



2007 European Winter Conference on Plasma Spectrochemistry

18 - 23 February 2007

Taormina, Italy

ABSTRACTS

22 February 2007

- Speciation: Metallomics and Proteomics and Related Applications
- Stable and Radioisotope Analysis



and



EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre



Oral and Poster Sessions on Thursday 22 February 2007

Abstracts

KN 11

PROBING ELEMENTAL SPECIATION IN THE BIOLOGICAL ENVIRONMENT - THE ON-GOING CHALLENGE TO ICP (AND NOT ONLY!) MS. **Ryszard Lobinski**,

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Speciation of anthropogenic contaminants in biota by hyphenated techniques has been attaining maturity. On the other hand, the complexity and the generally poor knowledge of trace element metal complexes with biological ligands (most of these species have not yet been discovered!) often make the sheer definition of the target analyte problematic. Formation of biologically relevant metal sites usually requires a set of post-translational events, many of which can be influenced by environmental changes. These events are invisible to standard proteomics and the need to study them puts metals and their coordination environment into the centre of interest. This is expressed by a number of new terms increasingly used in recent literature such as, e.g. metallomics, often extended to encompass covalently bound heteroatoms (S, Se, and I).

The information on the metal-protein interactions is often either lost in the gas-phase (MALDI) or not acquired because of the insufficient detection limits in real-world salt-rich matrices (ES MS). Also, the ionization efficiency is dependent on the molecule which, while being of little consequence for structural analysis, renders the quantification without external standardization very difficult if not impossible. All these reasons encourage a closer look at the role ICP MS can still play.

The lecture overviews the state-of-the-art and highlights the recent advances in ICP MS of metalloproteins, such as laser ablation ICP MS detection in gel electrophoresis or nanoHPLC – ICP MS coupling for seleno- and metalloproteomics.

Th01

ASSOCIATION OF CD-CHELEX ASSAY WITH SEC-HPLC-ICP-MS FOR QUANTIFICATION OF TOTAL MT, APO-MT AND METAL BOUNDS TO MT IN BIOLOGICAL SAMPLES

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Metallothioneins (MT) are cysteine-rich proteins involved in regulating the intracellular availability of zinc (Zn) and copper (Cu) ions as well as in detoxifying the cell in presence of heavy metals such as cadmium (Cd) and mercury (Hg). Total MT, apo-MT and metals bound to MT are relevant parameters in biology not only to detect contaminations by toxic heavy metals, but also to assess the availability of intracellular zinc in physiological conditions and to evaluate the presence of stressing and inflammatory conditions. One of the most rapid and sensitive procedure to determine the quantification of MT is the Cd-chelex assay. However, this method is able to assess only total MT and fails when the sample contains an extremely high affinity ligand for MT such as mercury or excessive amount of copper. This limitations may be overcome by using a SEC-HPLC-ICP-MS system to separate the low-molecular weight fraction containing MT and simultaneously detecting their content of Zn, Cu, Cd and

Hg. A second injection of the same sample saturated with Cd allows to assess total MT in the sample. Whole tissues and cells extracts, with or without saturation with Cd, after a fast centrifugation step, may be injected directly into the HPLC system, thus avoiding oxidation or other undesired modification of MT. Total Zn, Cu and Hg bound to MT as well as total MT can be quantified comparing the area of the chromatographic peaks with those of MT standard saturated with the respective metal ions. Using this method, the following detection limits (signal to noise ratio higher than 3) were estimated (values given as total amount of injected substance): 0.5 ng for total MT (by Cd saturation assay), 0.1 pg for Zn, 0.3 pg for Cu, 0.01 pg for Hg. The present method was successfully applied in the quantification of total MT, apo-MT (calculated by the difference "Total MT" – "Metal Bound MT") and Zn, Cu and Hg bound to MT in human peripheral blood mononuclear cells and in hepatic tissues from not lethally Hg intoxicated rats.

Th02

STUDIES ON ELEMENTAL LABELLING USING ICP-MS BASED HYPHENATED TECHNIQUES

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Biochemical and clinical research are nowadays based on the structural elucidation of biopolymers and metabolites associated to any process in life sciences. Besides that their quantification has gained significant importance leading to the quantitative 'omics' science. As important tool for quantification purposes mass spectrometric techniques, e.g. ESI and MALDI, have been applied.

On the other hand inductively coupled plasma-mass spectrometry (ICP-MS) has opened the quantification of biopolymers by the direct determination of naturally occurring heteroelements like sulphur, phosphorus and selenium [1-3]. However, these elements suffer from low ionisation efficiency and/or spectral interferences, which particularly affect their detection at low concentration levels. In order to overcome these drawbacks, few labelling strategies have been developed with the aim of introducing an ICP-MS detectable element [4]. So far, the most promising technique is MeCAT (metal-coded affinity tag) [5].

In this presentation the strategy of biopolymer labelling will be presented on selected examples. The use of two different hyphenated techniques, namely gel electrophoresis (GE) and μ -LC coupled to ICP-MS, are applied to the separation and detection of DNA fragments and standard proteins, resp.. Besides the detection of the naturally occurring heteroelements, these analytes were labelled using different strategies. Initial results will be presented and a comparison of both methods will be given.

- [1] D. Schaumlöffel et al. (2002) *Anal. Bioanal. Chem.* 372: 155-163
- [2] M. Wind et al. (2003) *Angew. Chem. Int. Ed.* 42: 3425-3427
- [3] D. Schaumlöffel, R. Lobinski (2005) *Int. J. Mass Spectrom.* 242: 217-223
- [4] J. Bettmer et al. (2006) *Anal. Bioanal. Chem.* 386: 7-11
- [5] M. Krause et al. (2005) Patent DE 102 27 599 B4

Th03

COMPREHENSIVE CHARACTERISATION OF ZINC-BINDING PROTEINS IN BACTERIAL CELL LYSATES USING 2D LIQUID CHROMATOGRAPHY COUPLED WITH ICP-MS AND MALDI-QTOF-MS.

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There has been a sustained interest in the speciation of protein bound trace elements in biological systems. This research proposes a top-down intact protein separation approach whereby 2D liquid chromatography is combined with both ICP-MS and MALDI-QTOF-MS for comprehensive investigation of zinc-binding proteins in bacterial cell lysates. Preliminary experiments were performed with bacterial cell lysates obtained from genetically engineered *E. coli*. SmtA, a zinc-binding bacterial metallothionein thought to be involved in essential metal ion homeostasis was utilised to determine suitable methodology. Highly reproducible 2D separations were achieved using ion-exchange chromatography in conjunction with reverse phase separations using a monolithic column. This presentation will address aspects of method development including protein separation, on/off-line elemental measurements using ICP-MS and incorporate protein identification results obtained via MALDI-QTOF-MS. Results focus on successful protein separation which permitted the direct comparison of the control and experimental cell lysates, such that over expression of zinc-binding was observed. Further investigations will involve multi-element profiling of species responsible for metal ion transport in *E. coli*, this is of particular interest when cultures are grown in growth-limiting media.

Th04

COMPLEMENTARY BIOANALYTICAL AND BIOCHEMICAL TOOLS TO STUDY CIS-PLATIN INTERACTIONS WITH DNA NUCLEOBASES.

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The metabolic pathway of platinum drugs in tumoral processes starts with the interaction of such compounds with the DNA nucleobases and the irreversible formation of stable adducts which compromise tumoral cells ability to replicate. In this regard, cis-Pt (cis-diamminedichloroplatinum) was introduced as chemotherapeutic drug in the early seventies and the elucidation of its mechanism of action in tumoral cells has been widely studied ever since.¹ Although the formation of cis-Pt adducts with the DNA nucleobases has been reported by many authors along the years, ongoing studies on improving Pt-drugs efficiency by increasing drug selectivity and minimizing side-effects are still of medical interest². Recent studies have revealed a higher number of adducts in the patients responding to Pt drugs and, suggested that the formation of DNA-adducts with cis-Pt could be a pharmacokinetic parameter to optimize in cancer therapy with Pt drugs.

In order to study cis-Pt-DNA interactions with the final aim of reducing the side effects of this drug, several bioanalytical strategies have been developed within this ongoing project. This communication will illustrate the optimization of the chromatographic separation using ICP-MS detection (³¹P and ¹⁹⁵Pt simultaneously) for the analysis of DNA adducts. For the optimization of the whole system, the bidentate adduct [(NH₃)₂Pt(dGMP)₂] has been synthesized *in-vitro* and its molecular structure has been evaluated by ESI-Q-TOF working in positive and negative modes. Analytical performance characteristics of different separation methods will be critically compared and the chosen one will be applied to the analysis of DNA samples from *Drosophila melanogaster* (fruit flies) exposed to cis-Pt. The extracted DNA (using the phenol-chloroform method) is simultaneous used to perform bioanalytical (HPLC-ICP-MS) and biochemical (COMET and SMART assays) measurements. Comparative results using all these instrumental methods will be illustrated in the presentation.

¹ S. J. Lippard, J. Berg. *Principles of Bioinorganic Chemistry* (1994). Eds. University Science Books, CA, USA..

KN 12

MS-BASED PROTEOMICS TURNS QUANTITATIVE: AN EXCELLENT OPPORTUNITY FOR THE ICP-MS

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Mass Spectrometry (MS) has been most successfully used to characterise proteins in complex samples. However, results so far have largely been qualitative in nature.

Although there are recent approaches to obtain quantitative proteomic information all of them are “relative” because they rely on comparing the signals from a given peptide from two different experimental conditions. Absolute quantification (only one experiment) is much less addressed in proteomics. We will demonstrate how elemental detection by ICP-MS can provide a means to modern biochemists for absolute quantitative proteomics, particularly for the study of post-translational modifications (PTMs) of proteins.

