of organometallic ions/molecules, speciation developments for large biomolecules, such as iodinated proteins in edible seaweed by two dimensional polyacrylamide gel electrophoresis (2D-PAGE) hyphenated with laser ablation (LA) – ICP-MS, has also been performed. Similarly, the assessment of dissolved metal-protein complexes in seawater and marine sediment pore water, and in marine plankton (particulate metal-protein complexes) has also been addressed. Offgel electrophoresis combined with microfluidic lab-on-a-chip electrophoresis has been used for speciation of metal-protein complexes. In this case, electrothermal atomic absorption spectrometry and inductively coupled plasma – optical emission spectrometry have been used as specific detectors for metals. Finally, speciation studies based on determining free (labile) metals and metals bound to organic matter in seawater by using on-line SPE-ICP-MS procedures, as well as, on-line and off-line HPLC (two dimensional size exclusion and ionic exchange chromatography) – ICP-MS techniques have also been developed. Levels of organometallic species, metal-protein complexes included, in seawater, marine sediment pore water, marine biota, and atmospheric particulate matter in coastal environments by applying the proposed methodologies are finally given.

### **Acknowledgements:**

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## **THE INFLUENCE OF NITRATE ON THE UPTAKE OF SELENOMETHIONINE BY GREEN FRESH WATER ALGAE**

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Selenomethionine (SeMet) is assumed to be the key chemical species in the bioaccumulation of selenium (Se) in aquatic systems, as well as in Se ecotoxicity. We have recently shown that green fresh water algae take up inorganic Se oxyanions, convert them into SeMet, and release them back into the surrounding waters. In this follow up study, we now determined the mechanism by which SeMet is taken up by algae, as well as the influence of hydrochemical parameters on this process.

SeMet uptake by green fresh water algae was negatively correlated with nitrate concentration in the growth medium. Other common anions (sulfate and chloride), common counter cations (sodium and calcium) and pH had no influence on SeMet uptake. Experiments with nitrogen-starved algae showed higher SeMet uptake than for algae grown with abundant nitrate. This indicates that SeMet is taken up as an alternate nitrogen source when nitrate is sparse.

The uptaken SeMet was primarily incorporated into proteins under nitrate-deficient conditions. Nitrogen abstraction from SeMet by the algae was not observed. At abundant nitrate concentrations, much less SeMet was taken up and incorporated into proteins. In turn, SeMet conversion to inorganic Se species (selenite, selenite and selenocyanate) was observed, which were emitted back into the growth medium.

Our results on the interaction between nitrate and SeMet during algal uptake will be discussed in the context of developing site-specific Se criteria, as well as with respect to biological treatment technologies applied to industrial process waters containing both nitrate and Se.

## **SEX SPECIFIC FORMATION OF METALLOTHIONEINS BY THE CORAL PRAWN *METAPENAEOPSIS CRASSISSIMA***

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The coral prawn, *Metapenaeopsis crassissima*, is unique among crustaceans because the females of the species have significantly higher (100-fold) Cd concentrations in their tail muscle than do the males. To investigate this phenomenon, coral prawns from Shark Bay in Western Australia were collected and exposed to various concentrations of Zn, Cu, Cd and <sup>106</sup>Cd in water. Total concentrations of these elements were determined and an analytical protocol was developed to identify, and then quantify, the Cd-metallothioneins (Cd-MTs) by HPLC with post-column splitting and simultaneous measurement of the effluent by ICPMS and ESMS. The results are discussed in terms of detoxification processes and metal species formation.

### **Acknowledgements:**

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## **FROM MACRO TO NANO - SPECIATION OF HEAVY METALS IN WATER ECOSYSTEMS**

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Metals are commonly present in the environment as the integral part of ecosystems. There are many sources of heavy metals in the environment, both natural and anthropogenic. They can get there from the atmosphere as a result of intensive rain or snowfall, or they can be eroded out of the bedrock or soil. The great variety of sources and physico-chemical conditions means that an element can occur in many different forms. But, every year, the use of substances such as nanometals increases rapidly in fields such as biomedicine, pharmaceuticals, cosmetics, electronics, energy and environmental protection which leads to increased quantities in the environment, and particularly in the water environment. The forms of occurrence of metal such as size, magnetic characteristics, surface area, degree of oxidation, the combination with other substances, determine its toxicity or the synergistic relationships it enters into with other substances, which in turn determine its uptake and absorption by living organisms. That is why any assessment of the degree of contamination of the environment should be carried out not only from the point of view of the total amount of a metal found in environmental samples; it is also very important to know the contents of stable species of metals, in macro and nano size, constituting a potential reserve in the biocirculation.

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## CHROMIUM SPECIATION IN DRINKING WATER

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Chromium (Cr) exhibits different oxidation states. Elemental metal, trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] are the most commonly observed chromium species in environment. Chromium in water supplies can be either from naturally occurring sources or as the result of industrial activities. WHO has established a guideline value of 0.05 µg/L for total Cr in drinking water, many governments and safety regulatory agencies have also set maximum allowable limit for total Cr in drinking water to ensure safe consumption. However, toxicity as well as mobility and bioavailability are largely different for different Cr species. While the [Cr(VI)] is highly soluble, toxic, and carcinogenic; [Cr(III)] is less toxic and considered to be a micronutrient. Therefore, a thorough study on Cr species in drinking water is crucial for evaluating potential hazards and safeguarding the public health.

Many study programs have studied the examination of [Cr(VI)] in water. However, because of the great difficulty in preventing the interconversion between [Cr(VI)] and [Cr(III)] in water, only Cr(VI) was present in the testing samples. We present here the first preparation and verification of a stable drinking water sample which contains both [Cr(VI)] (prepared from a certified reference material of potassium dichromate) and [Cr(III)] (prepared from a coordination complex of chromium(III) acetylacetonate [Cr(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>]). The homogenized water sample was packed into HDPE bottles; all bottles were vacuum-sealed inside aluminium-coated bags and stored at room temperature. The bottled water samples are stable for long, in which chromium interconversion reactions do not occur at room temperature. The mass fraction of [Cr(VI)] was quantified by ICPMS. Both the between bottle heterogeneity and the stability of this material have been evaluated in accordance to ISO Guide 35:2006.

The material was selected as testing samples for the international comparison study “CCQM-K124(Part B): Key Comparison on Chromium Speciation in Drinking Water” organized under the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) of the International Committee for Weights and Measures (CIPM). Measurement results from 7 National Metrology Institutes and Designated Institutes were collected. Despite using different measurement techniques, most participants’ results on the mass fraction of [Cr(VI)] in the test material were found to be consistent; a Key Comparison Reference Value (KCRV) of 62.67 µg/kg was drawn successfully.

## **TRACING GADOLINIUM-BASED CONTRAST AGENTS FROM WASTEWATER, VIA SURFACE WATER TO DRINKING WATER**

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In recent decades, a significant amount of anthropogenic gadolinium has been released into the environment as a result of the broad application of gadolinium-based contrast agents (GBCAs) for magnetic resonance imaging (MRI). The kinetic and thermodynamic stability of the GBCAs makes these complexes quite resistant against wastewater treatment and environmental degradation. In order to follow the GBCAs from the wastewater discharge through the aquatic environment, sensitive and selective methods were developed for the species determination that allows the differentiation of complexed gadolinium from other (natural) Gd species occurring at background levels in the aquatic environment. In earlier studies it was shown that GBCAs are neither significantly retained nor degraded during wastewater processing. Using the developed methods for speciation analysis, the stability of frequently applied GBCAs towards UV radiation has been investigated. The contrast agents Gd-DTPA, Gd-DOTA and Gd-BT-DO3A showed a high stability in irradiation experiments applying a wavelength range from 220 nm to 500 nm. Nevertheless, the degradation of Gd-BOPTA as well as the formation of Gd-containing transformation products was observed by means of HILIC-ICP-MS.

In a second study the group followed the gadolinium species through different steps of drinking water purification. Water samples from six waterworks in Germany were analyzed, covering different techniques of drinking water purification. Applied purification techniques involve ground filtration, filtration through activated carbon as well as ozonation. Disinfection of the drinking water is carried out in those waterworks by addition of chlorine dioxide or UV irradiation. Using sector-field ICP-MS in combination with ultrasonic nebulization for sample introduction and a HILIC method for on-line separation of the GBCAs, very low detection limits between 8 and 14 pmol/l were obtained for the different contrast agents. This high detection power enabled to follow the frequently applied contrast agents Gd-DTPA, Gd-DOTA and Gd-BT-DO3A throughout the purification steps of the different water works. There was no evidence for additional Gd species or transformation products being present in the analyzed samples. Since sampling schemes were not sufficient for a mass balance throughout the water processing, an interpretation of the data regarding a possible removal of contrast agents was not possible. However measured concentration levels of Gd-based contrast agents did not significantly diminish through the process.

## **AUTOMATED MONITORING OF ARSENITE AND TOTAL ARSENIC IN A GROUNDWATER TREATMENT PROCESS USING VOLTAMMETRY**

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The use of groundwater containing inorganic arsenic (As) of geological origin has caused public health hazards in many developing countries in South-East Asia. The groundwater from the region typically contains both iron (Fe) and As, and because of the reducing conditions of the groundwater, often contains higher concentration of arsenite (As(III)) compared to arsenate (As(V)). Of the inorganic As species, As(III) is known to be more toxic and also more difficult to remove from water compared to As(V). To mitigate the health problems associated with the use of As containing water, we have developed a low-cost biological filtration (BF) technique utilizing indigenous Fe oxidizing bacteria in groundwater for simultaneous removal of Fe and As. In our pilot study in Vietnam, we have proved that BF technique can remove both As(III) and As(V) in groundwater by adsorption of As onto the biologically formed Fe hydroxides (BIO-Fe). Utilizing an X-ray absorption spectroscopy (XAS) technique, we monitored the chemical form of As adsorbed on the BIO-Fe and have elucidated the mechanisms of As(III) removal by BIO-Fe.

We also investigated the effect of As(III) /total As ratio in raw groundwater on the removal by BF, as well as the variation in As species in water during and after the BF treatment by a long-term monitoring of BF pilot system in Japan. For this purpose, an on-line monitoring system based on anodic stripping voltammetry (ASV) was used to periodically (e.g., every 24 hrs) collect raw and treated water samples, and analyze As(III) and total As. The water sample from our site contained a small amount of sulfide, an interferent in determination of total As by ASV, but the interference was removed by introducing an automated rinse step of the working electrode (solid gold) with  $10^{-3}$  M  $\text{KMnO}_4$  after analysis of actual samples. An ascorbic acid rinse step after total As analysis was used to remove residual  $10^{-3}$  M  $\text{KMnO}_4$  that oxidizes As(III) in the sample. After identifying many operating variables relevant to the analytical accuracy and eliminating interferences unique to the field deployed voltammetry instrument, the accuracy of the As(III) and T-As determination by the on-line voltammetry was validated by analysis of the same sample by LC-ICP-MS. In our treatment system, As(III)/Total As ratio in raw water had no apparent effect on the removal of As by BF. And As(III) was not oxidized to As(V) in an aeration unit installed before the raw water enters the BF system, but was oxidized in the deep part of the filter layer, resulting in the higher concentration of As(V) than As(III) in the treated water. The trend was consistent throughout the monitoring period.

## **ARSENOBETAINE IN SEAWATER: DEPTH PROFILES FROM THE NORTHWEST ATLANTIC**

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Arsenic occurs in seawater at low concentrations (ca 1 µg As/kg or 13 nM), primarily as the inorganic species arsenate. Marine animals, however, contain very high levels of arsenic (typically 2,000-20,000 µg As/kg wet mass), mainly as arsenobetaine. Despite this predominance of arsenobetaine in marine animals, it has never been reported in seawater. Previous attempts to detect arsenobetaine in seawater have been thwarted by the complex salt matrix as well as very low analyte concentrations. We report a method capable of measuring arsenobetaine in seawater at the ng As/kg level, and present the first depth profiles (2 m – 5,000 m) for this arsenic species.

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## **SESSION 8**

Elemental speciation in soil and plant interaction

## ON THE USE OF NON-ROUTINE APPROACHES TOWARDS UNDERSTANDING CHEMICAL SPECIATION IN PLANTS

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Increased attention is focus on the investigation of the mechanisms of biotransformation and translocation of various species in plants, which become to be of fundamental interest on the ecological plant physiology. In this presentation various scenarios tailored towards obtaining complementary information of the biological and chemical characterization of the plants cells, organelle and tissues, will be discussed.

Allium test was used to evaluate the grown of roots and its mitotic activity in apical meristem. Also, the biomass was found to deliver important information. Total content of elements of interest was determined by inductively coupled plasma mass spectrometry (ICP MS). High-performance liquid chromatography (HPLC), coupled to ICP MS, was used for the evaluation of chemical speciation. In this case the use of species specific IDMS procedure was used. Moreover, several imaging techniques were used for the investigation of the special distribution of the element of interest over the plant's tissues. The imagines from confocal and light microscopy were compared with the distribution maps obtained by LA ICPMS.

To conclude, in this presentation the advantageous of multi-technique approach towards obtain complementary information about the metabolism in plants will be highlighted and exemplified by the investigation of selected elements biotransformation and translocation in plants.

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## ARSENIC SPECIATION AND CADMIUM DETERMINATION IN TOBACCO LEAVES, ASH AND SMOKE

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The concentrations of arsenic (As) and cadmium (Cd) in the tobacco leaf, ash and smoke of 10 kinds of cigarettes collected from different countries worldwide were determined by ICP-MS after microwave-assisted digestion. Total As and Cd concentrations in the tobacco leaves ranged from 0.20 mg kg<sup>-1</sup> to 0.63 mg kg<sup>-1</sup> and 1.8 mg kg<sup>-1</sup> to 9.9 mg kg<sup>-1</sup>, respectively. On the other hand, As and Cd in tobacco leaves were not substantially vaporised by burning and most amounts of them remained in the tobacco ash after burning. Only 1.2 % to 7.4 % of As and 0.1 % to 1.5 % of Cd in the tobacco leaves were vaporised into smoke through the burning. By the speciation analysis of As in tobacco leaves and ash by HPLC-ICP-MS following acid extraction, arsenite [As(III)] and arsenate [As(V)] were determined and trace amount of monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsine oxide (TMAO), tetramethylarsonium (TeMA) and some unidentified As species were also found. Arsenic speciation for the smoke absorbed in an aqueous solution was carried out. The sum of As species in tobacco leaves, ash and smoke was in good agreement with the result of total As determination in each sample, and the recoveries of speciation were 100 ± 10 %. The distributions and the behaviours of As species were clarified. It was found that some of the Arsenic species were formed through smoking process.