Glycosilation of transferrin is a good example: it is known that abnormal Tf isoforms, commonly referred to as carbohydrate-deficient-transferrins (CDTs), are excellent biochemical markers for congenital disorders of glycosylation (CDG) and also for chronic alcohol consumption. As such CDTs are still able to bind one or two Fe(III) atoms per molecule, we have investigated the usefulness of typical "iron speciation" strategies to develop a method of enough resolution and sensitivity to enable the determination of individual Tf glycoforms and so to develop a biomarker of CDG. The method is based on high performance liquid chromatography (HPLC) coupled on-line with ICP-MS with an octapole reaction system (ORS). This allowed the straightforward detection of six Tf glycoforms in healthy human serum after adequate iron saturation. Intact serum Tf glycoforms analysis by MALDI-TOF and by ES-Q-TOF will be discussed for identification, while isotope dilution analysis using ⁵⁷Fe isotope will be described for absolute and accurate Fe-Tf isoforms determinations.

Another most important PTM of proteins is phosphorylation. It is well documented that phosphorylation processes determine the activity, subcellular localization, signalling potential, turnover and interactions of a given protein with other proteins, DNA or bioligands. Thus, phosphoproteomics is now an extense and active field of research demanding new ideas for quantification. The use of element-specific ICP-MS detection of phosphorus for phosphopeptides detection and determinations by capillary HPLC-ICP-MS analysis of proteins tryptic digests will be described. The high accuracy (around 2%) and precision attained using just a single reference phosphorous containing compound [Bis(4-nitrophenyl) phosphate] for calibration of all phosphopeptides of a tryptic digest of the protein make this strategy ideal for the investigation of small quantitative protein changes in functional and temporal studies. This approach is also most valuable to study and determine phosphorylation degrees in previously known proteins as demonstrated for commercial α -casein.

Th05

EVALUATION OF ICP-MS AS DETECTION SYSTEM FOR QUANTITATIVE ELEMENT-TAGGED IMMUNOASSAY

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In a research program dealing with the development of innovative methods in proteomics, an element-tagged immunoassay with ICP-MS detection was devised to determine hidden allergens in foods. Attention was focused on the peanuts proteins Ara h1 and Ara h3/4.

Taking advantage of the sensitivity of enzyme-linked immunosorbent assays (ELISAs), a non-competitive sandwich method was developed. The microtiter plate (coated with anti total soluble peanut protein polyclonal antibodies) was exposed to samples, to anti-Ara h1 and -Ara h3/4 monoclonal antibodies (Ab I) and then to europium-labeled rabbit anti-mouse polyclonal antibodies (Ab II). After digestion with 7M HNO₃ (100 µl, 1 hr, room temperature), 25 µl sample were injected into the flow injection analysis-ICP-MS system.

Ab I and Ab II concentrations were optimized as a function of the assay, since the results showed that limits the dynamic range of this method at low concentration of antigen is limited by the non-specific binding. These findings suggested that in order to detect very low amounts of antigen it is necessary to maintain a low background of Eu and a low amount of proteins that can form non specific binding to the anti Ara h1 and Ara h3/4 antibodies.

In addition, different incubation times and temperatures were tested both on the sample and on the standard solutions. Calibration curve of the ICP-MS-linked Eu-labeled antibodies was calculated in the 0.6 nM-0.15 µM range showing excellent linearity of the method.

The method has been applied to the detection of peanuts allergens in foods and the results showed that ICP-MS represent a powerful detection system both in terms of sensitivity and linearity, although the non-specific reactivity of the reagents used in the immunoassay protocol could be the bottleneck of the application.

Th06

SPECIATION OF ESSENTIAL AND/OR TOXIC ELEMENTS IN HUMAN AND FORMULA MILK BY ELEMENTAL AND MOLECULAR MASS SPECTROMETRY.

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During the first months of human life, milk constitutes the unique source of nutrients. A correct supply of all macro and micronutrients (proteins, lipids, carbohydrates, minerals, enzymes) from milk is necessary in order to assure baby's health, therefore human milk can be regarded as the optimal natural nutrient for the new born (1).

Nevertheless, the biological behaviour (absorption and bioavailability) of a given elements strongly depends on the chemical form in which this element occurs in milk. Nowadays the chemical forms (species) of the elements that are transferred to new born are not known. This fact explains the need to carry out speciation studies in milk, as well as the current interest to identify the specie(s) to which the element is bound (2).

In this work, we describe the element speciation studies carried out in milk samples by coupling of different chromatographic techniques (HPLC) with an element-specific detector,

such as ICP-(ORC)-MS. For this purpose chromatographic separation was carried out using size exclusion chromatography (SEC) and cationic exchange chromatography (Mono S). The results obtained for the speciation of essential and toxic trace elements (Fe, Cu, Zn, Se, I, Cr, Co, Mn, P, S, Al, Cd y Pb) in human and formula milk whey and this association to proteins like albumin, transferrin, lactoferrin, lactalbumin and lactoglobulin will be presented. Further, molecular identification and characterization results of the previously mentioned presented biomolecules (metal binding proteins in human and formula milk), by using molecular technique will be showed. The use of MALDI-TOF has made possible the determination of protein molecular weight and “mass-fingerprinting”.

(1) A. Ballabriga, A. Carrascosa. “Nutrición en la infancia y la adolescencia”. Ediciones Ergón S.A., Madrid, (2001)

(2) R. Cornelis , J. Caruso , H. Crews, K. G. Heumann. “Handbook of Elemental Speciation, Handbook of Elemental Speciation II: Species in the Environment, Food, Medicine and Occupational Health” .John Wiley and Sons Ltd . England (2005).

Th07

NEW APPROACHES TO CISPLATIN METALLOMICS

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Cisplatin (cis-diamminedichloroplatinum (II)) is the most important of the platinum containing antitumoral drugs. It is used in the treatment for a variety of cancers. However, this drug presents several side effects as nephrotoxicity and ototoxicity. Studies about the interaction of the drug with different biomolecules present in body fluids and cells are essential to understand the toxicity mechanisms that are still not fully characterised.

The experiments designed in this work are focused to the study of cisplatin interactions with different target biomolecules present in serum and in tissues of rats treated with the drug. The objective of this work is the development of an analytical methodology to separate and characterise the cisplatin-biomolecule species formed. For that purpose it have been used chromatographic (FPLC, SEC) and mass spectrometry techniques, for elemental and structural determination (ICP-MS, MALDI-TOF, ESI-Q-TOF).

Incubation experiments with significant serum proteins such as Apo-Transferrin (Apo-Tf) and human serum albumin (HSA), has demonstrated the high affinity of HSA for cisplatin. This is also true for real human serum incubations. Triptic digestion of the formed adducts and the analysis of the peptides produced by MS results in peaks with isotopic pattern characteristic from peptides adducts with platinum.

Incubations were made, as well, with cytosolic biomolecules like metallothioneins (MT) and glutathione (GSH), studying the effect of the incubation time on the formation of adducts. It has been demonstrated the rapid interaction of the drug with MTs. MS analysis of the adducts formed in vitro with standard proteins and proteins from tissues of rats treated with the drug, confirm the identity of the species and provide information about the interaction drug-biomolecule.

The combination of traditional techniques for protein separation, like 2D gel electrophoresis, with the bidimensional chromatographic methodology developed for the characterisation of specific interaction cisplatin-protein in tissues has been studied.

Th08

CAPILLARY HPLC-ICPMS: A GENERIC APPROACH FOR ABSOLUTE QUANTITATIVE PHOSPHOPROTEOMICS

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Protein phosphorylation is a key event in signalling processes. A single protein can be phosphorylated and de-phosphorylated on different sites at different times. These phosphorylation changes can only be detectable if quantitative information is available. Unfortunately, quantification of protein phosphorylation is a very challenging task often hampered by low relative amounts of phosphoproteins and lack of adequate analytical methods. In special, absolute phosphoprotein quantification at given phosphorylation sites is not commonly addressed and reported methods so far require chemical synthesis of each individual phosphopeptide, which should be known beforehand. Interestingly, the elemental response by ICP MS, operated under certain conditions, could be directly proportional to the absolute amount of phosphorus present. Therefore, ICP MS may become a great alternative for specific and quantitative phosphopeptide analysis before their final characterization by ESI-MS.

In our method, the use of a post-column sheath flow in conjunction with a total consumption nebulizer and the addition of a commercially available phosphorus standard to the sample were able to provide reliable and simultaneous quantitative results for all individual phosphopeptide present, initially expected or not. Accuracy and precision attainable were investigated using commercially available phosphopeptides and robustness of the method was evaluated in casein proteins. The absolute information obtained by ICPMS allowed to compute phosphopeptide recoveries for every step, keeping the whole analysis under control. This new approach can be invaluable to address quality assurance requirements urgently needed in quantitative (phospho)proteomics.

Th09

SECTOR FIELD ICP-MS FOR QUANTITATIVE PROTEOMICS USING METAL CODED AFFINITY TAGS (MECAT)

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The identification and quantification of complex protein and peptide mixtures plays a key role in proteome analysis. Therefore a new simple and efficient method, called MeCAT (Metal Coded Affinity Tag) was developed by Proteome Factory AG. Metal chelate complexes are linked to all cysteines of model proteins, which were then analyzed and quantified by ICP-MS. Rare earth elements such as Lutetium and Holmium were used with the MeCat reagent to label the proteins. The benefit of using ICP-MS includes the possibility of absolute quantification, a large dynamic range and highest reproducibility. The advantage of using high resolution ICP-MS is the superior signal to noise ratio which allowed quantifications of proteins down to the attomol and femtomol range. This application was examined with two model proteins (BSA, α -Lactalbumine) with two lanthanoid metals (Ho, Lu). High resolution ICP-MS allowed absolute quantification and screening of MeCAT labelled proteins and peptides, offering a new and powerful tool for quantification in proteomic research.

KN 13

ISOTOPE RATIO MEASUREMENTS IN MASS SPECTROMETRY: NEW SOLUTIONS FOR OLD PROBLEMS

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The measurement of isotope ratios using Plasma Source Mass Spectrometry has been applied to solve different technical and analytical problems, from the provenance of archeological artifacts to the detection and correction of species degradation in speciation analysis. The analyst however has to face different challenges to obtain accurate and precise isotope ratio measurements and to apply those measurements to obtain relevant analytical information.

From the technical point of view, isobaric interferences from other elements, such as Rb-Sr or Nd-Sm, need to be eliminated. Traditionally, off-line separations are performed prior to the isotope ratio measurement. In our laboratory we have evaluated on-line HPLC separations with large volume injection in combination with multicollector ICP-MS instruments with satisfactory results in terms of precision and accuracy. Mass bias correction is another technical problem which needs to be reevaluated. We have observed that using weighed least squares we can reduce significantly the uncertainty in the mass bias correction factor which will reduce their effect in the uncertainty of the corrected isotope ratio.

From the application point of view, single isotope ratio measurements, as traditionally applied in isotope dilution analysis, can be substituted with isotope patterns and isotope pattern deconvolution models opening new alternative and challenging quantitation procedures with simplified and intuitive mathematical background. Classical speciation problems including Cr(III)-Cr(VI) and Hg(II)-MeHg⁺ can be easily solved with this alternative tool.

The study, both *in vitro* and *in vivo*, of the metabolism of trace elements is simplified using isotope pattern deconvolution. When an enriched isotope of the element to be studied is added to the system this enriched isotope could be found latter in different chemical species. The isotope enrichment for each chemical species (tracer/tracee ratio) will depend on the background concentration of the natural element in the system and the amount of enriched isotope incorporated in each particular species. We have developed a mathematical model based on isotope pattern deconvolution in which a second enriched isotope is used to quantify the amount of the element in each chemical species while the isotope enrichment is calculated from the other enriched isotope. The possible study of differential expression of proteins using enriched sulfur isotopes will be described.

Th10

DETERMINATION OF TRACE ELEMENTS IN SEDIMENTS BY SEQUENTIAL CLOUD POINT EXTRACTION AND ISOTOPE DILUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY.

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The weakly-bound trace elements fraction in sediments extracted with 1 mol/L HCl was preconcentrated using sequential cloud point extraction CPE. Spikes of ¹¹²Cd, ⁶⁵Cu, ²⁰⁶Pb and ¹¹⁷Sn performed the quantification by Isotope Dilution ICP-MS. The ligand *O,O*-diethyldithiophosphate (DDTP) and the surfactant Triton X-114 followed by heating at 40 °C until attaining the cloud point concentration producing a micelle. A step of centrifugation followed by cooling in an ice bath facilitated the micelle separation. This micelle was digested with HNO₃ plus H₂O₂ heating to 120 °C and a volume closed to 3 mL was analysed by ICP-MS measuring isotope ratios characterized by RSD <0.5%. The digestion of the micelles reduced the C content to 1% improving the precision of isotope ratio measurements to less than 0.5%. The analysis of Lake Ontario Sediment WQB-1, demonstrated that with DDTP more than 93% of these analytes were extracted, as well as other elements such as As and Sb. The poor surfactant residual phase had the pH adjusted to 5 and the chelating reagent 4-(2-pyridylazo) resorcinol (PAR) mixed with Triton X-114 was added. The sequence to attain the CPE was repeated and a second micelle containing Co, Cr, Ni, V, Ti and Zn was obtained.

Th11

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY DETECTION OF GOLD LABELLED NUCLEIC ACIDS

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Labelling nucleic acids and other bio-molecules with elemental tags has many advantages compared with determining them through their phosphorous and sulfur content. Principally these relate to greatly increased sensitivity and the avoidance of isobaric and polyatomic interferences.

This paper will concentrate on the application of ICP-MS in nucleic acid research. The labelling of nucleic acids with Nanogold particles will be discussed and methods for functionalising nucleic acids for elemental labelling will be described. Separation of the functionalised bio-molecule from reagents and excess label will also be detailed.

The paper will conclude with discussion of potential applications of ICP-MS detection of elementally labelled nucleic acids.

Th12

HIGH ACCURACY ISOTOPE RATIO MEASUREMENTS USING MULTI-COLLECTOR ICP-MS: SOLUTIONS TO WIDESPREAD PROBLEMS

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Multi-collector ICP-MS has proved to be a very powerful tool for measuring high precision and accuracy isotope ratios. Application of this type of instrumentation, in combination with different isotope-ratio techniques, to real world problems is discussed.

A method, using ^{129}I as the spike, has been developed for the analysis of iodine in foodstuffs by MC-ICP-IDMS which does not require iterative matching of samples and standards. This reduces time of analysis and makes the sample pre-treatment easier. Tolerances of the double IDMS method for iodine determination have been explored and small variations of the amount of ^{129}I spiked or the amount of ^{127}I in blends have no effect on recoveries. In addition, by limiting the procedure to only using standards that do not exceed at any point a maximum activity of 0.4 Bq g^{-1} ($61 \text{ ng g}^{-1} \text{ }^{129}\text{I}$) then the method can be adopted by a wider range of laboratories outside of radiological control. This method has been applied to the production of a reference material for iodine in foodstuffs. Despite the need for monitoring low levels of iodine in foodstuffs, the provision of food matrix certified reference materials is limited. This new material will be of use to food analysts.

The second application is the use of isotope ratios for authenticity testing. The potential of isotope ratio measurements for the detection of counterfeit pharmaceutical tablets has been previously investigated but the lack of widespread methodologies for the measurement of delta values and the application of different approaches to correct for mass discrimination effects makes the comparison of values between different laboratories a difficult task. Furthermore the data from these studies could be presented as evidence in court and therefore methods need to be validated to support their credibility.

Can the analytical community produce reliable/traceable natural isotope ratio delta values when using a multi-collector ICP-MS? It is also crucial to be able to produce uncertainty values associated to the delta measurements. These will vary depending on the correction applied for mass bias and the uncertainty associated to the delta value of the working standard. A method for $\delta^{34}\text{S}$ sulfur measurements has been investigated, different working standards and approaches for mass discrimination have been used and values will be compared. A case of study using pharmaceutical tablets from different batches/origin will be discussed.

KN 14

ISOTOPIC FINGERPRINTS – A UNIQUE PIECE OF INFORMATION (?)

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Authenticity of goods and products as well as information of provenance of (pre-/historic) humans or animals is creating a lot of challenging questions to our scientific community. Isotope ratio analysis is a very elegant approach in order to add an additional piece to the puzzle: Where does it come from?

Due to increasing precisions of ICP-MS technology, it has become a mature and widely applied analytical technique for a still increasing number of isotopic systems. Laser ablation adds the advantage of direct solid sampling to this technique. Nonetheless: The better the instrumentation becomes, the more important is the fact not to draw conclusions out of scientific artefacts.

We have widely investigated a number of isotopic systems in order to meet the claim to provide accurate and precise data. Since we now can determine small differences, a new 'old' question raised: how reliable is the isotopic fingerprint as unique information? Therefore, transfer pathways of elements as well as diagenetic processes have to be considered. Examples on the application of (LA)-(MC)-ICP-MS for authentication studies of artefacts and agricultural products as well as migration studies of prehistoric human cultures and recent animal systems by different isotopic systems are discussed within this presentation.

Tu13

³¹P ELEMENT SPECIFIC DETECTION: A NEW APPROACH FOR CHEMICAL WARFARE AGENT DETECTION

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Recent increases in terrorist activity and the threat of chemical weapon attacks has lead to the demand of a rapid and reliable method for analysis of chemical warfare agents (CWA) and their degradation products. The nerve agents Sarin and VX, as well as many others, pose a deadly threat to the human population if released. These phosphorus containing nerve agents along with their degradation products present difficulties for ultra-trace analysis due to their low volatility and lack of a good chromophore. Previous studies have successfully utilized methods such as gas chromatography/mass spectrometry (GC-MS), ion mobility/mass spectrometry (IMMS), and liquid chromatography/mass spectrometry (LC-MS) for the analysis of organophosphorus containing degradation products with detection limits in the ng/mL range¹⁻³. Chemical warfare degradation product analysis by inductively coupled plasma mass spectrometry (ICP-MS) coupled with ion-pairing reversed phase high performance liquid chromatography (IP-RP-HPLC) has recently been shown as a rapid and reliable speciation technique with detection limits in the pg/mL range⁴.

In this study the use of HPLC and GC separation techniques coupled with ICPMS detection are described for the analysis of common degradation products of Soman, Sarin, Tabun, RVX and VX chemical warfare agents. To date these are the first studies utilizing ICPMS for the ultra-trace analysis of chemical warfare agent degradation products.

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Th14

PRECISE DETERMINATION OF $^{44}\text{Ca}/^{40}\text{Ca}$ ISOTOPE RATIOS BY USING ICP-MS WITH DYNAMIC REACTION CELL AND ITS POTENTIAL FOR FOOD AUTHENTICITY STUDIES

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Collision cell and dynamic reaction cell (DRC) technologies are applied in inductively coupled plasma mass spectrometry (ICP-MS) mainly to enable the determination of traditionally 'difficult-to-analyse' isotopes like ^{40}Ca , ^{56}Fe , ^{80}Se , which suffer from interference by argon-containing ions. During almost a decade of availability to the analysts, DRC-ICP-MS has been found advantageous for a number of applications including precise isotopic analysis of Fe, Se, Pb and other elements. It has been shown, that application of collisional damping in the DRC in combination with fast scanning allows to obtain isotope ratio precisions close to the counting statistics error [1]. However, precise determination of $^{44}\text{Ca}/^{40}\text{Ca}$ isotope ratios still remained a challenge.