## SPECIES ANALYSIS TO UNDERSTAND THE BEHAVIOR OF GADOLINIUM IN MAIZE PLANTS

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Earlier studies [1] showed the influence of Gd on the nutrient balance and very high concentrations of Gd in the root tissue, with low transport to shoot tissue. Therefore, speciation and imaging of Gd in root tissue and xylem sap samples were conducted to understand the behavior of Gd in the plant compartments.

High content of Gd was found in the dried bulk samples of the roots after aqua regia digestion. Gd was analysed in spots of high concentrations at the epidermis of the root by ToF-SIMS. The typical isotope pattern was identified for Gd as well as for Gd species bound to oxygen. The expected Gd-phosphates could not be found in these spots. The occurrence of the spots in the epidermis might explain the low transfer rates of Gd from solution into the plants. For the first time, ToF-SIMS analysis with a spatial resolution of 5  $\mu\text{m}$  was used to locate these spots and to obtain information on the species of the Gd in the plant root [2].

The Gd concentrations in the xylem sap were analyzed in relatively high concentrations of 300 – 500  $\mu\text{gL}^{-1}$ . A speciation method (HPLC-ICP-MS) was developed to analyze the potential complexes of Gd with low molecular weight organic acids (LMWOA). The concentration of the LMWOAs has a strong influence on the retention time of the Gd-complexes. As a consequence, a matrix adapted calibration with concentrations of the LMWOA concentrations similar to the xylem sap was found to be a suitable approach.

In the end, we could identify the reason for the high concentrations of Gd in the roots and to explain the high tolerance of the plants. Additionally, we found an answer why the Gd can be analyzed in high concentrations in the xylem sap in the presence of phosphate without formation of phosphate precipitates.

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## THE USE OF STABLE ISOTOPES TO PROBE IRON SPECIATION IN PLANT SAPS

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Despite the essential role of iron in plant physiology, its high concentrations in soil can lead to serious environmental pollution; some of the most affected areas can be found in Brazil - the second largest Fe producer. The recovery measures proposed include revegetation of these areas with plants able to assimilate high contents of iron. Knowledge of the physiological and molecular mechanisms of this cost-effective approach to environmental rehabilitation is essential to design, optimize and improve strategies of revegetation of the post-mining areas impacted by excess of iron.

Studies of very complex homeostatic networks controlling the uptake and tissue distribution of iron in plants require analytical techniques able to supply qualitative and quantitative information on the molecular details of the species involved. So far, the viable analytical methods available are scarce owing to the low content and – in many cases – lability of iron-organic ligand coordination complexes.

The approach proposed is based on the state-of-the-art methodology involving the coupling of hydrophilic interaction liquid chromatography (HILIC) with elemental and molecular mass spectrometric detection. The essential part of the analytical development is the control of species stability by stable isotope spikes which undergo the same processes as the species originally present in the sample. The quantification is carried out on the basis of species formed in plant saps from known quantities of isotopic spikes and excess of naturally occurring ligands.

The method was applied to the identification and quantification of iron-metabolites in two plants species (*Setaria parviflora* and *Paspalum urvillei*) native to South America, tolerant to excess Fe and recommended for the recovery of degraded areas impacted by post-mining waste disposal. The species present include citrate and mixed citrate-malate iron complexes. The knowledge of the tolerance mechanisms of these species to iron will help in the selection of new candidate species in the use of revegetation of the iron-polluted areas.

## STUDY OF $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Eu<sup>(III)</sup> AND HUMIC SUBSTANCES INTERACTIONS USING ESI-FTMS

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Modelling of the environmental behaviour of Eu requires knowledge on Eu sorption species forming at soil mineral surfaces. Of particular interest is the sorption of humic substances (HSs), which is known to enhance surface reactivity and sorptive capacity of minerals towards Eu, at low pH of soils. HSs are expected to fractionate during sorption, as they are complex mixtures of organic compounds with specific chemical nature, structure and reactivity. To address the effect of HS sorptive fractionation on Eu sorption, we investigated the (co)sorption of Eu(III) and a reference fulvic acid (Pahokee Peak Fulvic Acid, PPFA) onto alumina colloids, with the aim of gaining molecular-scale insights on chemical identity of sorbed PPFA compounds by using ESI-FTMS analysis of solutions before and after sorption.

Batch (co)sorption experiments of PPFA (25mg.L<sup>-1</sup>) and Eu<sup>3+</sup> (10 $\mu$ M) at pH 5 in 25g.L<sup>-1</sup>  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> colloid-solution suspensions showed that sorption of PPFA induced (i) surface charge reversal of the colloids and (ii) almost quantitative sorption of Eu, suggesting strong Eu-PPFA-alumina-surface interactions. ESI(-)-MS analysis of native PPFA solution confirmed the complex nature of PPFA. Thanks to high resolving power and mass accuracy of mass spectrometer, ca. 8000 compounds were detected. A chemical formula was ascribed to 5040 compounds, which belonged to three classes, namely polycyclic aromatic compounds (PAC), not-condensed aromatics (NCA) and aliphatics.

Examination of MS spectra of supernatants from batch experiments evidenced a strong sorptive fractionation of PPFA. It was inferred that 28% of the compounds identified in native PPFA solution were quantitatively sorbed, and the others were partitioned between solution and alumina surface to very varying degrees. A main result is that the quantitatively sorbed molecules were mostly aliphatics and NCAs with a high O/C ratio (>0.6) and some highly unsaturated PAC, while the more aliphatic compounds of low/intermediate O/C showed very weak affinity for surface. Therefore, the PPFA compounds showing the highest affinity for alumina surface were aliphatics and NCAs exhibiting multiple oxygen functionalities. It is suggested that these highly reactive compounds are those involved in the sorption of Eu at acidic pH at alumina surface.

## **SESSION 9**

Elemental speciation methods of colloids  
and nano-particles  
Speciation analysis in petroleum chemistry  
Remediation technologies

**MERCURY TOXICITY IN MARINE ANIMALS –  
ACCUMULATION AND DETOXIFICATION  
OF Hg AND MeHg**

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Mercury is a well known toxic element which can occur in different forms, and the implications of neurotoxic MeHg exposure to humans have been shown drastically with the Minamata event which left many people dead and thousands chronically ill. Despite its high toxicity, MeHg is readily accumulated in the marine food chain, with concentrations in the high mg per kg range in fish and marine mammals at the highest trophic level.

In this presentation, we will explore the bioaccumulation and possible detoxification in organs of marine mammals, here in a pod of Long Finned Pilot Whales stranded at the Scottish east coast. We present Hg levels and Hg speciation results in five different organs of these animals (Liver, Kidney, muscle, brain and blubber) and evaluate the findings with correlations versus age, tissue type and mercury species. We suggest that neurotoxic MeHg is detoxified by Selenium, forming non-bioavailable inorganic HgSe clusters.

## **TRANSFORMATION AND FATE OF SILVER AND CERIUM OXIDE NANOPARTICLES IN THE AQUATIC ENVIRONMENT**

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Natural transformation processes, such as aggregation or degradation, can control the environmental fate and behavior of nanoparticles (NPs) released into the environment. Among nanoparticle properties, their size distribution has a tremendous impact on the evaluation of their potential effects. This study investigated the fate of silver (Ag) and cerium oxide (CeO) nanoparticles and NP transformation products in different types of natural water. Following a transformation period, size distribution of NP forms in waters was determined by ultrafiltration and SP-ICP-MS techniques and NP shape and size were confirmed by electronic microscopy. The set of analytical tools also allowed to characterise their transformation products. Particle size distributions changed significantly under different experimental conditions where most material was also found in coarse colloidal fractions (< 100kDa). Water chemical properties such as organic carbon had significant impacts on the fate and changes in forms of both NP Ag and CeO. AgNPs formed aggregates in water with relatively high values of organic carbon concentrations. AgNPs were also degraded as observed with the stars formation. In contrast, no Ce was found in the truly dissolved fraction indicating no evident NP degradation for CeO. More than 90% of NPs CeO was found as large colloids. NPs CeO were preferably accumulated in fish gills, likely adsorbed onto gill surface, and accumulation was the highest in green waters. Even NPs CeO were less accumulated than NPs Ag, NPs CeO were more harmful as they induced fish mortality. The high level of natural organic matter in water can reduce the global toxicity of the NPs Ag and CeO; nonetheless some of them in small aggregates induced toxic effects. Future research on nanotoxicity should consider potential transformation for an improved risk assessment of released nanoparticles.

### **Acknowledgements:**

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## **NEW FRONTIER OF METAL SPECIATION: DETECTION AND CHARACTERIZATION OF NANOPARTICLES IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES BY MEANS OF SINGLE PARTICLE ICP-MS**

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The use of engineered nanoparticles (ENPs) in several technological applications and in consumer products has increased significantly in recent years. This widespread use leads to their release into the environment, raising serious concerns about their potential impact. For this reason, the sustainability of nanotechnology implies a reliable risk assessment of nanomaterials and nanoparticles in relation with human health and the environment. The development and implementation of regulatory policies relies on the availability of methodologies for the detection, characterization and quantification of inorganic ENPs in the different types of samples. Going a step further, the correct interpretation of the results strongly depends on the determination of the physico-chemical form of the element and hence knowledge of speciation is essential.

For example, it is critical to know whether the toxicity observed by cytotoxicity assays with human cells is due to the inorganic ENPs themselves or the ions released by them; in studies of bioavailability of inorganic ENPs in plants it is also important to determine whether a plant takes up intact ENPs and to delineate the processes the latter can undergo (dissolution, aggregation, etc). Moreover, the detection of NPs may complement other speciation studies since natural occurring nanoparticles could be the “invisible species” which are not observed by common speciation techniques. In this context, the method of single particle ICP-MS will be outlined and illustrated using the results of three different studies: characterization of nickel NPs in human skin cells, uptake and accumulation of platinum NPs by plants and detection of naturally occurring selenium NPs in yeast.

### **Acknowledgements:**

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## ACQUIRING INFORMATION ON SPECIATION OF SILICON IN FUELS OF DIFFERENT ORIGIN USING FAAS AND WD XRF

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Determination of silicon is a hot topic of spectral elemental analysis of petroleum – related samples. It is also a challenging task due to, among others, high risk of contamination / analyte losses and strong interferences [1-4]. However, in authors' opinion the most difficult problem in determination of Si as well as in Si speciation analysis is the different behaviour of various analyte forms in an analytical procedure. For example, such difficulties were observed in direct analysis using flame atomic absorption spectrometry (FAAS) [4], inductively coupled plasma optical emission spectrometry [2] and inductively coupled plasma mass spectrometry (including chromatography samples introduction) [1,3]. In the most sophisticated approaches, detection limit about 1  $\mu\text{g kg}^{-1}$  [3] or detection and quantitative determination of about 100 organic Si compounds were possible [1].

The aim of this work was to develop an analytical scheme to acquire information on silicon speciation in petroleum products / alternative origin fuels which can contain not only various organic, but also inorganic Si forms.

Four groups of Si forms were distinguished: very volatile organic, volatile organic, non-volatile organic and inorganic (represented by hexamethyldisiloxane, b.p. 101 °C, octamethylcyclotetrasiloxane, b.p. 176 °C, modified polydimethylsiloxane and silicon dioxide, respectively). FAAS and WD XRF (wavelength dispersive X-ray fluorescence) were applied as analytical techniques. Samples were analysed in an organic solution or in an aqueous solution (after mineralization and fusion with lithium metaborate). The advantages / drawbacks of particular procedures made it possible to differentiate the behaviour of particular Si forms. For example, too high result of direct FAAS analysis indicates enrichment of very volatile Si forms in a gas phase of the system, while too high results of WD XRF analysis can indicate SiO<sub>2</sub> sedimentation.

The developed analytical scheme was applied for analysis of model as well as real samples, such as Diesel oil, marine fuel, oil contaminated with modified polysiloxanes and oils from waste processing (processed plastics, processed tyres).

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## LESS STUDIED SPARINGLY-SOLUBLE ELEMENTS: HOW TO DEAL WITH THEIR SPECIATION IN CULTURE MEDIA

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Substantial progress has been achieved over the last 30 years in our understanding of metal fate in environmental systems and their interactions with organisms but also a huge amount of research proved useless. The reason is that, in ecotoxicity and toxicity studies, solution chemistry was generally overlooked: the use of oversaturated solutions, uncontrolled complexation of trace metals, pH variations during experiments, etc. have been more the rule than the exception. When the situation looked under control for some notorious elements such as lead, mercury or arsenic, many elements that had remained essentially unused are becoming essential components in a variety of applications ranging from information and communication technologies, semiconductors, electronic displays to 'green energy' related technologies [1]. Nothing, or very little, is known about their (eco)toxicity. Among these elements, many are sparingly soluble, which raises again problems already experienced with other elements such as Cr(III) [2] or Sb(III) [3] in the past. The complexity of some current culture media (e.g., [4]), together with the lack of equilibrium and solubility constants for these elements, probably requires approaches different from the calculation of the speciation in solution in order to know what the organisms are being exposed to.