This talk will summarize recent experiences in optimization of DRC-ICP-MS for precise measurement of $^{44}\text{Ca}/^{40}\text{Ca}$ isotope ratio with a special emphasis on improving precision and reducing apparent mass bias in isotope ratio measurements. In the second part, practical aspects and potential application of this method for food authenticity studies will be discussed with an example of comparative analysis of calcium isotopic composition in asparagus samples originating from different areas including those registered by European Commission in PGI system (Protected Geographical Indication).

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Th15

FRACTIONATION OF MERCURY ISOTOPES IN THE ENVIRONMENT AND PRECISE MEASUREMENT OF MERCURY ISOTOPE RATIOS BY MC-ICP/MS

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This paper discusses techniques for measuring precise isotope ratios of mercury using a continuous-flow cold-vapor technique coupled to MC-ICP/MS. The optimized method achieved a precision of better than 0.001 % RSD for mercury isotope ratios at concentrations of ~10 ng/mL. To correct for instrumental mass bias during the measurement, a thallium solution with known $^{203}\text{Tl}/^{205}\text{Tl}$ ratio was measured simultaneously. The method was applied to measure natural variations of mercury isotope ratios in sediments. Variations in mercury isotope ratios were confirmed in the uppermost horizon of long sediment cores (representing modern time mercury). The newly deposited mercury appeared to be enriched with heavier isotopes compared to the mercury down core (representing background mercury). A fractionation of close to 0.60 ‰ between surface and deeper sediments was observed. Precise mercury isotope ratio measurements were further applied to track sources of mercury at contaminated sites. The fractionation that occurs during reduction of Hg(II) to Hg

(0) and subsequent evaporation of Hg(0) was systematically investigated and Raleigh fractionation factors calculated.

Th16

Sr ISOTOPIC ANALYSIS OF HUMAN BONE AND TOOTH TISSUE EXCAVATED AT THE CEMETERY OF THE SINT-SERVATIUS CHURCH (MAASTRICHT, THE NETHERLANDS) USING MULTI-COLLECTOR – ICP – MASS SPECTROMETRY

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The Saint Servatius basilica in Maastricht, The Netherlands, is considered as important cultural heritage. There, archaeologists have discovered a huge collection of artefacts, such as valuable objects, sarcophagi, fragments of architecture and human remains, testifying of its 1600 year rich history.

In this work, multi-collector ICP-MS has been used to study the Sr isotopic composition of human bone and tooth tissue, excavated at the cemetery of the Saint Servatius basilica. The goal of these studies is to investigate the heterogeneity and possible migration of its past population. There is considerable difference in the Sr turnover rate between bone tissue and tooth enamel. While the Sr isotopic composition of bone tissue is governed by the location where a person has been living during the last years before his death, tooth enamel reflects the place of that person's birth and infancy.

Complete sample digestion with quantitative Sr recovery has been accomplished by use of a microwave-assisted acid digestion for bone tissue, and open dissolution on a hot plate for tooth tissue. Preceding isotope ratio measurements, Sr has been isolated both quantitatively and in pure form using a commercially available extraction chromatographic resin (Sr specTM, Eichrom Technologies Inc.). For isotope ratio measurements, a large geometry Nu 1700 multi-collector ICP-MS instrument was used. The results of these measurements, a comparison to these obtained by single-collector ICP-MS and conclusions about the population will be presented.

Poster Session Thursday 22 Feb 2007

ThPo1. TWO-DIMENSIONAL SEPARATION SCHEMES FOR THE ASSESSMENT OF METAL PROTEIN INTERACTION BY ICP-MS

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Determination of metallo-biomolecule association in biological applications is one of the most challenging tasks of speciation analysis. Measuring these interactions on different levels of complexity (1) in experiments with selected proteins or other relevant biomolecules and (2) attempting comprehensive mapping of adducts in-vivo is of crucial importance in many research fields as e. g. bioinorganic chemistry and biomedicine. The potential of the complementary use of both elemental and molecular mass spectrometry in these specific applications is evident.

ICP-MS is the unrivalled detector capable of dealing with trace concentrations of metals bound to proteins. The key advance of ICP-MS relies in the fact that quantitative results can

be obtained with species unspecific standards. The determination of metal to sulfur ratios can be exploited to assess stoichiometry of metal binding in biomolecules, since the sulfur containing amino acids exhibit a natural abundance of 4 %.

As a drawback mostly these investigations have to preserve physiologic conditions reducing the number of applicable separation mechanisms, as limited stability of the metal-protein adducts may result in de-metallation during the separation. Furthermore, sample matrices are extremely complex. So far comprehensive mapping of metalloproteins was attempted by exploiting methodological approaches stemming from proteomics. Gel electrophoresis was combined with laser ablation ICP-MS for detection of metals. As a drawback these separation schemes are mostly not native and hence data validation of these approaches is difficult.

Our elemental proteomics approach will comprise isoelectric focusing by free flow electrophoresis as first separation dimension prior to orthogonal SEC-ICP-MS analysis. For the first time we will explore the potential of combining the two techniques with subsequent SEC-ICP-MS determination in the analysis of metal-protein association.

ThPo2. PHOSPHOPEPTIDE ENRICHMENT STUDIES USING ICPMS

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Protein phosphorylation is one of the most important post-translational modifications, which is critically involved in many significant cellular processes. Phosphorylation is often a sub-stoichiometric process mostly occurring in low abundance proteins involved in many signaling networks. Therefore, phosphopeptide enrichment is usually a prerequisite before analysis by element and molecular mass spectrometric techniques. Unfortunately, these preconcentration procedures are usually not completely controlled. Interestingly, in contrast to molecular MS techniques, ICPMS can provide absolute quantitative information. This feature can be very useful to address quality assurance requirements urgently needed in quantitative phosphoproteomics.

The objective of this work was the development of a new strategy to enrich the sample for phosphorylated peptides reducing the number of co-eluting non-phosphorylated peptides to a minimum. This was obtained by using a multi-mode column, a combination of gel filtration, reversed phase and ion exchange modes. Phosphopeptide recoveries for every step included in the analysis (enrichment and chromatographic separation) were computed using the absolute information obtained by ICPMS, which allowed their optimization.

ThPo3. SEPARATION AND QUANTIFICATION OF PROTEIN MIXTURES WITH THE HYPHENATION OF CAPILLARY HIGH PRESSURE LIQUID CHROMATOGRAPHY AND INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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Proteins are the active species in every living organism. Their appearance is manifold, both with respect to their primary structure and different modification state. Besides the structural elucidation, protein quantitation has become very important in many fields, e.g. diagnostics, but remains still a great challenge for the analytical methods.

The contribution of inductively coupled plasma-mass spectrometry (ICP-MS) to protein analysis is the ability of element-selective and species-independent quantification. Its

hyphenation to capillary high pressure liquid chromatography (cHPLC) is a highly successful approach and enables gradient separations with high organics content. Whereas peptide separation is straightforward, protein separation is to some extent still a challenge. Typically, ion-exchange or size-exclusion chromatography need high flow rates, but satisfying reversed-phase separations suitable for cHPLC are more difficult to obtain. Exceptionally high separation efficiencies are achieved using polymer-based monolithic columns. In this pilot study, we investigated their potential for protein analysis by cHPLC-ICP-MS.

Essentially all proteins contain sulphur, which can be used for their quantification.¹ Since sulphur holds more than one stable isotope, all proteins with known number of sulphur atoms in a given mixture may be quantified by species-unspecific isotope dilution analysis (IDA). For instance, IDA of sulphur was successfully applied to the analysis of metallothionein isoforms² separated by capillary electrophoresis. The application of IDA to intact proteins is highly relevant, since there is an urgent need for reliable and accurate reference methods in clinical and biochemical research. Therefore, we probed the applicability of IDA for sulphur-based label-free quantification of large proteins by cHPLC-ICP-MS.

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ThPo4. COUPLING OF HPLC-ICP-MS AND μ -HPLC-ICP-MS FOR THE DETERMINATION OF CIS-PT ADDUCTS WITH DNA NUCLEOBASES AND STRUCTURAL CHARACTERIZATION BY ESI-Q-TOF

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The antitumoral effect of *cis*-platin [cis-diamminodichloroplatinum(II)] in mammals seems to be related to its binding to DNA components. Previous studies have revealed the stoichiometry of this interaction by electrospray mass spectrometry (ESI-Q-TOF). Initial *in-vitro* incubation of the drug with the pure nucleotide (deoxyguanosine 5'-monophosphate) provided a MW of 921 Da which was slightly different to the one obtained with the oligonucleotide of sequence 5'-TCCGGTCC-3'. This difference is explained for the internal phosphodiester bridge between the two adjacent guanines (once they are forming the complex with *cis*-Pt) in the oligonucleotide that does not occur with the individual nucleotides.

The chromatographic separation of the adducts formed with *cis*-Pt has been carried out by coupling high resolution liquid chromatography (HPLC) to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) monitoring simultaneously ³¹P and ¹⁹⁵Pt. Two different chromatographic columns have been evaluated for this purpose: A narrow-bore RP-C₈ using a mobile phase containing 60mM ammonium acetate (pH 5.8) and 7.5 % methanol and a capillary RP-C₈ using as mobile phase consisting of a gradient of methanol:water.

Detention limits of both systems were of 2.4 ng ³¹P and 0.1 ¹⁹⁵Pt for narrow-bore RP-C₈ and 0.7 ng ³¹P and 2.1 pg ¹⁹⁵Pt for the capillary RP-C₈. The resolution of the chromatographic peaks improves with the capillary system, though the best separation of the four DNA nucleotides has been obtained using conventional HPLC.

Both methods have demonstrated the capacity of the hybrid system HPLC-ICP-MS to satisfactorily separate the free nucleotides (monitoring ³¹P) and the adduct formed between *cis*-Pt and dGMP

ThPo5. EFFECT OF SELENIUM-METHYLSELENOCYSTEINE IN HUMAN HEPATOMA HEP G2 CELL LINE. PROTECTION AGAINST OXIDATIVE STRESS AND METHYLMERCURY.

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Selenium is an essential micronutrient for humans and also a constituent of enzymes (such as glutathione peroxidase and 1-iodothyronine 5-deiodinase). In addition, it is recognised that Se-compounds provide protection against various forms of cancer, specially as Se-Methylselenocysteine (Se-MeCys). On the other hand, the interactions between Mercury and Selenium are arousing high interest because several authors reported a protective function of Se against toxic effects caused by mercury.

In this in-vitro study, the protective effect of selenium (as Se-MeCys) against oxidative stress and toxic effects caused by methylmercury in human hepatocytes (Hep G2) were evaluated.

Cell culture was treated, as a first approach, with Se-MeSeCys and later with the oxidative stressor tert-butyl hydroperoxide (t-BOOH) during 3 hours, with the aim to observe a response against oxidative stress. Cell viability, and some parameters related to the redox status, such as reactive oxygen species (ROS), reduced glutathione and the activity of reductase glutathione (GR) and glutathione peroxidase were measured. The results show that Se-MeSeCys at micromolar level is able to protect cells against oxidative stress produced by t-BOOH.

Finally, speciation studies were carried out using HPLC-ICP-MS; the results obtained suggest that Se-MeSeCys remains unaltered over the whole process. By using SEC-ICP-MS, differences in profiles of metallobiomolecules associated to Cu and Zn were observed within control cells, cells treated with t-BOOH and cells treated with t-BOOH plus Se-MeSeCys.

Concerning selenium-methylmercury interactions, in vitro studies were carried out with the culture cell Hep G2, where Se-MeSeCys and methylmercury (MeHg) were coadministred and left for 18 hours. Protection against cell damage caused by mercury was observed in presence of Se-MeSeCys. In order to deeper understand the protection mechanisms of Se-MeSeCys, speciation studies were carried out with ICP-MS coupled to different separation techniques.

ThPo6. STUDIES ON THE BEHAVIOR OF MEGLUMINE ANTIMONIATE AND ITS METABOLIC SPECIES IN THE HUMAN BODY

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Clinical applications of antimonials in the treatment of leishmaniasis are a unique opportunity to investigate the metabolism of antimony and its species in the human body. In this work, which is a continuation of previously reported studies, ICPMS without or in combination with ion chromatography and flow injection hydride generation, has been used for the determination of total [Sb], Sb³⁺ and Sb⁵⁺ in clinical samples (whole blood, plasma, urine, hair and fingernails) of patients treated with N-methyl meglumine antimoniate (MMA) under low-dose administration (5 mg Sb⁵⁺/ kg of body mass). Samples from a reference group were analyzed for comparison. Studies were performed on species-spiked water, urine, whole blood and plasma samples to get information on the chemical stability of these species. Concentrations of total [Sb], Sb⁵⁺ and Sb³⁺ in urine and blood plasma samples, determined

weekly during the administration period of MMA, showed rapid excretion of the drug and no significant metabolism. However, indications for drug metabolism and bio-reduction of Sb^{5+} to Sb^{3+} were obtained from urine samples during the slow elimination phase. Total [Sb] in scalp hair and in fingernail samples of patients matched their drug administration history. Even after longer time periods since the last drug administration (>150 days), patients showed elevated [Sb] levels in newly grown hair and in urine. These results give further support to the hypothesis of peripheral body compartments from which the excretion kinetics of Sb is much slower and in which active *in vivo* conversion of the organic antimonial drug occurs, including the formation of the more toxic Sb(III) species.

ThPo7. ON-LINE COUPLING OF GEL ELECTROPHORESIS AND ICP-MS FOR THE DETERMINATION OF FE IN METALLOPROTEINS

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Gel Electrophoresis (GE) is a powerful separation technique for the characterization and analysis of proteins and biomolecules. The combination of inductively coupled plasma mass spectrometry (ICP-MS) and GE takes advantage of the high separation capacity of GE and the multi-elemental capability of ICP-MS for metal analysis. The on-line coupling of gel electrophoresis and ICP-MS was already described for the determination of dsDNA fragments by W. Brüchert. Electrophoresis is a separation method based on the differential mobility of large biomolecules under an applied electric field. The gel was made with different concentrations of acrylamide monomer, and cross-linking produced different sized polymer mesh networks. Several different concentrations of gels were tested for suitability in separating the proteins. Denaturing GE separations using Sodium-Dodecyl Sulphate (SDS) or Native (isoelectric point) separations were used for proteins with differing forms of iron complexation: Hemoproteins, such as Cytochrome C and Hemoglobin, have iron-porphyrin as a prosthetic group, in which the iron is strongly bound. These proteins require separation by SDS-GE and post determination of iron by ICP-MS. Alternatively, native GE can be used to avoid the loss of Fe^{3+} ions in Ferritin and Transferrin, where the iron ions are weakly complexed within a hollow protein shell. On-line UV Absorption analysis is used to identify the arrival time of the protein to the ICP-MS.

The development of different GE separation techniques for coupling with MS for the analysis of iron-protein complexes reported in here will pave the way towards protocols for the analysis of a vast spectrum of metalloproteins.

ThPo8. NEW DEVELOPMENTS IN NANOHP LC WITH PARALLEL ICP MS AND ESI MS/MS DETECTION FOR HETEROATOM BASED PROTEOMICS

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Many proteins contain in their structure a covalently bound heteroatom such as sulphur, phosphorous or selenium, and are therefore detectable by inductively coupled plasma mass spectrometry (ICP MS). In many studies, total elemental analysis is insufficient for understanding the functional role of elements in biological systems. Identification of the molecules in which these elements are present, or ligands complexing them, by molecular mass spectrometers is necessary. Due to the large number of compounds usually present in a sample, their identification necessitates a separation step prior to detection. Miniaturized

chromatographic techniques, such as nanoHPLC, enable high resolution separation even for very small sample volumes.

The coupling of nanoHPLC - ES MS/MS has largely contributed to a progress in high throughput identification and structural characterisation of proteins via peptide mapping. However, the electrospray ionization is strongly compound-dependent, is often suppressed by the presence of the matrix and the quantification is practically possible only via differential approaches using isotopically labelled tags. Therefore new ways for quantification of peptides and proteins are intensely sought for. The specific detection makes ICP MS an attractive technique for quantitative analysis. Its principal advantages include the high sensitivity, the independence of the response of the molecular environment of the heteroelement, large dynamic range and high tolerance to matrix. The development of an interface enabling the direct hyphenation of nanoHPLC to ICP MS was achieved through the invention of the nanonebulizer. It became possible to perform parallel nanoHPLC - ICP MS and nanoHPLC - ESI MS coupling and to obtain elemental and molecular information of the sample constituents. The complementarity of these two detection modes greatly facilitates the identification and quantification of heteroatom-containing biomolecules.

Analytical strategies taking advantage of the synergistic effect of both atomic and molecular mass spectrometers as detectors for nano liquid chromatography are discussed in this contribution for the identification and quantification of proteins and selenoproteins. First, species separation and selenium or sulphur specific detection are carried out by nanoHPLC coupled to ICP MS. The same sample is injected a second time to nanoHPLC with a molecular mass detector such as tandem electrospray mass spectrometer to characterize the structure of the molecules of interest. The difficulties encountered in quantitative proteomic analysis with molecular detection can thus be avoided by the specific detection and quantification of sulphur by ICP MS for sulphur containing species. Furthermore, unspecific isotopic dilution analysis permits the absolute quantification of hetero-element containing biomolecules of unknown identity.

ThPo9. DETERMINATION OF RARE EARTH ELEMENTS IN CONTRAST AGENTS USING ICP-MS

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Magnetic Resonance Imaging (MRI) is a non invasive imaging technique, widely used in hospitals, for visualizing biological processes in vivo via active targeting of an imaging contrast agent (CA). Clinically accepted agents for MRI contrast enhancement allow for detection limits in the μM range. However, since the concentration of relevant biological targets usually does not exceed the pM range, the sensitivity of these agents is far too low to enable molecular imaging. One approach to achieve an amplification of the effective CA concentration is based on the combination of many CA molecules in large liposome nanoparticles. Therefore Philips Research is trying to develop new liposomal-based contrast agents. Experiments show that the gain in sensitivity obtained for the Yb-dotam-containing liposome nanoparticle with respect to a single Yb-dotam molecule is roughly proportional to the number of Yb-dotam units present in the particle. An accurate determination of the amount of Yb in these liposomal-based contrast agents is done using ICP-MS.

ThPo10. CERULOPLASMIN ASSAY BY IMMUNOAFFINITY CHROMATOGRAPHY AND HPLC-ICPMS

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Ceruloplasmin (Cp), a copper metalloprotein in human serum has been a valuable diagnostic marker in Wilson's disease where Cp levels tend to be low while high Cp levels in human serum were associated with myocardial infarction, neoplastic and inflammatory conditions.

There is no standardized reference method for Cp and current immunologic assays and the bichromatic assay have a number of drawbacks. The method presented here uses immunoaffinity chromatography to remove six of the most abundant proteins from a serum sample and high-pressure liquid chromatography (HPLC) with a size-exclusion column to separate Cp from other serum proteins and any free Cu prior to analysis of ^{63}Cu and ^{65}Cu by inductively-coupled plasma mass spectrometry (ICPMS).

Cp identification is based on retention time match of the unknown protein in the serum sample with the Cp external standard and the presence of ^{63}Cu and ^{65}Cu at a ratio of 2.2 ± 0.1 . The method accuracy as established independently by two of the authors with a certified reference serum is 98 to 101% and the coefficient of variation is 6.4% and 5.4%, respectively. The assay was used to analyze 167 human sera for Cp from patients with MI, pulmonary embolism (PE), rheumatoid arthritis (RA), systemic lupus erythematosus (SLE), other forms of arthritis, and a set of healthy patients as normal controls. Our data show that Cp concentrations tend to be higher in MI, RA, and SLE patients, higher in female as compared to male patients, and we did not observe a correlation between Cp concentration and patient's age for the limited set of 70 patients for which we had gender and age information.