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## SYNOPSIS OF DIVALENT METAL IONS SORPTION ON TITANIUM(IV) PHOSPHATE ION-EXCHANGERS

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Titanium (IV) ion-exchangers have been extensively studied regarding water purifications due to their high mechanical and thermal stabilities, high resistance to oxidation and high sorption capacity towards various transition metal ions. It has been demonstrated that their physicochemical properties and their structural characteristics can be selectively altered when different synthetic conditions are used. This work focuses on the synthesis and sorption properties of TiP sorbents towards  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  ions. The Ti(IV) ion-exchangers are all obtained at different *mild* synthetic conditions. It is shown that a careful change of the titanium and sulfuric acid contents in the primary solutions combined with successive washings with HCl can lead to either crystalline  $\alpha$ -TiP (composed of  $-\text{HPO}_4$  groups), amorphous dihydrophosphate  $\text{TiO}(\text{OH})(\text{H}_2\text{PO}_4)\cdot\text{H}_2\text{O}$  (TiP1) or amorphous TiP products containing both  $-\text{H}_2\text{PO}_4$  and  $-\text{HPO}_4$  functional units.

The sorption characteristics towards the transition metal ions were investigated and it was found that the obtained TiP1 sorbent had imminent ion-exchange kinetics and a higher exchange capacity than the data reported so far. The sodium uptake of TiP1 was estimated to be  $6.3 \text{ meq}\cdot\text{g}^{-1}$  which is among the highest values found in literature. The maximum sorption capacity of the Na-TiP1 form towards divalent metal ions was determined to be  $3.1\text{-}3.9 \text{ meq}\cdot\text{g}^{-1}$  with a selectivity order as follows:  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+}$ .

Furthermore, the TiP1 sorbent has shown very promising sorption behaviour when batch experiments with industrially polluted waters were performed.

### **Acknowledgements:**

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# **POSTER SESSION**

## NEW METHODS FOR THE DETERMINATION OF TRACE CONCENTRATIONS OF <sup>99</sup>Tc IN WASTEWATER

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Technetium (Tc) is the lightest element without stable isotopes and occurs naturally only in trace amounts. Nevertheless, nowadays Tc occurs even more often than some stable elements. The most relevant nuclide is <sup>99</sup>Tc, which is generated in high amounts in nuclear waste and possesses a half-life of 214,000 years. The present abundance of <sup>99</sup>Tc is almost exclusively the result of anthropogenic contamination resulting from processes like nuclear weapon testing, reprocessing of spent nuclear fuel, nuclear accidents as well as nuclear power plants.

The nuclear isomer <sup>99m</sup>Tc is widely used in radiopharmaceuticals in diagnostic medicine (scintigraphy) for the imaging of target organs or tumours. After administration, the radiopharmaceuticals are excreted by patients, access the wastewater and subsequently the environment. Tc is believed to evolve to an important contributor to the future collective dose affecting the population. Additionally, <sup>99</sup>Tc is considered to be the most important radionuclide in risk assessment of radioactivity in the environment as well as in the decommissioning of nuclear facilities and the management of nuclear waste. Up to now, the determination of Tc in environmental samples is mostly done by means of beta radiation counting, which requires long measurement times and is less sensitive than methods such as inductively coupled plasma mass spectrometry (ICP-MS). Furthermore, there are no studies available dealing with the long term input of Tc into the environment due to diagnostic facilities.

In this work, two methods for the ultra trace analysis of Tc in environmental samples were developed and the input into the environment due to diagnostic facilities was studied. Wastewater samples were taken within the catchment area of a nuclear diagnostic facility and finally analysed by means of sector field ICP-MS. Due to polyatomic interferences a solid phase extraction method was developed and used, which furthermore preconcentrates Tc. Rhenium (Re), which is known to possess a comparable chemistry, was used as internal standard. Quantification was carried out by means of a new dilution method called isobaric dilution analysis, where a Tc sample is spiked with a Ru standard exhibiting an isobaric isotope with  $m/z$  99. By recording isotope ratios and considering different element specific responses, elevated concentration in the lower pg/L range could be determined, which are associated with the discharge of a local diagnostic facility. The method was further improved and automatized by means of an online extraction with a post column dilution set up enabling the calibration of transient signals.

## ALUMINUM FOIL – A POSSIBLE SOURCE FOR FOOD CONTAMINATION?

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Aluminum is the most abundant metal in the Earth's crust. Because of its low density and for its ability to resist corrosion it is widely used, especially in the industry. Furthermore we find it in everyday products like cosmetics, drugs and sun creams or we use it as aluminum foil in the kitchen. But some studies suggest that aluminum plays a role in diseases like Alzheimer disease<sup>[1]</sup> or breast cancer<sup>[2]</sup>. Also possible accumulation in the lung, bones, liver or brain can cause problems. To evaluate the contribution of aluminum foil in contact with food to our daily exposition, three different approaches were used. On the one hand different foodstuff (e.g. meat, fish and potatoes) were wrapped into aluminum foil and then baked in an oven for about 45 minutes at 180°C to simulate a normal cooking procedure. On the other hand several food samples were wrapped in aluminum foil and then stored in a refrigerator for either one day or three days to simulate the typical handling of food leftovers. Furthermore some food samples were placed on a steel plate and then covered with aluminum foil for again one day and three days. After exposition to aluminum the food was freeze-dried and digested using a microwave assisted acid pressure digestion. Analysis was performed with ICPMS. For quality control the reference material "bovine muscle powder", blanks, drift standards and internal standards were used. Results suggest at least a slight increase of the food aluminum concentration in all food samples after contact to the aluminum foil. The concentration further increases on the one hand due to longer exposure time and on the other hand with additional contact to a material with a higher standard electrode potential like for instance a steel plate.

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**COLORIMETRIC DETERMINATION OF LITHIUM IN  
NATURAL WATER USING THE AZO COMPOUND THORIN  
(C<sub>16</sub>H<sub>11</sub>AsN<sub>2</sub>O<sub>10</sub>S<sub>2</sub>)**

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Lithium (Li) is arguably the most important element when it comes to the energy needs of the future. Li batteries are currently the most efficient chemical energy accumulators making Li a crucial component in modern battery technology. Li batteries are fundamental to the future production and availability of mass produced electric vehicles (EVs) which are already starting to populate our streets. This EV rush has created a market for lithium resources, a demand that mining companies are keen to meet. Li is too reactive to occur in nature un-combined nonetheless there are some areas in the world where Li has accumulated into economically viable deposits. The most accessible sources of Li on our planet are located in the high altitude brine aquifers of the South American salt flats. Geochemistry has also deposited mineable amounts of Li rich minerals in crystalline igneous rocks called pegmatites. The South East of Ireland hosts several occurrences of these Li rich pegmatites.

The possibility of Li being extracted from Irish rock comes with potentially negative environmental issues associated with mining. Mining processes, no matter how environmentally aware, present some very real dangers to natural waters particularly by metal infiltration. There is a need to establish baseline levels of Li in the natural waters of the area prior to any mining activity. The current work involves the quantification of trace amounts of Li in the natural waters of the area. Lithium is often overlooked when it comes to natural water analysis and there is very little literature regarding its quantification in aqueous environments. Li is normally determined using either emission or absorbance flame spectroscopy which are both expensive processes. Developing an inexpensive colorimetric method for the determination of Li was desired for this project.

It has long been known that azo compounds combine with certain metallic ions to form characteristically coloured complexes. Thorin (Disodium 4-[2-(2-arsonophenyl)hydrazin-1-ylidene]-3-oxo-3,4-dihydronaphthalene-2,7-disulfonate) is one such azo compound that is currently used mainly in psychiatric pharmacology as a chromogenic agent for colorimetric determinations of Li in biological samples, in association with the treatment of certain conditions like bipolar disorder. Thorin was first used in the colorimetric analysis of Li in mineral ore samples, by the Oak Ridge National Laboratory, USA in the 1950s. The Thorin method used in our analyses of natural waters was adapted from the Oak Ridge mineral ore analysis protocol.

## NATIVE FLUORESCENCE DETERMINATION OF TETRACYCLINE RESIDUES IN MILK PRODUCTS BY SILICA-COATED MAGNETIC NANOPARTICLES

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The presence of antibiotic's residues in food represents a risk for human health, and it should be correlated to the occurrence of strain resistance to antibiotics, allergic syndromes, and disorder of intestinal flora, with concomitant reduction of microbial production of vitamins. The concentration of tetracycline in milk and milk products a maximum residue level of 100 µg/kg has been established. Various methods have been used for the determination of antibiotics: HPLC, spectrophotometry, electrochemistry, fluorescence and etc. Surface functionalized magnetic iron oxide nanoparticles are new kind functional materials, which have been widely used in sensing and biotechnology. In this study, magnetite nanoparticles modified with ions Eu(III) was used for development of optical sensors for antibiotics determination.

In this work we report preparation of iron oxide nanoparticles with amino- and phosphonic-derivatives by means two different routes. One of them the most popular rout is based on the covered Fe<sub>3</sub>O<sub>4</sub> with a chemically inert a think silica layer consist amino (-NH<sub>2</sub>) and then phosphonic(-PO<sub>3</sub>H<sub>2</sub>) groups. The other ways is based on dopamine anchors covalent bonded with surface of Fe<sub>3</sub>O<sub>4</sub>. Nitrodopamine, was used as a precursor to prepared this nanoparticles. Thereafter, the dopamine-doped nanoparticles of magnetite was functionalized phosphonic(-PO<sub>3</sub>H<sub>2</sub>) groups. The magnetic nanoparticles have been synthesized by chemical co-precipitation method.

The using of phosphonic-derivatives allows to obtained core-shell particles with complexing properties. Isotherm adsorptions of ions europium(III) on surface silica-coating Fe<sub>3</sub>O<sub>4</sub> nanoparticles refers to the L-type. Sorption of europium(III) was quite rapid and equilibrium was achieve after 15 min. The optimum concentration of europium ions on surface magnetite nanoparticles for the determination of trace amounts of tetracycline in aqua solution is 2.5·10<sup>-5</sup> mol/l for Tetracycline in concentration range 1.0·10<sup>-5</sup> M–1.0·10<sup>-8</sup> M.

A preliminary series of experiments were obtained in water solution of tetracycline and showed that maximum intensity was achieved for pH close to 7. Similar measurements run on blank milk samples evidenced a different behavior: The maximum emission intensity was found for pH=7-7.2.

In the optimal experimental conditions, linear relationships were obtained, between intensity of fluorescence and concentration of tetracycline in milk samples.

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## COMPARISON OF THE CONTENTS OF SELECTED XENOBIOTICS IN HONEY BEES WITH REGARD TO THEIR HABITAT

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Colony collapse disorder (CCD) is the phenomenon that occurs when the majority of worker bees in a colony disappear and leave behind a queen, plenty of food and a few nurse bees to care for the remaining immature bees and the queen. During last few decades there was observed a drastic rise in the number of disappearances of honey bee (*Apis mellifera*) colonies. Colony collapse disorder causes significant economic losses because many agricultural crops worldwide are pollinated by honey bees. Several possible causes for CCD have been proposed, but no single explanation has gained widespread acceptance. Very likely CCD is caused by a combination of factors such as infections, malnutrition, various pathogens, genetic factors, immunodeficiency, loss of habitat or its pollution. Founding apiaries in the cities allows to avoid some of these factors, although new risks emerge due to the industry and traffic. The purpose of this study was to compare the contents of selected elements (Zn, Cd, Pb, Cr, Al, Se, Co, Mn, Cu, As) and pesticides in bees from hives located in urban and rural areas. Also it was checked whether these elements are accumulated on the surface or inside the bee's body. The samples of bees were washed (optionally) and dried and then selected parts or whole bees were mineralized using conventional heating. Determination of selected elements was carried out using inductively coupled plasma mass spectrometry. Larger contents of As and Cd are observed in samples of bees coming from urban areas. Other elements are present in the bees in comparable amounts. In the case of rural bees, significantly higher amounts of Cr and Zn were found on the surface of the insect's body.

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## **DETERMINATION OF Se IN DIETARY SUPPLEMENTS BY PHOTOCHEMICAL VOLATILE SPECIES GENERATION ATOMIC ABSORPTION SPECTROMETRY**

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The technique of volatile species generation has recently seen renewed interest due to the development of new generation approaches. The main advantage of this technique is the separation of the analyte from the sample matrix and the subsequent possibility to decrease spectral interference and improve the limits of detection in comparison with the direct analysis of liquid samples by atomic spectrometric methods.

Regular intake of selenium is recommended for its cancer protective effects and for improving the state of human skin, hair and nails. [1] For these reasons it is a common component of dietary supplements. However, regular intake of high doses of Se may lead to garlic breath, poor dental health, disorders of the nervous system and skin and hepatic toxicity caused accumulation in liver. It may also increase the risk of type II diabetes. [2] At the moment, contents of constituents of dietary supplements are subject only to a limited regulation, which is set by the Regulation (EC) No 1925/2006 of the European Parliament and of the Council. It is necessary to continue developing sensitive and accurate methods of Se determination suitable for control of dietary supplements.

This contribution proposes determination of Se in multivitamine dietary supplements containing either sodium selenite or sodium selenate. The determination is based on the photochemical generation of volatile compound of selenium from the medium of acetic acid with the aid of the TiO<sub>2</sub> photochemical catalyst. The generated volatile compound was transported into the quartz tube atomizer and determined by AAS. The necessity to reduce selenate prior to the generation of volatile species of Se is eliminated as the prereduction step takes place during the generation process and similar sensitivities were observed for Se (IV) and Se (IV). Nevertheless, their behaviour during the extraction step is very different requiring different extraction procedures.

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## HIGHLY SENSITIVE IMPEDIMETRIC SENSORS FOR MERCURY IN AIR AND IN WET DEPOSITIONS

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Recently, global traceability of mercury has been addressed with a network approach using automated and/or semi-automated systems for its sampling and detection in air and/or wet deposition based on commonly used analytical procedures for the determination of mercury in precipitation in global network. These latter require significant running costs for sampling and shipping samples to the reference laboratories, especially in remote regions such as Antarctica or in underdeveloped areas that do not have basic infrastructures. The sustainability of global scale monitoring networks for measuring mercury in air or precipitation samples depends on the development of advanced online (bio)sensors capable to quantify total mercury or even better speciated mercury concentrations. These advanced sensors should be robust, traceable and do not require gas carrier, significant energy supply and highly qualified technical expertise.