ThPo11. CHARACTERISATION OF CADMIUM BINDING PROTEINS FROM PLANT EXTRACTS BY USE OF HYPHENATED TECHNIQUES

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Heavy metals are present in soils from natural and anthropogenic sources. Cadmium is one of the most widespread but non-essential metals which is highly toxic to living beings. Cadmium can enter directly to the human food chain due to its accumulation in the nutritional plants. The concentration of Cd in foods depends on its level in the soil and bioavailability. Some leafy crops like lettuce or spinach and root crops such as carrots or parsnip are able to accumulate more than other plant foods. Furthermore, non-nutritional species such as e.g. *Arabidopsis halleri* can hyperaccumulate Cd and can be used to clean up the contaminated soil by using the phytoremediation method. However, it suffers from the lack of understanding of the basic physiological, biochemical and molecular mechanisms involved in heavy metal hyperaccumulation. This leads to the difficulties with the optimization of the phytoextraction technique and its further commercial applications. Therefore, a requirement for development of the suitable analytical methods allowing deeper insight in these mechanisms is sought. The comparison of these mechanisms in hyperaccumulating and non hyperaccumulating plants could be useful and interesting.

A model organism chosen for this study in the first set of experiments was a nutritional plant, namely spinach. The aim was to develop analytical tools allowing *in-vivo* screening of cadmium containing proteins. Laser ablation was utilised as a sample introduction system for coupling of gel electrophoresis to ICP-MS. Characterization of metal-protein complexes was performed using size-exclusion chromatography coupled with ICP collision cell MS and by means of molecular MS.

ThPo12. HYPHENATION OF CAPILLARY LC WITH COLLISION CELL ICP-MS AND ON-LINE MICRO FRACTION COLLECTION FOR MALDI-TOF ANALYSIS

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Capillary and nano HPLC are the methods of choice for many separation problems due to their good compatibility with the ESI process. Recently different interface systems have been described in the literature allowing the complementary application of ICP-MS and ESI-MS under exactly the same chromatographic conditions, which is a pre-requisite for a proper matching and pre-selection of peaks due to their elemental tag.

Capillary-LC-ESI-MS is often limited especially due to matrix effects and signal suppression as a result of the composition of the used LC eluent.

Furthermore MS-MS experiments have to be planned very carefully since data acquisition is often restricted to short time events, defined by the small elution windows of the separated peaks.

The combination of capillary LC with micro fraction collection on a MALDI target plate allows the “quasi” on-line coupling of LC and MALDI-TOF, which helps to overcome some of the limitations of capillary-LC with on-line ESI-MS detection.

This contribution will describe the combination of capillary LC with online ICP-MS detection for element and off line MALDI-TOF analysis for a molecule specific detection of the separated compounds. The setup developed based on a nano flow splitting device and a micro fraction collector system, which allows the direct spotting of the HPLC eluent and matrix addition on either re-usable and disposable MALDI targets. First results will be presented.

ThPo13. QUANTITATIVE DETERMINATION OF CD-METALLOTHIONEINS IN PRAWN SAMPLES BY HPLC-ICPMS

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Metallothioneins (MT) are ubiquitous, cysteine-rich proteins that have been ascribed various biological roles including involvement in metal detoxification processes. Earlier aquarium experiments with crabs exposed to cadmium showed that they produce a particular and unusual isoform at high exposure, and in a follow-up field study, this same MT isoform was identified as one of at least five MTs in the muscle of female coral prawns collected from a site naturally high in cadmium. These data suggested that the MT isoform in coral prawn may be formed in response to high Cd exposure, and hence it could be a selective biomarker of excessive, and toxic, Cd levels.

We report studies on the development of an HPLC-ICPMS method for the quantitative determination of the various Cd-MTs in coral prawn. Effort has been directed to developing a simple extraction procedure to give intact Cd-MTs in an extract which is compatible with direct injection onto a reversed-phase HPLC column followed by selective detection of Cd and other metals with ICPMS. Factors investigated include extraction efficiency under various conditions, the stability of the MTs at each stage of sample preparation, and HPLC column recoveries of Cd. Besides parameters influencing the chromatographic separation special attention has been paid to ICPMS instrumental factors influencing quantitative results. The data on the prawn abdominal muscle so far show that several Cd-MT isoforms are present, and that the pattern of these MTs is related to the total concentration of cadmium.

ThPo14. METALLOMICS STUDY OF TISSUE EXTRACTS FROM THE GENETICALLY SEQUENCED *Mus musculus* COMPLEMENTED BY PROTEOMICS AND GENOMICS APPROACHES

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The use of multidimensional analytical approaches mainly based on orthogonal chromatographic techniques, mass spectrometry and inductively coupled plasma mass spectrometry (ICP-MS) are increasing concern. The main advantage of this tool is the use of metals bound to biomolecules (heteroatoms) as markers that simplify the traditional proteomic approaches.

The usual analytical methodologies for metallomics involve the use of size exclusion chromatography in combination with other complementary separation techniques with heteroelements monitoring by ICP-MS. This atomic specific detector copes for most of elements with biological significance. For unknown metallobiomolecules the identification step is covered by the powerful of organic mass spectrometry, namely MALDI-TOF and Qq-TOF, this later for MS/MS analysis.

In the present work, *Mus musculus* from which the genome is well known, has been study using the new approach. The different organs (liver, kidney, brain and spleen) were frozen and the cytosolic fraction extracted. Metals bound to biomolecules were purified using a membrane based separation combined with dialysis and the ICP-MS was further used. Finally, unknown metallobiomolecules were characterised by using MALDI-TOF and Qq-TOF.

A traditional proteomics approach was applied in parallel on the basis of 2D-PAGE separation, tryptic digestion of the spots and protein characterization and sequencing by MALDI-TOF and Qq-TOF. The results obtained from both studies were compared and correlated with the *Mus musculus* genome data base.

ThPo15. INVESTIGATION OF METALS IN RIBOSOMAL PROTEINS

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Ribosomes, the protein workshop of the cell, are responsible for the production of proteins in all living organisms. The ribosome is a ribonucleoprotein (RNP) complex composed of both ribosomal proteins and ribosomal RNA. The exact role of ribosomal proteins, other than simply providing structural scaffolding, is not presently known. A fundamental prerequisite for understanding the biochemical interactions that occur within the ribosome during protein synthesis is a detailed knowledge of the structure of the ribosome. This work focuses on the investigation of metals in ribosomes, specifically, screening for metals that are involved in ribosomal protein chemical secondary structure and ribosomal protein/RNA structural interactions. The ribosomal proteins were first analyzed via LC ICP MS to screen for the presence of metals in the samples and the amount of metal(s) present in each sample was determined. Size exclusion as well as reversed phase liquid chromatography have been employed to analyze the ribosomal proteins themselves as well as the intact ribosome. This information will provide insight into how much metal is required for proper folding of the ribosomal proteins. It will also be useful to investigate where the metals are incorporated from during bacterial growth and if their presence is necessary for proper ribosome function.

ThPo16. CE-ICP-MS FOR STUDYING URANIUM BINDING TO HUMAN TRANSFERRIN AND ALBUMIN SERUM PROTEINS

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About 20% of uranyl ions in human serum are associated with the protein pool. Albumin and transferrin, the most abundant proteins in serum, are both supposed to bind uranium. To obtain a better explanation of the biochemical toxicology and kinetics of U in the human body, the competition effects between both proteins must be known. Capillary Electrophoresis (CE) is used for the separation of Transferrin and Albumin, and a high-resolution ICP-MS (Element2) for the subsequent detection of U bound to the proteins. Both instruments are coupled *via* the CETAC CEI-100 interface. The torch of the ICP-MS is connected to the spray chamber using a shielded Teflon tube (70 cm long, 4 mm i.d.). We present a protocol for U binding to Transferrin and Albumin under physiological conditions, which is optimized to the requirements for CE analysis. The competition for U binding between the proteins is shown.

ThPo17. DETERMINATION OF MERCURY BINDING BIOMOLECULES USING HPLC COUPLED SIMULTANEOUSLY TO ICP-MS AND ES-MS

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Mercury is one of the most important elements to consider when environmental pollution is concerned. Recognised as global pollutant, mercury is not only hazardous as a metal itself, but most importantly due to its occurrence in different species. The most prominent example here is methylmercury, which is known for its biomagnification in the food chain and its enhanced bioavailability, also highly influencing mercury toxicity towards biological systems.

Mercury and methylmercury have been shown to bind to large sulfur containing biomolecules, and it was proposed that mercury and methylmercury transport in biological systems might occur via these compounds, and that mercury biomolecules do also govern mercury toxicity. While the existence of Hg bound to the sulfur function of biomolecules such as cysteine or glutathione has been evidenced, no direct identification of an Hg containing bio-molecule was achieved through organic mass spectrometry so far.

The work presented in this paper describes the determination of Hg-biomolecule complexes with cysteine, glutathione and phytochelatins (PC2-4) using HPLC coupled simultaneously to ICP-MS and ESI-IT-MS. Structural identification on a molecular level is discussed using the fragmentation pattern obtained from ESI-IT-MS.

In addition, ab-initio calculations are being performed for MeHgCys in order to investigate preferred protonation state of the amino and carboxyl termini of the Cysteine and the possibility of non-covalent interaction between the Hg and these termini.