Taking into consideration all the above, preliminary results on several sensors based on electrochemical impedance spectroscopy (EIS) for mercury speciation in air or wet deposition are reported:

- 1) Hg(I) and Hg(II) from wet deposition are electrochemically reduced to Hg(0) and deposited on a gold micro-electrode.
- 2) Similarly Hg(0) from air spontaneously reacts on gold electrode to create amalgam.
- 3) Hg(II) selectively reacts with oligonucleotides (12 bases) made of thymine. EIS, a powerful and sensitive technique, allows querying the electrode surface.
- 4) Hg(II) ions specifically interact with limonene based polymers.

After EIS measurement Hg(0) can be easily removed from the gold surface by electrochemical oxidation and Hg(II) with imidazole. Minimal volumes (600 nanoL) and surfaces play a role in sensors performances. High sensitivity, L.o.d.= 0.06 ppq, L.o.q.=0.10 ppq and a sampling rate from 3 to 12 samples/h have been obtained.

## **DETERMINATION OF TELLURIUM IN FLAVOURED MINERAL WATERS BY ELECTROCHEMICAL HG-AFS**

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Tellurium is one of the heavier trace elements and its high amounts in environment are not welcome. It belongs to the group of elements which readily form volatile hydrides. This makes a hydride generation coupled with atomic spectrometry the first choice method for its analysis. Hydride generation is a sample introduction technique commonly used in atomic spectrometry. Its main advantages are an easy separation of the analyte from a matrix, possibility to use milder atomization temperatures and reduction of atomization interferences leading to an increase of the determination sensitivity. Conventionally the hydride generation is performed chemically, but the main disadvantage of this conventional method is the necessity to use tetrahydridoboritanes. These are very reactive and unstable and need to be prepared daily or stored frozen; in addition to their high cost. One of alternatives to the chemical approach is the electrochemical generation, using electrical current as the reductant and a solution of a strong mineral acid as a source of hydrogen.

The presented study focuses on the investigation of the electrochemical tellurium hydride generation and its atomization in microflame AFS. A laboratory-made electrolytic cell was designed for the purpose and the generation setup was optimized and subsequently the analytical figures of merit were determined; the obtained limit of detection is  $4 \text{ ng} \cdot \text{ml}^{-1}$  (4 ppb). In addition an interference study was carried out. The studied interferents were chosen from various groups of metals: i) other hydride forming elements, ii) transition metals, iii) alkali metals and iv) alkali earth metals. The great performance of the method, especially for the last two mentioned interferent groups, suggests that it allows water samples to be analyzed without any pre-treatment. This also brought up the question of interference of organic compounds. Mineral water with artificial flavorings was chosen as model sample contaminated with organic interferents. Unsweetened mineral water and several randomly chosen flavors were acidified, spiked with tellurium standard solution and analyzed. Even though more complex water matrices presented some problems, the analytical process was practically not influenced by the majority of flavors and sugar; with exception of raspberry flavored water, which interfered strongly. The developed electrochemical hydride generation method coupled with AFS thus proved to be a complex method capable of direct determination of tellurium in real samples.

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## STUDY OF pH EFFECT ON EXTRACTION OF GLYPHOSATE AND AMINOMETHYLPHOSPHONIC ACID FROM EUCALYPTUS MATRIX USING HPLC-ICP-MS/MS AS DETECTION SYSTEM

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Glyphosate [N-(phosphonomethyl) glycine] (GLY) is an organophosphorus non-selective post-emergent herbicide, which is absorbed by leaves and translocated through the plant and widely used in eucalyptus culture for weed control. There are few studies about the effects of GLY in the eucalyptus growth due to challenges related with trace determination of this herbicide in the plant matrix. Usually, the separation and analysis methods used for the determination of GLY and its metabolite, aminomethylphosphonic acid (AMPA), are based on GC or HPLC. However, the absence of chromophoric groups and low volatility of these compounds requires derivatization step before analysis. HPLC-ICP-MS/MS has some advantages in this application such as no requirement of derivatization step, specific element detection (P), high sensitivity and capacity to eliminate interference from matrix. In this study it was studied an extraction method of GLY and AMPA in eucalyptus wood for subsequent quantification by HPLC-ICP-MS/MS. Samples of eucalyptus wood were spiked with GLY and AMPA. Then in these samples were added 5 mL of ultrapure water with pH properly adjusted to 1, 3, 5, 7, 9, 11 and 13. The system was homogenized by shaking for 60 s and centrifuged at 4000 rpm for 10 min. The supernatant collected was reduced and the concentrated extract was resuspended into 3 mL of mobile phase (50 mM acetic acid/ammonium acetate + 5mM tetrabutylammonium + 1% methanol, pH = 4.7). The chromatographic separation was performed using analytical column Zorbax SB-C8 (4.6 mm x 150 mm, 5 µm) at 30 ° C and the mobile phase (above mentioned) flowing at 1 mL min<sup>-1</sup>. The quantification was done by ICP-MS/MS in mass shift mode with O<sub>2</sub> where P was detected as PO<sup>+</sup> at m/Z 47. The best GLY recovery was 72 ± 4%. AMPA showed recovery above 100% maybe due to phosphorus based compounds present in the matrix with the same retention time which may require a clean-up step. This work shows the potential of the HPLC-ICP-MS/MS for trace level determination of GLY and AMPA in eucalyptus.

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## **FIT FOR PURPOSE ANALYTICAL METHOD FOR DETERMINATION OF LOW LEVEL MERCURY IN SEAWATER: EXTENDED VALIDATION STUDY**

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With the eventual ratification of the Minamata Convention on Mercury, United Nations/IAEA Member States will be required to establish or strengthen environmental mercury monitoring efforts. Among its many tasks, the IAEA Marine Environment Studies Laboratories (IAEA-MESL) in Monaco acts as the analytical support center for IAEA Member States' laboratories and is the pillar of the IAEA Quality Assurance program for determination of contaminants in the marine environment. As such, IAEA-MESL has developed and validated a method for ultra-low level analysis of total mercury (THg) in seawater in order to better assist Member States' laboratories with mercury analysis and mercury data quality assurance.

An analytical procedure using cold-vapor atomic fluorescence spectrophotometry (CVAFS) along with improved cleaning and sample processing methods was optimized and validated according to the recommendations of ISO-17025 standard and Eurachem guidelines. Importantly, a limit of detection and limit of quantification, after extensive cleaning and careful sample preparation, was possible at ultra-low levels (LOD = 0.01 ng/kg; LOQ = 0.04 ng/kg) using a relatively small sample volume (25ml). However, these values were variable over time and highly dependent on clean analytical technique. Additional parameters such as recovery, working range, repeatability, intermediate precision and combined uncertainty (28%,  $k=2$ ; ~ 0.2 ng/kg concentration levels) were also carefully estimated.

All sample preparation steps were carried out in a clean laboratory environment under clean hoods (Class 100).

The traceability of obtained measurement results was also demonstrated. Particular attention was paid to the correct definition of the measurand in this validation study. The mass fraction of mercury dissolved in seawater and mercury associated with solid particles was estimated for a coastal seawater sample from the Mediterranean Sea and the respective mass balance provided.

As part of the method validation, sample preservation methods, sample preparation methods and stability of samples were also investigated. As was found in previous research, preservation of seawater samples with 0.1% (v/v) nitric acid was acceptable for short-duration (up to 1 month) holding times. In this instance, nitric acid proved effective for sample stability for both unfiltered and filtered sample processing at concentrations around 0.47 ng/kg and 0.20 ng/kg, respectively.

Additional validation of the proposed analytical procedure was achieved by participation in an Inter-Laboratory Comparison (ILC) study. The results provided were in excellent agreement with the assigned values of the ILC.

## A LEAD ISOTOPE STORY OF A PINE TREE

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The soils contamination by lead (Pb) in the region "Riesenbecker Osning", the northwestern part of the Teutoburg Forest in the Northwest German lowlands, is assumed to originate from coal combustion. A lead isotopic analysis of the affected trees, soils, and waters in this region provided some unexpected values and a high variance. It was hypothesized that hat a source other than soil was of importance, especially in the trees. Intensive fighting between German and British troops took place during the last month of World War II in that region. Lead ammunition in the wood of trees could be such a different lead source.

A tree (*pinus sylvatica*) was sampled together with the soil profile in the direct environment. The selected tree was about 130 years old. With a metal detector the locations of bullets in the wood were identified and the wood samples of this section were analyzed for lead concentrations (ICP-MS, Agilent 7700) and lead isotope ratios (MC-ICP-MS, Neptune Thermo) after digestion.

The wood around the bullets was clearly affected. We found strongly elevated lead concentrations as well as the same isotope ratios as in the bullets. Two different isotope ratios of the bullets were identified. Both these ratios differ significantly from the lead isotope ratio in the contaminated soil.

Additionally, branches and needles of the pine tree were investigated for lead concentrations and lead isotope ratios. Some of these samples show a clear influence of the bullet lead in their isotopic ratios. This seems to be a suitable explanation for the previously observed unexpected isotope ratios in this region.

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## **EFFECT OF ORGANIC AND INORGANIC AMENDMENTS TREATMENT ON BIOAVAILABILITY OF METAL(LOID) IN PADDY SOILS**

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This study was aimed to investigate the effect of some organic and inorganic amendments application to paddy soils, for the purpose of reducing metal(loid) uptake by rice, on the soil-rice plant continuum. Pot experiment was conducted to evaluate the effect of lime, organic matter, iron and sulfur on the changes in Cd solubility in soils and the uptake by rice. Cadmium content in polished rice for iron chloride and (iron chloride+organic matter) treatments was only 16-23% compared to control and 25-37% compared to lime treatment, however, sulfur treatment rather increased the rice Cd. To examine the effect of sulfur and soil amendments on metal(loid) uptake by rice, a field study was performed. The maximum As reduction rate in brown rice after steel slag application was 40%. The effect of organic amendments application to paddy field on the release of soil As was also evaluated. Addition of several organic matter to paddy soils increased the As content in soil solutions than control. After application of organic matter, the As content in soil solutions from As-rich soils increased in all treatments excepting swine liquid manure treatment than control. Among As species, As(III) was dominant in soil solutions. Total As content in brown rice harvested from excessively contaminated soils with As were higher in rice hull, cattle manure and fowls manure (0.5%) treatments than control. And the content from highly contaminated soils with As were higher in fowls manure and swine liquid manure treatments than control. On the other hand, dominant As species in brown rice from excessively contaminated soils was As(III) in all treatments excepting rice hull and rice bran treatments. However, dominant As species in brown rice from highly contaminated soils were As(III) and DMA.

## **RHODIUM ACCUMULATION IN WHITE MUSTARD PLANT**

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Rhodium is the least frequently occurring platinum-group elements (PGES). Due to the unique properties is widely used in industry and jewelry, but nearly 80% -90% of annual supplies of rhodium is consumed in the production of automotive catalytic converters. Not less important is its use in the preparation of anticancer drugs. From various sources, this element may get into the environment, where it is taken up by plants. Under stress related to the presence of metals, plants trigger defense mechanisms, which include, among others, phytochelatins synthesis - stress metabolites, whose role is to complex xenobiotic and thus to reduce its negative impact on plant vegetation.

The aim of the study was to determine the degree of Rh taking from the ground and its transport to the aerial parts of *Sinapis alba* L, cultivated under controlled conditions in hydroponics. During undertaken work the accumulation and translocation factors were calculated. A very efficient transport of rhodium to mustard leaves was illustrated. Moreover a special attention was paid to the synthesis of phytochelatins in plant tissues. High performance liquid chromatography with fluorescence detector and electrospray mass spectrometry were applied. Phytochelatins PC<sub>2</sub>, PC<sub>3</sub> and PC<sub>4</sub> in all plant organs were identified.

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## **SPECIATION OF MERCURY (II) AND METHYLMERCURY IN SEDIMENTS BY HPLC-ICPMS**

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Mercury has several species that differ in their availability, mobility and toxicity. By biotic and abiotic processes natural transformation of these species occurs in different environmental areas [1]. The high mobility and toxicity of methylmercury is one reason for the particular interest in this species. Due to the low concentration of methylmercury in sediments and possible species transformation the determination of these species brings challenges to the developer [2].

For the analysis of the total mercury concentration in sediment samples a direct mercury analyzer has been used. The separation and detection of mercury (II) and methylmercury was performed by HPLC-ICPMS. L-cysteine and 2-mercaptoethanol are two common used additives for the extraction and determination of mercury species [3]. Because of the harmful effect of 2-mercaptoethanol we only performed experiments with L-cysteine. On this basis, this poster deals with the effect of different L-cysteine concentrations on the extraction and separation efficiency.

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**INFLUENCE OF CULTIVATION CONDITIONS ON  
BIOTRANSFORMATION OF SELENIUM IN ONION  
(*Allium cepa* L.)**

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The aim of the study was to investigate the biotransformation of selenium in plants of *Allium cepa*, as well as the identification of factors that may affect these changes.

*Allium cepa* plants were cultivated hydroponically or in soil enriched with Se (IV) or Se (VI). Selenium speciation was determined by HPLC-ICP MS. TEM was used to evaluate the condition of plants treated with selenium.

Metabolism of selenium (IV) and (VI) depends on the conditions of plant culture. During cultivation of *A. cepa* plants in soil containing selenium, biotransformation of Se was found to be different than in the plants grown hydroponically. It was observed that during the cultivation in soil enriched with Se (IV) the organic forms of selenium are metabolized less efficiently than in the case of hydroponic culture. At the same time, plants grown in soil enriched with selenium (VI), were found to have increased proportion of organic forms of selenium, including SeMetSeCys, than plants grown hydroponically.

As the ultrastructure analysis of cells showed, the cause of the differences may be different oxygen conditions in the liquid medium and the soil. They may affect mitochondrial activity of the cells and, consequently, the entire bioenergy of the cells. The results obtained under hydroponic cultivation cannot be directly extrapolated to the processes occurring in natural conditions, where the plants grow in soil.