ThPo18. USE OF ISOTOPICALLY LABELED MOLECULAR MERCURY COMPLEXES TO TRACK AND UNRAVEL THE ORIGINS OF THE ARTIFICIAL TRANSFORMATIONS OF MERCURY SPECIES IN NATURAL BIOLOGICAL REFERENCE MATERIALS

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A double spike speciated isotope dilution (DS-SID) methodology was developed to investigate the inadvertent transformations affecting methylmercury (MeHg) and inorganic mercury (iHg) measurements in biological tissues, using alkaline digestion, derivatization and gas chromatography inductively coupled plasma mass spectrometry (GC/ICP-MS). Labile enriched inorganic mercury (²⁰¹iHg) and IRMM-670 methylmercury (²⁰²MeHg) isotopic standards and their synthesized cysteine-complexed analogs were applied as isotopic calibrants to compare five natural mussel and/or oyster tissues standard reference materials (SRMs) present in freeze-dried (SRM 1566b, 2976 and 2977) and cryogenic fresh-frozen forms (SRM 1974a, 1974b). The results indicated different transformation yields (methylation and demethylation) between the two classes of material when labile enriched spiking standards were applied. Significant differences were also observed when their molecular cysteine-complexed analogs were employed. These findings suggested that under the condition of analysis, labile and complexed isotopically labeled mercury species behaved differently and/or were not transformed at the same rate as native, matrix-bound mercury species. It also suggested that the textural aspects of the matrix investigated might also play an important role. Systematic experiments were conducted across the different analytical steps to investigate the origins and the reliability of the transformations yields. The results revealed that the accuracy of the transformation yields was directly linked to the aptitude of the spiking standards to match the complexation patterns of native mercury species in the sample matrix and during sample preparation steps. Inorganic mercury was found to be more subject to this bias as compared to MeHg due to its higher binding strength and complexation level with sulfhydryl groups. These results suggest the need to investigate more deeply the aptitude of speciated isotope dilution procedures to handle the problem of lability/complexation and ligands interactions between enriched and native mercury species in natural environmental matrices and control materials used for method validation.

ThPo19. ON-LINE ISOTOPE DILUTION ANALYSIS ICP-MS: THE IDEAL SOLUTION FOR ROUTINE TESTING LABORATORIES

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Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a relatively modern analytical technique that was commercially introduced in 1983 and has gained general acceptance in many types of laboratories. ICP-MS is rapidly becoming the technique of choice in many routine testing laboratories for the accurate and precise measurements needed for today's demanding applications. From 1993 until today around 60 ICP-MS instruments have been installed in Spain with an exponential growth in the last years. Many accredited private and public environmental laboratories use ICP-MS today routinely for the analysis of water samples.

Isotope dilution analysis (IDA) is a well-known analytical technique based on the measurement of isotope ratios in samples where their isotopic composition has been altered

by the addition of a known amount of an isotopically enriched element. IDA methodologies provide superior accuracy and precision compared to more common calibration strategies. However, the use IDA in combination with ICP-MS as routine technique in testing laboratories is often judged as a costly and complicated analytical method. Today, the cost of enriched isotopes needed for trace and ultratrace analysis of water samples at concentration levels lower than 100 ng g^{-1} is only of a few cents of euro per element and sample. On the other hand, the “complicated” procedure can be simplified applying on-line IDA where a mixture of enriched isotopes is mixed on-line with the sample prior to the ICP-MS nebuliser. This allows also easy automation of the procedure as samples and QC standards are supplied by an autosampler. In this presentation we describe the development and validation of an ICP-MS method for the simultaneous determination of trace elements in water samples by on-line IDA which could be immediately applied in routine testing laboratories.

ThPo20. DETERMINATION OF PRECISE ^{93}Zr CONTENT IN IRRADIATED SAMPLES USING ISOTOPE DILUTION IN AN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER WITH MULTICOLLECTION. APPLICATION TO THE MEASUREMENT OF THE HALF-LIFE OF ^{93}Zr

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The zirconium isotope ^{93}Zr is a long-lived pure β particle emitting radionuclide, with maximum beta energy of 56 keV and a half-life of 1.53×10^6 years. It is produced by both nuclear fission and neutron activation of the stable ^{92}Zr , which is present in different quantities in the structural components of nuclear reactors. Determination of ^{93}Zr concentrations with high precision is a major issue for waste management.

Isotopic composition of Zr is difficult to measure by conventional Thermal Ionisation Mass Spectrometry (TIMS) because of the low ionisation efficiency due to its high ionisation potential ($I_{\text{Zr}}=6.84 \text{ eV}$). On the contrary, Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) is a technique of choice for the measurements of isotopic composition of zirconium at high precision.

We will present an analytical procedure for the determination of ^{93}Zr concentrations in nuclear materials by isotope dilution MC-ICPMS, using ^{96}Zr -spiking of Zr. The uncertainty obtained for the concentration of ^{93}Zr in nuclear materials after chemical purification is lower than 0.5%. This procedure was applied to the determination of the half life of ^{93}Zr using a purified solution. The activity per unit of mass of solution was measured by liquid scintillation counting using an efficiency tracing method with a ^3H standard. The combination of mass and activity concentration of ^{93}Zr in the solution allows a precise and reliable determination of the half life of this radionuclide.

ThPo21. ANALYSIS OF NATURALLY OCCURRING STABLE Fe ISOTOPE RATIOS IN PLANT MATRICES: SAMPLE PREPARATION AND MEASUREMENT TECHNIQUES

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Although plants accumulate Fe as an essential micronutrient in normal tissue at around $100 \mu\text{g g}^{-1}$, mechanisms of uptake and subsequent translocation remain poorly understood. Measuring naturally occurring fractionation of the stable isotopes of Fe holds great promise in

studying these fundamental plant physiological processes. There are, however, well known analytical problems - Fe has unfortunate isotope masses with respect to analysis: Sample derived and carrier gas based isobaric interferences on ^{54}Fe , ^{56}Fe and ^{57}Fe challenge high precision measurements.

We developed an analytical method to achieve high precision Fe isotope measurements in plant matrices. In preparation for measurement, two anion-exchange chromatography steps gave adequately purified samples (removing plant derived interferences and allowing subsequent isotope measurements to be plotted on a theoretical mass dependent fractionation line in three isotope space). The *IsoProbe* MC-ICPMS hexapole collision/reaction cell, containing H_2 and Ar, was optimised to reduce intensities of argon polyatomic species ($^{40}\text{Ar}^{14}\text{N}^+$ and $^{40}\text{Ar}^{16}\text{O}$) and plant matrix effects. The hexapole gas phase reactions were also studied theoretically and practically, with thermodynamic calculations indicating the possible reaction pathways.

This study used an in-house grass standard (Imperial College HRM-14) in order to develop reproducible Fe isotope measurements. The resulting procedure gave sample duplicates with inter-sample reproducibility of $\pm 0.2\%$ (2 S.D) for $\delta^{56}\text{Fe}$.

ThPo22. DEVELOPMENT OF AN IN-LINE FI Sr/MATRIX SEPARATION METHOD FOR ACCURATE DETERMINATION OF $^{87}\text{Sr}/^{86}\text{Sr}$ ISOTOPE RATIOS

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Isotope systems provide unique information like the age of geologic formations, environmental or biologic pathways, migration behaviour or the provenience of raw materials and products. Due to continuing endeavours in authentication of miscellaneous commercial products, isotope ratio analysis is gaining economic relevance. The advent of multi collector ICP-MS (MC-ICP-MS) has enabled time efficient high precision isotope ratio determination for numerous elements. Nonetheless, sample pre-treatment is still the time limiting step. Analyte/matrix separation, like separation of Sr from interfering Rb and Ca, is often a prerequisite for accurate isotope ratio determination. Fast and reliable procedures are required to overcome this limitation. Flow injection (FI) combined with in-line matrix separation offers a gateway for increasing the sample throughput. Reduced risk of contamination, reduced use of chemicals - especially costly ion exchange resins - and increased reproducibility favour FI procedures to traditional manual sample preparation procedures. We introduce a newly developed in-line FI method for Sr/matrix separation and subsequent determination of Sr isotope signatures from the transient signal by (MC)-ICP-MS. The presentation gives a short description of the development process, the full validation of the analytical setup as well as results obtained on biologic and geologic samples with varying Rb/Sr ratios.

ThPo23. COMPARISON AND APPLICATION OF DIFFERENT MULTIPLE ISOTOPE SPIKING APPROACHES FOR THE STUDY OF ORGANOMETALLIC SPECIES REACTIVITY IN THE ENVIRONMENT

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The basis of the multiple isotope spiking approaches relies on the labelling of different elemental species with different isotopes. Such isotopic labelling is normally used for two main purposes: first, to study the formation and/or degradation processes of elemental species

in natural ecosystems or living organisms and second, to correct for species transformation reactions that may occur during the chemical analysis.

Depending on the complexity of the interconversion model and the availability of the isotopically enriched species, different specific complementary mathematical approaches must be developed to support the experimental data and calculate the extent of possible transformations of the species of interest. During the last years, different multiple species-specific spiking methodologies have been proposed for a wide variety of analytical, environmental and toxicological applications. This work will summarise and compare such approaches highlighting their main advantages and limitations. Different applications (such as field incubations in aquatic environments or laboratory incubations versus anaerobic bacteria) will be shown to study the reactivity and the interactions of organometallic contaminants of Sn and Hg.

ThPo24. CLINICAL APPLICATIONS OF THE VARIAN 810/820 ICP-MS

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Elemental analysis is an important tool in the clinical laboratory, and the drive to lower detection limits is making ICP-MS the preferred technology for this job.

There is a growing interest in the distribution of metals originating from chemotherapy drugs and implanted components. This is demanding in terms of the sensitivity of the technology. Additionally, the range, variety and complexity of clinical matrices results in many spectroscopic interferences in ICP-MS, which can significantly impact the detection limit of specific elements

To meet these varied demands a flexible instrument, which is capable of minimising polyatomic interferences but also configurable for uncompromised sensitivity, is required. In the following presentation the ease and simplicity of configuring the Varian ICP-MS to meet these needs will be described and the performance characteristics will be detailed in real clinical sample matrices.