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## SPECIATION OF AS(III) AND AS(V) IN SOIL SAMPLES BY HPLC-ICP-QQQ

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The toxicity of arsenic depends on chemical forms in which it occurs in the environment. Inorganic species, As(III) and As(V), are considered the most toxic forms, while organic As compounds, such as arsenobetaine or arsenocholine, are much less toxic. Studying the chemical forms of arsenic helps to elucidate its mobility and biological availability. Therefore, it is necessary to determine As species in different compartments of the natural environment, including soils.

The aim of the study was to develop a method of determination of inorganic forms As(III) and As(V) in soil solutions using high performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry (HPLC-ICP-QQQ). A mass spectrometer (8800 QQQ, Agilent Technologies) and a high performance liquid chromatograph (1260 Infinity, Agilent Technologies) were used in the study. In order to eliminate spectral interferences, oxygen as reaction gas and mass shifting arsenic to AsO at m/z 91 were used, which provided lower detection limits and freedom from polyatomic and doubly charged interferences and thus allowed for reduced chromatographic injection volumes. Chromatographic separation was conducted with isocratic elution using the mobile phase: 1 mM phthalic acid, 10 mM EDTA<sub>Na2</sub>, pH=4.5. The IonPac<sup>®</sup> AG7 Dionex guard column and IonPac<sup>®</sup> AS7 Dionex anion-exchange column were used. The time of analysis was 4 min. The obtained detection limits (LD) were 0.08 µg·L<sup>-1</sup> and 0.07 µg·L<sup>-1</sup> for As(III) and As(V) respectively. Accuracy, determined as recovery of As for real samples with addition of a known amount of the element, ranged from 97% to 102%.

Soil samples examined in this study were acquired from one of the biggest mine spoils remaining in Złoty Stok (Poland). In the laboratory conditions, the samples were placed in pots and maintained at constant moisture. Soil solution was collected for analysis by microporous suction samplers (MacroRhizon), after 2 days, 1, 2 and 4 weeks. Arsenates As(V) proved to be predominating species of As in all soil solutions, however, an increase in As(III) concentrations was observed with prolonged time, as related to the changes of pH and Eh. The maximum concentration of As(V) in soil solution was determined at 16.9 mg·L<sup>-1</sup>. The developed method of separation and determination of As(III) and As(V) species in soil solution can be a valuable tool for analysis of environmentally relevant arsenic present in soils.

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## **SPECIATION OF ANTIMONY IN PORE WATER OF SHOOTING RANGE SOILS - THE EFFECTS OF REMEDIATIVE AMENDMENTS**

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Antimony, a trace metalloid, attracts increasing attention because of its toxicity and poorly understood environmental fate. Bioavailability and ecotoxicity of soil antimony (Sb) depend on its total concentrations and speciation. Sb usually occurs in soils in the form of inorganic compounds - Sb(III) or Sb(V), depending on redox conditions; it may also form organic derivatives. Sb(III) is much more toxic than Sb(V). The concentrations of Sb in Polish soils are generally very low ( $< 1 \text{ mg}\cdot\text{kg}^{-1}$ ), however, the soils in ore mining regions and in military shooting ranges may be considerably enriched. This study was aimed to examine the speciation of Sb in soils of two military shooting ranges – in Wrocław and Oleśnica. The effects of soil amendment with FeOx-rich wastes (FeW) and compost (Co), commonly used for immobilization of metals, were examined, with focus on the solubility of Sb and its speciation in soil pore water. Five soil samples, representative for firing posts and earthy stop butts, containing up to  $116 \text{ mg}\cdot\text{kg}^{-1}$  Sb, were collected and examined. Non-amended and treated soils were incubated for 1 month at various moisture (80% and 100%), and soil pore water was periodically collected with MacroRhizon suction samplers. Sb(III) and Sb(V) in pore water samples was determined by HPLC-ICP-QQQ (HPLC 1260 Infinity and 8800 QQQ, Agilent Technologies).

Sb concentrations in pore water were in the range  $61\text{-}908 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ , exceeding by manifold a threshold for good quality underground water and drinking water ( $5 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ ). Soil amendment with FeW reduced Sb solubility by ca. 50-75%, particularly at the beginning of incubation, and this effect decreased with time. On the contrary, Co-treatment caused small initial reduction of Sb solubility, better expressed, however, after a longer time. The contributions of Sb(III) in pore water were at the beginning extremely low ( $<1\%$ ), and tended to increase, depending on pH, Eh and treatment.

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## SOLUBILITY OF ARSENIC IN HISTORICAL MINE DUMPS AS AFFECTED BY DECOMPOSITION OF FOREST LITTER

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Arsenic is considered one of the most toxic elements that has been included in the WHO list of ten chemicals of major public concern. The environmental risk, associated with soil enrichment in arsenic, depends on its potential and present solubility as well as on its speciation. Arsenic present in water and in soil solution may occur both in inorganic forms of As(III) and As(V), of which As(III) is particularly toxic, and as organic compounds with much lower toxicity. The problem of soil pollution with arsenic occurs in Poland only on a local scale, but in the Sudeten Mts. and in their Foreland, there are several sites where arsenic was mined in the past, among them one of the world leading arsenic industry centers Złoty Stok. This study focused on arsenic speciation in soils of a large (2.6 ha) mine dump in Złoty Stok, built of waste rock material that contains up to 4.5% of As. The dump was in the past covered with a thin layer (5-10 cm) of exogenous soil, and was declared a protected area because of numerous individuals of early-purple orchid (*Orchis mascula*) growing on its surface. The dump is surrounded by beech forest; therefore it seems likely that it will be colonized by beech in the future.

The aims of this study were: i) to determine the solubility of As in soil material collected from the dump, ii) to examine its speciation in soil solution, and iii) to examine related effects that may be caused by a decomposing beech litter. Two soil samples containing over 4% of As, were incubated for 1 month at the moisture of 80% and 100%, and soil solution was periodically collected with MacroRhizon suction samplers. As(III) and As(V) in soil solution were determined by HPLC-ICP-QQQ. Arsenic concentrations in soil solutions obtained from untreated soils were in the range 6.9-13.8 mg·L<sup>-1</sup>, and exceeded drastically the threshold values for good quality groundwater (0.02 mg·L<sup>-1</sup>) and drinking water (0.01 mg·L<sup>-1</sup>). These data prove a considerable risk to biota and humans. Application of beech litter to soils resulted in increased solubility of As (by 2-4 fold), with maximum As in soil solution 89 mg·L<sup>-1</sup>. Initial As(III) was very low (<1% of soluble As), but its concentrations increased with prolonged incubation, depending on pH, Eh and the presence of dissolved organic matter.

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## BIOAVAILABILITY OF ARSENIC SPECIES IN RICE SAMPLES

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Rice is the principal food in many countries for billion of people and one of the most consumed cereals in the world. Rice plant has the ability to bioaccumulate essential and toxic trace elements such as arsenic. The toxicity of the elements depends on their concentration but also of their chemical form and their bioavailability. The inorganic forms of arsenic are more toxic than organic forms and the toxicity increases with decreasing oxidation states ( $\text{AsH}_3 > \text{As}^{\text{III}} > \text{As}^{\text{V}} > \text{MMA} > \text{DMA}$ ) [1]. Children under three years of age are the consumers of rice in Europe most exposed to inorganic arsenic thorough the diet (rice-based food). Recently, the European Commission established the maximum levels of inorganic arsenic in foodstuffs. This regulation establishes a maximum level of inorganic arsenic of 0.10 mg/Kg in rice destined for the production of food for infants and young children [2].

Bioavailability study of As species in rice was performed in order to know if a change in As species occur during gastrointestinal digestion process. Rice samples were subjected to simulated gastric conditions (use of pepsin at pH 2.0, orbital – horizontal shaking at 150 rpm, 37°C, 2 hours) followed by a simulated intestinal digestion (use of pancreatin and bile salts at pH 7.4, orbital – horizontal shaking at 150 rpm, 37°C, 2 hours) with dialysis membranes (10kDa).

Arsenic species were then determined in the dialyzate fraction by high performance liquid chromatography coupled to inductively coupled plasma mass spectrometry (HPLC-ICP-MS). A Hamilton PRP-X100 (150 x 4.1 mm, 5 µm particle size) column was used for the separation of arsenic species, using 25 mM  $\text{NH}_4\text{H}_2\text{PO}_4$  (pH 6) as mobile phase operating at a flow rate of 1 mL min<sup>-1</sup>.

The proposed method has been applied to different rice samples acquired in local market. Obtained results of As bioavailability in rice confirm the As species transformation after *in vitro* digestion procedure.

### **Acknowledgements:**

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## **TiO<sub>2</sub> NANOPARTICLES ASSESSMENT AND BIOACCESSIBILITY STUDIES IN SURIMI (CRAB STICKS) BY SINGLE PARTICLE – INDUCTIVELY COUPLED PLASMA – MASS SPECTROMETRY**

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Titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) are commonly used as an additive (E171) in many foods, and it also used in personal care products, mainly sunscreens because their effective capacity for UV filtering. Although the presence of TiO<sub>2</sub> NPs in food has been shown qualitatively, quantification and characterization is difficult. Similarly, little is known about toxicity of TiO<sub>2</sub> NPs.

In this communication, TiO<sub>2</sub> NPs in surimi (crab sticks) were quantified and characterized by single particle – inductively coupled plasma – mass spectrometry (SP-ICP-MS). A preliminary study was performed for selecting the best extracting solution, as well as the operating conditions, for TiO<sub>2</sub> NPs extraction. Ultrapure water, 1.0 % (m/v) lactose and 1.0 % (v/v) glycerol led to low TiO<sub>2</sub> NPs recoveries. However, high TiO<sub>2</sub> NPs yields were assessed by enzymatic hydrolysis with pancreatin and lipase (pH 7.4, orbital – horizontal shaking at 200 rpm and 37°C overnight). Under these conditions, the size of TiO<sub>2</sub> NPs was not changed. This fact was verified by subjecting several TiO<sub>2</sub> NPs standards of certain size to the optimized procedure and analyzing the size distribution of the standards before and after the proposed enzymatic hydrolysis procedure.

Results have shown the presence of TiO<sub>2</sub> NPs in most of surimi samples (concentrations ranging from 7.5 10<sup>5</sup> to 2.8 10<sup>8</sup> TiO<sub>2</sub> NPs per gram). The size of TiO<sub>2</sub> NPs was within the 100 - 350 nm range.

Regarding toxicity, an *in vitro* procedure based on bioaccessibility was used to determine TiO<sub>2</sub> NPs bioavailability in surimi. Grinded samples were subjected to simulated gastric conditions (use of pepsin at pH 2.0, orbital – horizontal shaking at 150 rpm, 37°C, 2 hours) followed by a simulated intestinal digestion (use of pancreatin and bile salts at pH 7.4, orbital – horizontal shaking at 150 rpm, 37°C, 2 hours). High values of TiO<sub>2</sub> NPs were found in the bioaccessible fraction, although the size of the TiO<sub>2</sub> NPs (approximately mean size of 90 nm) was lower than those determined in surimi sample. This fact implies that TiO<sub>2</sub> NPs are altered (the sizes are reduced) during the *in vitro* bioavailability procedure.

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## NEW CE-ICP-MS METHOD FOR THE EXAMINATION OF GOLD NANORODS SPECIATION UNDER SIMULATED PHYSIOLOGICAL CONDITIONS

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Cancer is one of the biggest challenge of public health care and economy nowadays. New methods of early diagnosis and cancer treatment are still needed. Currently, a lot of scientists examine the possibility of using nanomaterials in cancer therapy. Their unique physicochemical properties may be relevant to the development of new diagnostic tools [1]. Gold nanorods (GNRs) are one of the most promising metal-nanomaterials in biomedical applications such as drug delivery, cell imaging and photothermal therapy.

Up to now, capillary electrophoresis (CE) has been widely used to examine various nanomaterials (gold nanoparticles,  $\text{Fe}_3\text{O}_4$  nanoparticles, quantum dots [2]). Due to the fact that nanorods enter the blood circulation system at small doses, the use of highly sensitive detector is required. Inductively coupled plasma mass spectrometer (ICP-MS) is a reasonable choice, as it allows detection of nanoparticles at low concentration.

The main aim of this study was a development and optimization of CE-ICP-MS method for examination of gold nanorods speciation under simulated physiological conditions. Type and concentration of background electrolyte, applied voltage and sample loading were optimized in order to obtain signals of the highest intensity and minimum half width of the peak. Analytical method parameters, such as reproducibility (intra- and inter-day), recovery, and limit of detection were calculated. The optimized CE-ICP-MS method can serve as a tool for studying interactions between GNRs and human serum proteins.

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## **STUDIES ON THE SEPARATION OF SILVER NANOPARTICLES AND SILVER(I) BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY**

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Silver nanoparticles (AgNPs) have a broad spectrum of antimicrobial activity and therefore are incorporated into various consumer products (e.g. anti-odour sportswear, underwear, socks, disinfecting sprays, food contact materials, washing machines, pillows and mattresses, toothbrushes, water filters, cosmetics). The rapid growth in the commercial application of AgNPs will certainly increase the exposure to silver among humans and in the environment. Size of metal-based nanoparticles is an important factor determining their physical and chemical properties as well as their bioavailability and toxicity.

Speciation analysis of various forms of silver, namely silver nanoparticles and silver ions is essential when assessing the potential impact of nanomaterials on human health and the environment. The unique surface structure and reactivity of nanoparticles increase the possibility of their dissolution into ionic constituents. Since nanoscale metal particles and metal ions may have independent or combined toxic effects, it is important to know whether the ecosystem is exposed to nanoparticles, ions or both. Therefore, analytical methods are required for the simultaneous determination of these forms in different matrices (consumer products, biological and environmental samples).

The possibility of application of high performance liquid chromatography for the separation of nano and ionic forms of silver with post-column ICP-MS detection is presented in this work. The chromatographic separation was performed on Nucleosil C18 column (7  $\mu\text{m}$  particle size, 1000  $\text{\AA}$  pore size, 250  $\times$  4.6 mm). Several different compositions of the mobile phase were investigated in order to obtain good resolution and ensure the stability of silver nanoparticles. In order to decrease the irreversible adsorption of AgNPs onto the column packing material, surface-active substances like SDS, Triton X-114, Tween 80 were used as the constituents of the mobile phase. To elute Ag(I) from the column, different complexation agents were tested such as  $\text{Na}_2\text{S}_2\text{O}_3$ , NaSCN, EDTA, L-cysteine.

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## AMINO ACID BASED SORBENTS FOR SPECIATION AND DETERMINATION OF PLATINUM AND GOLD IN COSMETICS BY SOLID PHASE EXTRACTION

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Trace metal analysis and speciation is most frequently based on the application of suitable selective separation and enrichment methods. Among them solid phase extraction is widely used as simple, easy to perform and fast analytical procedure. As far as the sorbent properties are the core of these procedures, agents with high selectivity, have been synthesized and investigated. In the present study new chelating sorbents, prepared by physical immobilization of different sulfur containing amino acid derivatives on the surface of silica gel have been tested as efficient sorbents for the enrichment of noble metals. Sorption behavior of Pt and Au towards new sorbents has been studied in batch and column mode. The influence of various chemical parameters: sample acidity, type and concentration of eluent, sample and eluent flow rates have been optimized for quantitative sorption and elution of Au and Pt. In acidic media the sorbents showed high selectivity toward studied noble metals in the presence of significant amounts of base metals. The influence of a reducing agent on the sorption of Pt (IV)/Pt (II) was examined. The noble metals ions retained on the sorbent were eluted with solution of thiourea in HCl. The measurements of Pt and Au in effluante and eluate solutions was executed by ICP-OES. The optimized procedure was used for preconcentration, speciation and determination of platinum and gold in noble metal containing cosmetics samples. Feasibility of the proposed method was proved by application of the procedure to several cosmetics samples.

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## SEPARATION AND DETERMINATION OF TiO<sub>2</sub> NANOPARTICLES IN WATER BY CLOUD POINT EXTRACTION AND ICP-MS

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Titanium dioxide nanoparticles are widely used in the industry due to their variety of uses, such as paints and varnishes, additive in many foods and personal care products. Due to its intensive use nanoparticles are released to the environment allowing for a potential health risk for humans and the eco-system.

In this study, an analytical method for the separation and determination of titanium dioxide nanoparticles in water samples has been developed. The separation was performed by Cloud Point Extraction (CPE) with Triton X-114. Titanium dioxide nanoparticles were then analyzed in the extracts by inductively coupled plasma-mass spectrometry (ICP-MS).

Parameters related to the CPE procedure such as Triton X-114 and NaCl concentrations were evaluated. Optimum concentrations of 0.03% and 0.19mM of Triton X-114 and NaCl, respectively were selected to develop this study. The TiO<sub>2</sub> nanoparticles extracted were then digested using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in a ultrasonic bath for 10 minutes at 60° and analyzed by ICP-MS.

The analytical characteristics of the method (calibration, limits of detection and quantification, precision and recovery) were evaluated. Finally, the method was applied for the determination of TiO<sub>2</sub> nanoparticles in environmental water samples.

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## HPLC-MS/MS AND HPLC-ICP-MS FOR CHARACTERIZING METAL BINDING PHYTOCHELATINS IN EDIBLE SEAWEEDS

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Phytochelatins (PCs) are non-enzymic metal-binding proteins characterized by low molecular weight, high content of cysteine residues, and have been described as physiologically multifunctional because they are involved in the transport, storage and detoxification of metals. Their sulphhydryl-rich primary structure confers them with a high capacity for metal binding.

In this communication, three PCs (PC2, PC3, PC4) have been isolated from edible seaweeds and characterized by high performance liquid chromatography (HPLC) with tandem mass spectrometry (MS/MS) and with inductively couple plasma – mass spectrometry (ICP-MS). PCs have been isolated from edible seaweeds by using a Tris/HCl buffer (pH 7.4) as an extracting solution after grinding in a mortar under liquid nitrogen. PCs were separated under reverse phase conditions using 0.1%(v/v) formic acid in water (mobile phase A), and 0.1%(v/v) formic acid in methanol (mobile phase B). Under optimized condition, PCs were resolved in 15 min (retention times of 2.8, 6.0, and 11.0 min for PC2, PC3, and PC4, respectively). Several edible seaweeds (Wakame, Kombu, Sea spaghetti, Nori, Dulse, Sea lettuce, Fucus, and Spirulina) were analyzed for metals binding PCs. Similarly total metal contents in the samples were assessed by ICP-MS after microwave assisted acid digestion. Metals such as As, Cd, Pb, Mn, Cu, and Zn were found to be bound to PC2; whereas only Cu was found to be bound to PC4. Repeatability and analytical recovery of the method was finally established.

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## MODIFYING THE SPECIATION OF IODINE IN SALINE MATRICES FOR QUANTIFICATION BY ICP-MS

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Nowadays, one of the major tasks for humanity is the development of a high level nuclear waste (HLW) disposal in deep geological formations. In order to ensure the compliance with safety standards for more than a hundred thousand years, it is essential to know the important interaction processes between the radioactive waste and the surrounding formations.

Apart from U, Am, Cs and a few other elements, especially Iodine is a relevant element for nuclear waste repository.  $^{131}\text{I}$  is a main fission product of  $^{235}\text{U}$  and very hazardous for human beings despite its short half-life ( $t_{1/2} = 8$  d). Small amounts of  $^{129}\text{I}$  with long half-life ( $t_{1/2} = 15.7$  Ma) are produced as well. Owing to its high volatility and mobility, which is related to its anionic nature in ground water as iodide, this beta emitter can contaminate for example seafood and milk within a long-ranged area. As a consequence of this, consumption of these products often leads to thyroid cancer.

In order to warrant the safety of a potential HLW disposal site, the retention capability of the environmental geological formations has to be known as well.

In this study iodine is quantified simultaneously with other elements (U, Eu, Cs) by inductively-coupled plasma mass spectrometry (ICP-MS) in complex matrices, for example in solutions with high salinity (up to 5 M NaCl). Nevertheless, the quantification of iodine is problematic due to the formation of volatile  $\text{I}_2$  and HI under acidic conditions which produce an unstable signal and a significant memory effect. To avoid the formation of volatile compounds, the speciation of iodine has to be modified. As known from the literature, the free anionic  $\text{I}^-$  can be trapped as a non-volatile  $\text{NH}_4\text{I}$  complex under basic conditions. However, this method suffers from several slightly soluble hydroxide complexes of high-valent metals and is not suitable for complex matrices. In this work, iodine will be completely oxidized to iodate by sodium hypochlorite at room temperature to enable acidic measurement conditions. With this method, it is possible to quantify I, U, Eu and Cs in saline matrices at once. As a result of this, the sorption isotherms of these elements in clay, which serves as potential geological formation for a HLW disposal site, can be determined and the retention coefficients can be estimated.

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## **A POLYMER INCLUSION MEMBRANE DEVICE FOR SAMPLING OF VANADIUM FROM WATERS**

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Vanadium is used in producing rust-resistant steels, in ceramics, as a catalyst as well as in the production of superconductive magnets. It occurs naturally in soil, water, and air. Natural sources of vanadium release to water include wet and dry deposition, soil erosion, and leaching from rocks and soils. Anthropogenic releases to water and sediments may include leaching from the residue of ores and clays, vanadium-enriched slags, urban sewage sludge, and certain fertilizers. Vanadium cannot be degraded in the environment, but may undergo various precipitation or ligand exchange reactions. Vanadium in compounds may undergo oxidation-reduction reactions under various environmental conditions. Vanadium can be complexed by various ligands present in the environment (e.g., fulvic and humic acids). In natural waters, dissolved vanadium exists as vanadium (IV) or vanadium (V) and these species have different toxic properties; therefore, it is important to monitor the concentration of individual oxidation forms of vanadium in the environment to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites. One way to perform a continuous monitoring of toxic elements in the environment involves the use of passive sampling devices.

In this work, first results on the study of the potentiality of a polymer inclusion membrane (PIM) system as a passive sampling device for monitoring vanadium concentrations in waters are reported. An optimization of the sampling systems in terms of membrane (extractant –Aliquat 336– and plasticizer –2-orthonitrophenyloctylether), and aqueous phases (donor pH, NaOH concentration in the acceptor phase) composition is presented and the influences of species and humic acids concentrations as well as vanadium oxidation state in the uptake regimen are evaluated.

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## **SPECIATION ANALYSIS OF METALS IN BOTTOM SEDIMENTS FROM THE PORT CHANNELS AND DUMPING SITES IN THE SOUTHERN BALTIC SEA**

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The aim of the work was to investigate the influence of processes occurring during deposition of dredged material in dump sites on the bonding of metals in the sediment. Dumping Sites are separate areas of the seabed, where may be deposited dredged sediments generally from port channels. Currently, there are more than 20 offshore dumping sites in South-Eastern Baltic Sea, which are used for depositing of dredged material from port areas and navigation channels. The sea areas administered by the Polish Maritime Offices have nine active Dumping Sites. About toxicity of polluted sediments are deciding not only concentration of macro- and micro- elements but, also the chemical form in which they exist. This form has considerable influence on their assimilation on different trophic levels (including human). Knowledge of quantitative elemental composition of sediments including chemical speciation is a very important element in predicting the potential risk of trace metals in relation to the living, marine resources and human health.

The investigated material were sediments from port channels and the same sediments after deposition on the Dumping Site in the south region of the Baltic Sea. Sequential analysis was carried out using the Tessier and BCR methods. Metals after extraction were determined by ICP-OES and ICP-MS.

The results of the carried out investigations indicated that the concentration of the trace metals were decreasing in sediments deposited on the dumping sites. Grain size analysis demonstrated a significant decrease of clay fraction in sediments from dumping site by comparison with the depositing sediments. The sequential analysis proved that the percentage of the particular forms of the metals (especially Pb and Cd) was changing in the sediments deposited in the dumping site. The changes of salinity, mechanical mixing during excavation, oxygen concentration may result in freeing the labile forms into the water column, especially the exchangeable and carbonate forms, which are loosely connected with the sediment, and these conditions may be sufficient to free these forms.

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## HYDRIDE GENERATION OF 'ARSENOSUGARS' FROM ALGAE SAMPLES

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Arsenate is the dominant form of arsenic in the sea water. The arsenate is transformed to the organic compounds in the marine organism. Therefore, a high concentration of arsenic is quite common, but only a small fraction of arsenic is inorganic arsenic. The dimethylarsinoylribosides (arsenosugars) are the predominant arsenic species in the algae. The glycerol-ribose, phosphate-ribose, sulfonate-ribose, and sulfate-ribose are four arsenosugars which are usually present. It was found that these arsenic species are 'hydride active' *i.e.* they can be by reaction with tetrahydridoborate converted to the volatile arsanes. The hydride generation (HG) is usually used as postcolumn derivatization step which increases the sensitivity and removes interferences and therefore lowers the limits of detection. The efficiency of HG from arsenosugars is quite low so far so that analytical performance of HG based determination is rather poor. A better understanding of HG of arsenosugars can improve situation. Unfortunately, arsenosugars species are not commercially available - they must be synthesized or isolated from natural source (algae). In this work, water extract of the Nori (red algae genus *Pyropia*) containing 95% of phosphate-ribose was used as a 'standard' for optimization of HG. Two hydride generators were employed: batch, and flow injection. Our preliminary results suggest that it's much easier to generate arsenic species from the arsenosugar standard in the batch generator, with the maximum HG efficiency  $63 \pm 3\%$ , than in the flow injection mode with  $19.0 \pm 0.2\%$ . It should be highlighted that only flow injection mode HG generator can be used as in the postcolumn derivatization step.

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## THE IMPORTANCE OF THE PRESENCE OF $\text{Fe}_2\text{O}_3$ AND $\text{Cr}_2\text{O}_3$ NANOPARTICLES ON THE GROWTH OF SELECTED BACTERIAL STRAINS UNDER ENVIRONMENTAL CONDITIONS

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Nanosized particles of two metal oxides ( $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ ) were characterized by X-ray diffraction and Fourier-transform infrared spectroscopy. X-ray diffraction results confirmed the single-phase formation of two nanomaterials. These nanoparticles were used to evaluate their antibacterial activity against both Gram-negative (*Escherichia coli*, *Proteus mirabilis*, *Pseudomonas aeruginosa*) and Gram-positive (*Staphylococcus aureus*, *Enterococcus hirae*) bacteria. Firstly, serial dilution method of bacterial suspensions were performed. Next, optical density (OD) by spectrophotometer at the wavelength of 600 nm was measured and finally, antibacterial activity was determined by minimal inhibitory concentration method (MIC). The solvent as negative control was used, while antibiotic tetracycline as a positive control. After overnight incubation at 37°C, the different levels of zone of inhibition was measured. It was observed that iron oxide nanoparticles showed slight bactericidal potential, while chromium oxide nanoparticles had no bactericidal activity. The order of antibacterial activity was demonstrated to be the following:  $\text{Fe}_2\text{O}_3 > \text{Cr}_2\text{O}_3$ . The results indicate that nanomaterials were most effective against Gram-positive bacterial strains.

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## METALS SORPTION ON THE ALKALI-ACTIVATED SLAGS

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New direction of research is represented by utilization of alkali-activated slag as sorbents for metal cations. The alkali activated materials have been usually used in the building industry to preparing of concrete. Alkali-activated concretes obtain higher resistance to reagents and pressure by utilization of alkali-activated slag. The alkali activated materials can be prepared from materials containing silicon and aluminium. The alkali-activation occurs under high alkaline conditions (pH value 12 -14). Type of activator, concentration of components, pressure and contact time have the highest influence on the final structure. The alkali-activation creates the amorphous and crystalline phases, most often zeolites, zeolitic precursors and hydrotalcites.

Steelmaking slag (SMS Basic) provided by ArcelorMittal Ostrava a.s. (Czech Republic) was used for alkali-activation. Commercial water glass ( $\text{Na}_2\text{SiO}_3$  KITTFORT s.r.o., Prague, Czech Republic) was used as the alkali-activator. The solution of water glass was adjusted with NaOH so that molar ratio  $\text{SiO}_2/\text{Na}_2\text{O}$  in the solution was equal to 1. The modified solution was added to the slag in the ratio 1:1 with contact time 7 days and then the suspension was filtered. The solid fraction from filtration was dried at two different conditions: at the ambient temperature for 7 days (AA SMS) and in the drier at 105°C for 8 hours (AA SMS 105). Characterization of the prepared slags by means of X-ray fluorescence, X-ray diffraction, and infrared spectrometry (DRIFT) demonstrates, that the alkali-activation forms a new structure. The sorption experiments were performed on these modified slags and the obtained data were compared with the original steel making slag. The sorption properties were studied for copper and lead cations. The sorption experiments were performed by batch technique with the optimal conditions: ratio sorbents: liquid 1:25, contact time 24 hours, ambient conditions and the concentrations of the metal cations in the range 2 – 140 mmol/L. The determination of the metals concentration in supernatant after sorption was performed by using of atomic absorption spectrometry with flame atomization (AA 240FS Varian).

The results of the performed experiments show the presence of new structures in the alkali-activated materials. The significant influence of drying process was found. The sorption experiments on the AA SMS and AA SMS 105 show that the modification of the slags influences the sorption properties. The removal amounts and the efficiency of the Cu(II) and Pb(II) removal is higher in the comparison to SMS Basic.

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## THE ASSESSMENT OF HALLOYSITE APPLICABILITY FOR THE IMMOBILIZATION OF HEAVY METALS

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Clay minerals of the kaolin subgroup are widely used in the industry and environmental protection as absorbents, ion exchangers and catalysts. The most important members components of the kaolin subgroup of minerals are kaolinite and halloysite. Halloysite is a two-layer mineral belonging to the kaolinite subgroup which is represented by the same chemical formula:  $Al_2Si_2O_5(OH)_4 \cdot nH_2O$ , where  $n$  is the number of water molecules that occupy the interlayer spaces of clay aggregates. The value of  $n$  is zero for kaolinite and up to four for halloysite.

Halloysite exhibits specific properties which are not observed in other kaolin minerals. These properties play an important role in terms of applications. Halloysite may be used for many purposes in environment protection, e.g. for the manufacturing of coagulants, municipal and industrial wastewater treatment as well as as a component of geosynthetic clay liners. Moreover, halloysite is commonly used in catalysts and fillers in polymers, plastics, composites and other similar materials.

Clay and clay minerals have also been explored as adsorbents for the removal of heavy metals from aqueous solution. The advantages of using clay minerals as alternative adsorbents for the removal of heavy metals are high ion sorption/exchange capacity, low permeability, swelling ability, chemical and mechanical stability and large specific surface area. Different types of clay minerals have been tested for the removal of heavy metal ions from water and wastewater.

The presented results concern the possibility of using halloysite as an efficient raw material for creating active barriers. Active barriers have capabilities to bind metals (other pollutants) and to immobilize them in the structure of the barriers. The conducted analyses of the selected sorption and physicochemical properties of halloysite included, among others, Scanning Electron Microscopy (SEM-BSE), X-ray Powder Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). In addition, a thermal analysis of analyzed samples with DTA - Differential Thermal Analysis and TGA - Thermogravimetric Analysis and porosimetric analysis was conducted. Kinetics of adsorption were described based on the pseudo-first and pseudo-second order of kinetic equations and intramolecular diffusion model. The release susceptibility of adsorbed Cu(II), Mn(II), Pb(II) and Zn(II) ions was set out, which determines the possibility of halloysite application as a permeable, active barrier in remediation of contaminated soils. The susceptibility of adsorbed ions was determined with BCR sequential fractionation method.

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## THE RECOVERY OF ZINC AND MANGANESE FROM Zn-Mn BATTERIES BY LIQUID-SOLID EXTRACTION WITH SULFURIC ACID

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Hydrometallurgical processes are an excellent alternative to recycling metals as oxides or other compounds, from dust with a non-metallic structure to precious metals. The hydrometallurgical method for raw material gives surprisingly good results which could not be achieved by conventional pyrometallurgical methods. Hydrometallurgy has some benefits compared to pyrometallurgical techniques including low cost requirements, possible recovery of leachants and the decrease of air pollution as there are no particles produced. However, some pre-treatment steps are required in order to improve metal dissolution rates in the aqueous phase, i.e. battery classification, dismantling, magnetic separation and leaching.

A recycling process for the recovery of zinc and manganese from Zn-Mn batteries is proposed in this paper. The aim of this work is to determine the optimal conditions of manganese and zinc extraction from black mass (prepared at Eco Hybres Company in a special pyrometallurgical process) of used zinc - manganese batteries. A single-stage extraction ratio from liquid to solid of 1:2, in the temperature of 40 °C in the time of 2 hours, using 15% sulfuric acid was obtained by the degree of extraction, equal to 75.54% for Zn, and 82.74% for Mn. Taking these degrees of metals extraction selected from the black mass into account, the results are satisfactory enough to achieve a recyclable of 50% of the zinc-manganese battery, considering the preparation of a black residue by EkoHybres.

The proposed single-stage extraction parameters of zinc and manganese are economical and highly efficient. At low ratios liquid to a black ground (1:2), the short extraction time (2 hours), low temperature (40 °C), achieve a good level of recovery, imposed by the European Union recovery requirement while maintaining the minimum amount of waste.

In the next step in recycling after extraction, can be recover manganese as manganese dioxide with a purity level of 99% and the zinc can be obtained as zinc sulphate solution, prepared for the zinc electrolysis process or to other processes in industries such as complex compounds, chelates etc. The proposed method gives very good results in the Zn-Mn battery recycling. The possibility of obtaining final products as examples on manganese oxide(IV) recycling the material creates the possibility use to in new batteries.

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## **IRON SPECIATION, FERRITIN CONCENTRATIONS AND Fe:FERRITIN RATIOS IN DIFFERENT MALIGNANCY BREAST CANCER CELL LINES: ON THE SEARCH FOR CANCER BIOMARKERS**

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Iron is an essential element for cell growth and division. Recent experiments have linked a deregulation of iron's metabolism with breast cancer progression, aggressiveness and recurrence [1]. Ferritin is a globular storage Fe protein, mainly accumulated in the liver hepatocytes and serum levels of this protein are the most valuable parameter in diagnosis and follow-up of iron deficiency and iron-overload diseases. The measurements of Fe in ferritin ratios has been reported to be superior to that of serum ferritin. It was hypothesized that these ratios could be an alternative biomarker for iron metabolism which is not confounded by inflammation [2].

This work has been focused on the comparative evaluation of part of the Fe metallome in two breast cancer cells of different malignancy: MCF-7 and MDA-MB-231. Evaluation of the total cytosolic iron as well as the ultrafiltrable iron content has been conducted using inductively coupled plasma mass spectrometry (ICP-MS) as Fe selective detector. Additionally, in this work has been done Fe-fraction experiments conducted by coupling size exclusion chromatography (SEC) to ICP-MS. Furthermore, in this work has been measured specific ferritin. For this purpose, a previously optimized sandwich immunoassay which is specific for human ferritin and contains a ruthenium complex in one of the antibodies that we use to monitor in ICP-MS [3] was applied to the cell lysates (cell lines MCF-7 and MDA-MB-231). For the determination of the Fe-content in the ferritin we use the antibody with biotin and we isolated the ferritin with magnetic particles with streptavidin and we measured total iron by ICP-MS.

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## DETERMINATION OF TOTAL ARSENIC AND ARSENIC SPECIES IN BIVALVE MOLLUSCS

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Arsenic (As) is one of the most toxic elements naturally occurring in the earth's crust and environmentally ubiquitous by natural and anthropogenic emissions. Because of the high mobility of arsenate ions, arsenic can be easily released to the atmosphere, transported, dissolved by water and readily taken up by aquatic organisms. High concentrations of As reported in common consumed seafood such as fish, crustaceans and molluscs, may pose a threat to the consumers health. Arsenic toxicity depends on its chemical form (As(III)> As(V)> MMA> DMA> AsB> AsC> TMAO> arsenolipids> arsenosugars), therefore to assess the health risk associated with seafood consumption, the speciation analysis is necessary.

An analytical method for speciation analysis of six arsenic species: arsenite As(III), arsenate As(V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine (AsB), and arsenocholine (AsC) was developed in one anion-exchange column by high performance liquid chromatography combined with inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Determination of total arsenic was carried out via ICP-MS. Reliability of results obtained within described method was verified by analysis of certified reference materials (CRMs). Proposed methods were applied to assess concentrations of total arsenic and six arsenic compounds in different species of bivalve molluscs available on the Polish market: dog cockle (*Glycymeris glycymeris*), Manila clam (*Ruditapes philippinarum*), Atlantic jackknife clam (*Ensis directus*), blue mussel (*Mytilus edulis*), Pacific oyster (*Crassostrea gigas*), great scallop (*Pecten maximus*), common cockle (*Cardium edule*) and hard clam (*Mercenaria mercenaria*). Samples originating from five countries were collected on local warehouses and markets according to the multi-annual monitoring programme "Protection of animal and public health".

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## ASSESSMENT OF METAL-ORGANIC COMPOUND COMPLEXES IN CHILEAN NATURAL WINES BY TWO DIMENSIONAL CHROMATOGRAPHY AND ICP-MS

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Itata Valley is one of the most important winemaking areas in Chile, and new trends in winery practices as well as growing grapes (minimum technological and chemical intervention) are addressed for the marketing new value-added products such as “natural wines”.

In this communication, inductively couple plasma – mass spectrometry (ICP-MS) has been used for assessing total contents of trace and ultratrace elements in wines, but also for assessing metals-low molecular weight organic compound (LMWC) complexes after two-dimensional chromatography [size exclusion chromatography (SEC), and ionic exchange chromatographic (AEC)] hyphenated with ICP-MS. A Superdex Peptide 10/300GL (SEC) was first used for separating low molecular weight compounds in natural wines (nine fractions of molecular weights ranging from 200 to 6690 Da monitored by UV detection). Elements such as B, Cu, Ni, Rb, and Ti were found to be bounded to compounds of molecular weights within the 200-2000 Da range. This SEC fraction was further characterized by AEC (use of PR-X100 column), and three compounds (UV detection), F1, F2 and F3 (retention times of 2.6, 3.2, and 3.8 min) were observed. AEC-ICP-MS showed the presence of B-, Rb-, and Li-LMWC complexes. B was found to be bounded to LMWC in fraction F2; whereas, Li was associated to fraction F1. However, other elements such as Rb and Mn, which were associated to the investigated SEC fraction, were not observed after AEC-ICP-MS analysis. These findings could imply high lability of Rb- and Mn-LMWC complexes.

Several white and red wines were analysed for total metal contents and also for metals associated to 200-2000 Da SEC fraction. Average concentrations of 0.053  $\mu\text{g L}^{-1}$  (Li), and 30.3  $\mu\text{g L}^{-1}$  (B) were found.

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## **THE DETERMINATION OF ORGANIC AND INORGANIC SILICON CONTAINING COMPOUNDS WITH HPLC-ICPQQMS**

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Silicon is omnipresent in our everyday life. On the one hand it is the second most abundant element in the earth's crust; on the other hand the anthropogenic silicone production is in the million tons per year range.

While naturally occurring silicon is usually in the form of silicates and silicic acids; siloxanes, especially polydimethylsiloxanes (PDMS) are the main anthropogenic products. Silicones are used in various areas (energy, construction, food, pharmaceuticals...) as silicone fluids, resins or elastomers.

It is of interest to quantify silicate in an aqueous sample matrix containing varying silicone derived compounds. For example when aqueous solutions are in contact with glass and silicone lubricants and the amount of silicon released from the glass container shall be determined. Chromatographic methods for silicate analysis include anion-exchange or ion-exclusion methods.

In order to quantify silicate in aqueous samples possibly containing also silicone oil derived components we combined a strong anion-exchange chromatography with ICPQQMS as element-selective detector. As the exact composition of used silicone oil lubricants was not known to us, a sample containing a high amount of silicone oil derived components was used to develop the separation. The triple quadrupole ICPMS (ICPQQMS) in oxygen reaction mode was successfully utilized to remove the wide range of polyatomic interferences on the different silicon isotopes. Reasonable column recoveries could be determined using flow injection analysis or the determination of total Si content of aqueous samples.

In the poster presentation the results from the chromatographic optimization as well as the silicon determination with the ICPQQMS are discussed.

## THE VEGETABLE AND SPROUTS AS A SOURCE OF HEALTH-RELEVANT COMPOUNDS OF SELENIUM IN THE DIET

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Selenium is an element of very great importance for the proper functioning of the human body, mainly due to its antioxidant properties. Selenium exhibits a preventive effect in the case of cardiovascular disease, the immune system, male infertility and inhibits the toxic action of other agents. Selenium is important for Hashimoto's disease. Intake of selenium in the diet slows the aging process. The biological and toxicological effects of selenium strongly depend on its chemical form. Some organisms for example: plant, yeast, are capable of metabolizing low bioavailable selenium compounds (inorganic selenium) into its high bioavailable forms (organic selenium).

The aim of this study was to investigate the bio-transformation of selenium by vegetable and sprouts towards the characterization of selenium metabolites. The selenium compounds in a plant was identified by high performance liquid chromatography (Agilent 1290 UHPLC) coupled with mass spectrometry (Orbitrap Fusion TMS).

Studies have shown that vegetable and sprouts can be a source of natural selenium compounds in the diet. In the analyzed varieties of sprouts (sunflower, radishes and onions) and vegetables (onion, garlic and leeks) mainly forms that were identified: Se-methylselenocysteine, Se-methionine,  $\gamma$ -glutamylSe-methylselenocysteine. Other forms of seleno-compounds that were found in the plants: 5'-adenosine, 2,3-DHP-selenolanthionine, Se-S-cysteine conjugate of selenogluthathione, 2,3-DHP-selenocysteine-cysteine, 2,3-DHP-selenocysteino-cysteinoalanina, glutathione-2,3-DHP or selenocysteine-glutamyl-N-glyciny1-2,3-DHP-selenocysteine.

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## **STUDY OF CHROMIUM SPECIATION IN ENVIRONMENTAL SAMPLES BY LIQUID CHROMATOGRAPHY COUPLED TO ICP-MS**

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The presence of chromium in the environment is mainly connected with human activity. Emission of dust and ash from industrial plants, discharge of wastewater into water and soil, and storage of solid waste produced during manufacturing processes contribute significantly to the pollution of the environment by this metal. Due to different biological activity of Cr(III) and Cr(VI) species, their chemical behaviour and toxic effects on humans and other living organisms, the speciation analysis of chromium in environmental samples is of great importance. However such analysis, even in surface or wastewaters, is still a difficult analytical task. Main problems arise due to the low concentration of analytes, their interconversion and strong influence of constituents of a complex sample matrix on analytical signal of chromium. Therefore, in order to obtain accurate and reliable results of speciation study, the selective separation procedures of chromium species based on chromatographic techniques should be combined with their sensitive determination.

In this work the ion exchange chromatography coupled to inductively coupled plasma mass spectrometry (IEC-ICP-MS) was used to study of chromium speciation in environmental samples. In order to separate Cr(III) from Cr(VI) on an anion-exchange column, the cationic forms of Cr(III) were transformed into anionic Cr(III)-EDTA<sup>-</sup> complex. The separated species were determined by ICP-MS using 8800 ICP-QQQ spectrometer. For elimination of spectral interferences during determination of chromium in mobile phase the reaction cell with oxygen gas was applied. Under optimal conditions the speciation analysis of chromium in surface water, municipal sludge and soil extracts was performed. On the basis of total concentration of chromium determined by ICP-MS and concentration of Cr(III) and Cr(VI) forms determined by IEC-ICP-MS the chromium species present in environmental samples were identified.

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## SEQUENTIAL INJECTION SPECTROPHOTOMETRIC DETERMINATION OF Cr(III) AND Cr(VI)

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Chromatographic systems are widely applied to speciation analysis. However, non-chromatographic methods performed in flow-based systems may be also useful as fast, cheap and easy to automate approaches, especially in case of determination of two species.

The work presents the development of a method for simultaneous determination of Cr(III) and Cr(VI) using the technique of sequential injection analysis (SIA). The SIA technique offers the possibility of automating the method and, compared to other flow-based methods, enables one to reduce significantly sample and reagents consumption, and therefore – waste production. The method based on a reaction of Cr(VI) with 1,5-diphenylcarbazide (1,5-DPC) in acid environment was applied to the determination of both analytes. Cr(VI) was determined directly and Cr(III) after its oxidation to Cr(VI) with the use of Ce(IV). The product of reaction was detected spectrophotometrically at 540 nm.

In the developed SIA system, known volumes of air, sample (subjected or not subjected the procedure of Cr(III) oxidation) and 1,5-DPC are introduced into the holding coil in an established sequence. Then the flow is reversed and they are directed to the detector to register a signal. The absorbance in the signal plateau is the measure of Cr(III) or Cr(VI) content in the sample. Because the signal for Cr(III) is influenced by the signal of Cr(VI), a calibration model covering the influence has been applied.

The method was verified on the example of determination of both analytes in synthetic and certified reference material of wastewater samples with good precision and accuracy for both analytes, Cr(III) and Cr(VI). Selected parameters of validation, like linear range, accuracy, repeatability and limit of quantification were established. The developed approach was employed to the determination of Cr(III) and Cr(VI) in a sample of industrial sewage.

## MERCAPTOBENZIMIDAZOLE AS COMPLEXING AGENT FOR SOLID PHASE EXTRACTION, DETERMINATION AND SPECIATION OF CHROMIUM IN TEXTILE FIBERS

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Speciation of Cr (III) and Cr (VI) is an important analytical task due to the significant differences in the toxicity, mobility and bioavailability of both chromium species. The determination of total chromium concentration is generally not sufficient for clinical and environmental considerations. Therefore, the Cr (III)/Cr (VI) analysis has reasonably become an important topic of the analytical research.

In this paper the sorption behavior of the mercaptobenzimidazole-modified activated carbon towards Cr (III) and Cr (VI) was studied at different experimental conditions and a solid phase extraction procedure has been established for chromium speciation prior to determination by flame atomic absorption spectrometry (FAAS). The adsorption experiments were conducted in batch mode. The optimal conditions for sorption, desorption and speciation processes were evaluated in terms of pH, eluent type and volume. The effect of solution acidity on the extraction behavior of Cr (III) and Cr (VI) from model solutions was studied in the pH range of 1–9. Under the optimized experimental conditions, the degree of sorption for Cr (III) was nearly equal to zero in all studied pH interval, however the adsorption percentage of Cr (VI) was in the range of 35–90%. The elution of Cr (VI) species was achieved by heating the loaded carbon with an acid mixture HNO<sub>3</sub>/HCl (1:1).

It was confirmed that carbon surface functionalization considerably improves its extraction efficiency and selectivity and ensures its successful analytical application. Analytical procedure developed consists of two steps: (i) determination of total Cr by direct instrumental measurement (ETAAS) and (ii) determination of toxic Cr (VI) after selective sorption and elution by using mercaptobenzimidazole modified carbon.

The optimized procedure was applied to the determination and speciation of chromium in textile fibers. The accuracy of the proposed method was proved by application to the certified reference materials and spiked model solutions.

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## **XAFS SPECIATION OF TRACE ELEMENTS IN BY-PRODUCT FROM COAL COMBUSTION PLANT**

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Recently, in order to prevent the environmental impact of chemical substances, emission controls and regulations has been strengthened worldwide. In this study, X-ray absorption fine structure (XAFS) spectroscopy was applied to determine the chemical form of trace elements in coal ash and by-product from coal combustion plant.

Coal combustion plant is widely utilized as a source of thermal and electric energy. It is well-known that coal contains trace elements such as boron, selenium, arsenic, mercury and so on. These trace elements are released into the flue gas as gaseous compounds or particle-bound forms during the coal combustion process. In the cleanup process of the thermo-electric power plant, most of trace elements are captured in coal ash particles from electrostatic precipitator (EP) and by-products such as gypsum and sludge from the wet flue gas desulfurization (FGD) unit. To safety control and effectively use of these by-products, it is necessary to get a chemical form of trace elements. There is no way to directly identify chemical forms of trace amount of elements in complex mixture of these combustion by-products. XAFS spectroscopy can be expected as one of the effective analytical techniques that it is possible to identify the chemical form of trace elements. However, it was difficult to apply the XAFS spectroscopy to trace amount of these elements in complex mixture with mercury, selenium, arsenic, zinc and lead compounds, under the effects of fluorescence X-ray signal from these matrix elements and scattered X-ray and so on.

In this paper, XAFS spectroscopy was applied to determine the chemical form of trace elements in complex mixtures such as coal ash, gypsum and sludge by using the multi-channels solid state X-ray detector (19-channels SSD), and the combination of a bent crystal Laue analyzer (BCLA) and 19-channels SSD, to develop the quick identification technique of selenium, arsenic and mercury.

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## MACRO- AND MICRO-ELEMENT CONTENTS IN RAT LIVERS AFTER INCREASED DIETARY SELENIUM INTAKE

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Selenium belongs to the most important essential elements for animals and various beneficial effects were reported [1]. The effect of Se-enriched defatted rape seeds [2] added to the diet on the response of essential micro- and macronutrients (I, Se, Cu, Ca, Fe, K, Mg, Mn, P, S, and Zn) in rat livers was investigated in model conditions. Special attention was paid to the interaction of iodine and selenium. The experimental diets for the individual experimental groups were prepared as follows: i) the control diet with 14% of the soybean meal; ii) 30% of the soybean meal in the diet was replaced with defatted rape seeds; iii) 60% of the soybean meal in the diet was replaced with defatted rape seeds; and iv) 100% of the soybean meal in the diet was replaced with defatted rape seeds.

In the rat liver, no significant changes of Se contents were observed as well as the changes of most of the investigated elements. Slight decrease in P, S, and Zn levels was observed in the control group whereas no changes occurred in the case of selenized groups of animals. The decreasing Cd contents in the rat liver with increasing Se content in the diet confirming antagonism of these elements was observed. In the opposite, selenized diet led to significant changes in the total iodine content, but no obvious dependence on the portion of selenized defatted rape seeds was observed. The abundance of inorganic iodine did not significantly differ between groups.

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## SPECIATION ANALYSIS OF COBALT IN FUNCTIONAL FOOD BY SEC-ICP MS

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Cobalt is an essential element needed in very small amount in the human diet. It is an integral component of vitamin B<sub>12</sub>, cobalamin, which supports red blood cells production and the formation of myelin nerve coverings. Cobalt, as constituent of vitamin B<sub>12</sub>, prevents anemia, it is also beneficial in some digestive disorders, and neuro-muscular problems. Human organism is not able to produce vitamin B<sub>12</sub> itself, so it needs to be acquired from food or supplements.

The project was focused on the determination of cobalt species in various functional foodstuffs (for example *Spirulina platensis*, Acai berries, Goji berries, *Physalis peruviana*). Cobalt species (its complexes with bioligands) were determined by fractionation followed by SEC-ICP MS analysis. In fractionation step samples were treated with buffer and enzymatic extraction media. Prior to speciation analysis of cobalt, its total amount was determined by standalone ICP MS.

Total concentration of metals in food does not characterize their bioavailability in the human organism. Such information can be obtained by SEC-ICP MS. Two step digestion model simulating gastric (pepsin digestion) and intestinal (pancreatin digestion) juices were used. *In vitro* simulation of gastrointestinal digestion helps to understand the process of bioaccumulation of elements by human body.

## DETERMINATION OF LEAD AND CADMIUM IN ENVIRONMENTAL REFERENCE MATERIALS USING THE ISOTOPE DILUTION TECHNIQUE

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Environment is polluted with numerous xenobiotics, which may have a negative impact on human health. Human industrial activity resulted in a significant increase in the level of pollutants in the environment. Cadmium and lead are listed among the elements of toxic nature for living organisms. Therefore, it is necessary to monitor the content of xenobiotics in the environment for human safety. To obtain the high quality results of analysis, certified reference materials are needed. The quality of results is an important issue in a whole range of scientific disciplines, in which chemical measurements are mandatory. It has been recognized by those interested in environmentally related investigations, that the quality of analytical results should be transparent and confident. Therefore, it is important to deliver accurate results and to be able to show their traceability. In this work, an isotope dilution approach for precise determination of cadmium and lead in candidates for environmental certified reference materials was performed. Isotope dilution mass spectrometry (IDMS) has capability of leading the highest quality results as a primary method of measurement. This technique is based on the measurement of isotope ratios in samples, in which the natural isotopic composition of the element has been altered by adding a known amount of isotopically enriched standard. Moreover, the entire IDMS measurements process demonstrating traceability to the International System of Units (SI): the mole, the kilogram and the second. From the other point of view, certified reference materials are recognized to be an essential tool in assuring the accuracy and establishing also the traceability of the results of measurements. Thus, there is a need to introduce new CRM's in order to fulfill the demand of the environmentally oriented studies.

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## WIĘCEJ PALIW Z KAŻDEJ BARYŁKI ROPY

Zasoby naturalne mogą nam dać dużo więcej niż się wydaje. W Grupie LOTOS umiemy z nich korzystać. Właśnie dlatego rozwijamy projekt efektywnej rafinacji. Dzięki niemu maksymalizujemy ilość i jakość paliw uzyskiwanych z każdej baryłki ropy. Kierujemy się troską o środowisko oraz korzyściami, które przyniesie ta inwestycja. Efektywna rafinacja opłaca się nam wszystkim.

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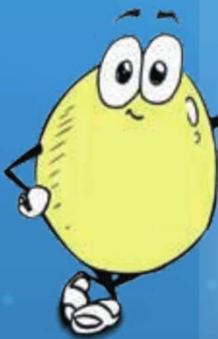
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## ICP-MS

Spektrometry ICP-MS umożliwiają czułą i szybką analizę ilościową i jakościową oraz analizę składu izotopowego próbek. Na przestrzeni ostatnich lat firma Shimadzu intensywnie rozwijała techniki ICP oraz MS, czego zwieńczeniem jest nowy spektrometr mas ze wzbudzeniem w plazmie indukcyjnie sprzężonej – ICPMS-2030.



Dzięki optymalizacji konstrukcji wewnętrznej oraz opracowaniu nowej komory kolizyjnej spektrometr ICPMS-2030 zapewnia wyjątkową czułość. Aparat ma najniższe obecnie zużycie argonu dzięki zastosowaniu opatentowanego przez Shimadzu Mini palnika oraz trybu ECO. System wprowadzania próbki oraz części linii jonowej, wymagające codziennej konserwacji bardzo łatwo utrzymać w czystości.

Oprogramowanie sterujące LabSolution ICPMS zawiera w standardzie nowatorskie, opatentowane przez Shimadzu moduły Asystenta Tworzenia Metody oraz Asystenta Diagnostycznego.

Funkcja „Asystent Tworzenia Metody” automatycznie dobiera optymalne warunki analizy ilościowej, m.in. wskazuje możliwe interferencje oraz proponuje sposoby ich usunięcia, zaś funkcja „Asystent Diagnostyczny” automatycznie wykonuje sprawdzenie poprawności danych po pomiarze oraz wskazuje w jaki sposób rozwiązać problemy z interferencjami. Funkcje te skracają czas pracy operatora, pomagają w tworzeniu bardziej efektywnych procedur analitycznych oraz znacznie zwiększają liczbę zanalizowanych próbek w danym czasie.

Zakres pomiarowy	Tło (cps)	Częstotliwość cewki indukcyjnej	Granica wykrywalności (ng/L *Be)	Komora kolizyjna	Czystość argonu	Eliminacja światła i cząstek obojętnych	Zużycie argonu	Opcjonalne techniki łączone	Wymiary (mm)
5-260 amu	< 1	27,12 MHz	< 0,5	Oktapol (Gaz kolizyjny – He)	99,95%	Ugięcie wiązki jonów	Typowo 11,5 L/min	LC/IC/LA	Szer. 870 x wys. 645 x głęb. 587

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