ThPo25. TRACE METALS IN ENVIRONMENTAL SAMPLES: WHAT DO WE DO WITH THE DATA?

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Cefas (the Centre for Environment, fisheries and Aquaculture Science) is an executive agency of the UK's Department for Environment, Food and Rural Affairs (Defra). The multi-disciplinary science undertaken by Cefas involves biological, chemical, ecotoxicological and physical studies to assess the health of the marine environment around the coast of England and Wales and, and to provide advice as to the impacts of human activities.

The activities undertaken within the chemistry function of Cefas are wide ranging and employ a large number of techniques. Here we present the work on trace metals analysis (methods and applications) and some of the results from the three UK-wide monitoring programs conducted under three main projects, each with a national remit:

- The National Marine Monitoring Programme: initiated in the late 1980s to provide an overview of the quality of the marine environment of the United Kingdom. Cefas has a

remit to monitor the concentrations of trace metals in the sediments and biota to assess their distribution and fate in the environment.

- Advice on disposal licenses: the deposit of substances and articles in the sea, now primarily dredged material, is controlled by a system of licences issued under Part II of Food and Environment Protection Act 1985. We analyse the concentrations of trace metals in dredged material prior to dredging in order to aid the decision-making process for new, and ongoing, licence applications.
- Monitoring of sea deposits: trace metals analysis is also carried out at dredged material disposal sites around the England and Wales coastline.

ThPo26. URANIUM ISOTOPE RATIOS DETERMINED BY MC-ICP-MS AND THE ASSESSMENT OF TOTAL COMBINED UNCERTAINTY BUDGETS

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Precise determination of uranium isotopic composition is required in nuclear technology, nuclear forensics and environmental monitoring. Particular applications imply determination of extremely low ^{236}U quantities in the presence of a large excess of ^{238}U and ^{235}U which represent severe sources of interference in determinations of ^{236}U .

This poster describes the application of MC-ICP-MS (Nu Plasma HR) equipped with an ion deceleration filter ('high abundance sensitivity channel') for rapid and sensitive determination of $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratios in aqueous samples and discusses measurement uncertainties. Comparative measurements by using sector-field ICP-MS with single ion detector are presented.

The ion deceleration lens system of the Nu Plasma MC-ICP-MS allows an improvement of the abundance sensitivity by about two orders of magnitude and offers the potential to analyse $^{236}\text{U}/^{238}\text{U}$ isotope ratios in the 10^{-8} to 10^{-7} range. On the other hand, using the ion deceleration lens for determination of $^{236}\text{U}/^{238}\text{U}$ isotope ratios above 10^{-5} is disadvantageous because it introduces potential additional sources of uncertainties. Accuracy of uranium isotope ratio measurements by MC-ICP-MS was evaluated by analysing unknown reference samples in the frame of a round robin exercise.

ThPo27. DIRECT ISOTOPE ANALYSIS OF URANIUM AND PLUTONIUM IN RADIOACTIVE PARTICLES USING LA-MC-ICP-MS

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Uranium and plutonium isotopic ratios in micrometer-sized particles is of greatest interest for nuclear forensics because they indicate whether the isotopes were intended for use in reactor fuel or nuclear explosives and can reveal undeclared use of nuclear materials. At present several extensive and sumptuous methods are employed for uranium and plutonium analysis in radioactive particles including e.g. nuclear track radiography, TIMS, SIMS, SEM.

Application of MC-ICP-MS in combination with laser ablation is a promising technique for direct isotopic measurements of actinides in individual solid particles due to good sensitivity and high spatial resolution of this method.

This poster describes sample preparation procedure and experimental arrangement of LAMC-ICP-MS for U and Pu isotopic analysis in individual particles extracted from contaminated soil and presents first results obtained on environmental samples. The developed method allows reliable detection of artificial nuclides such as ^{236}U and Pu as well

as the determination of corresponding isotope ratios at sub-pg level in micrometer-sized particles. Correlation of radionuclide ratios in particles originating from the reactor of Chernobyl is discussed.

ThPo28. ICPMS WITH COLLISION - REACTION CELL FOR RESOLUTION OF AR_2^+/SE^+ INTERFERENCES FOR ANALYSIS OF ^{79}Se IN SPENT NUCLEAR FUEL SAMPLES.

STUDY OF COLLISION/REACTION GASES FOR INTERFERENCES RESOLUTION.

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Laboratory of Nuclear, Elementary and Isotopic Analysis develops and implements high performance chemical specific separations and isotopes measurement techniques for analyses in spent nuclear fuel samples.

For example, selenium 79, formed during fissions of uranium 235 is a long life radio nuclide (half life in the order of 10^5 years) which is of prime interest as radio-contaminants concerned for long time entresposal due to its high capacity of migration in the environment. The measurement of the ^{79}Se , particularly complex because of its very low concentration in the solutions of irradiated fuel (few ppb), requires a very sensitive technique, reliable analysis, and the total absence of interferences during the measurement.

Furthermore, no source of ^{79}Se is available so it is necessary to make calibration curve with natural isotopes which are mainly interfered by argide ions formed directly in the plasma.

In this study, the influence of the experimental conditions of a quadrupole ICPMS with collision cell for analysis of the selenium was treated.

To determine the influence of the various factors on the obtained results while limiting the number of experiments, the technique of the experimental designs was used. The final goal of this study is to know the optimal conditions of analysis of selenium to obtain in a reproducible way, the best sensitivity at the mass 80 in a selenium solution and the minimum signal at mass 79 and 80 in the blank (nitric acid).

O_2 was used as reaction gas and different collision gas (He, Ne, N_2 , Ar) were studied in order to define its effect on the signal and on the operating conditions. Doehlert designs were used for all couple of gases and the difference of operating conditions will be discussed. The sensitivity will be compared for all the couples of gases and the interference reduction will be discussed in term of oxide rate, reduction of Gd^{2+} (which is also another interfering ion at mass 79 and 80).

The results concerning analysis of a Mox spent nuclear fuel sample will be presented with the use of the operating conditions obtained after analysis of the experimental designs.

ThPo29. DETERMINATION OF THORIUM, URANIUM AND OTHER ELEMENTS IN NARROWLEAF PLANTAIN (*PLANTAGO LANCEOLATA L*) AND THEIR INFUSIONS

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The leaves of *Plantago lanceolata L.* have a high content of tannin makes the leaves useful for all types of sores on the skin, cuts, bites and various inflammations. A tea brewed with the seeds is a treatment for diarrhea and dysentery and for bleeding in the mouth or other mucous membranes. The level of Th and U in plants is affected by the geochemical characteristics of a soil and by their bioavailability. In samples collected in different places in Europe values between 5 – 400 ng g⁻¹ d.w. of Th and 1 – 100 ng g⁻¹ for U were found with the maximum values in plant growing on the east border of Poland. The relationship of uranium isotopes

demonstrates that this pollution is a natural one. The results obtained in water extracts depend on the water quality. In deionised water a small part of elements is transferred in to liquid phase. In drinking water in which the Th or U concentration is higher than the concentration in plants an opposite effect is observed and the concentration in the solution dropt.

ThPo30. STUDY OF TRACE ELEMENTS IN PM 10 AIRBORNE PARTICULATE MATTER COLLECTED IN RIO DE JANEIRO, BRAZIL OVER A YEAR

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People who live in the vicinity of industrial areas and roads with intensive traffic flow are exposed to metals and metalloids in suspended particles, which are often above natural background levels. The release of these elements, contained in airborne particulate matter, can eventually affect human health, since they can be absorbed into lung tissues during the breathing. The nature and magnitude of this hazard in a given situation depend on a complex combination of many factors, including particulate size distribution, wind-speed range, airborne concentration, particle morphology, mineralogy and chemical composition.

High-volume samplers using glass fiber filters have been widely used for suspended particulate matter collection in a number of contaminated areas because of their high collection efficiency for the particles and low flow resistance.

This work presents the concentrations of trace elements in airborne particulate matter in Rio de Janeiro city, Brazil, for the period of January – December 2005. The sampling was performed in PM₁₀ glass fiber filters using a high-volume pump. The chemical elements Cd, Ce, Cu, La, Mo, Ni, Pb, Pd, Rh, Sb and Sn were correlated with the anthropogenic activities of the sites.

A method based on the EPA method for the determination of the elements in environmental particulate matter, using ultrasonic-assisted extraction and high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) was used. Spiked sampling filters were analyzed to check the accuracy of the analytical procedure, and the recoveries were between 88 and 115%.

ThPo31. DIFFERENT SAMPLE PREPARATION APPROACHES FOR THE MULTIISOTOPIC DETERMINATION OF Pu IN SEDIMENTS USING QUADRUPOLE AND SECTOR-FIELD ICP-MS.

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Plutonium is by far the most important transuranic element, and plutonium isotopes generally found in the environment are ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu and ²⁴²Pu. The ²⁴⁰Pu/²³⁹Pu, ²⁴¹Pu/²³⁹Pu and ²⁴²Pu/²³⁹Pu isotope ratios are potentially good tools to identify the different

sources of plutonium. The two most important and abundant plutonium isotopes are ^{239}Pu ($t_{1/2} = 24.110$ years) and ^{240}Pu ($t_{1/2} = 6.537$ years).

It has long been recognised that the physical and chemical form of plutonium influences its mobility and bioavailability in the marine environment. It is now well known that the chemistry of plutonium is complex due to its occurrence under various oxidation states. The distribution of Pu between water and sediment greatly depends on the oxidation state. For well oxygenated waters, most of the dissolved phase plutonium has been identified as Pu(V) and plutonium in sediments has been identified as Pu(IV).

Except in the close vicinity of industrial sources, plutonium concentration in marine sediments is very low (from 10^{-4} ng kg $^{-1}$ for ^{241}Pu to 10 ng kg $^{-1}$ for ^{239}Pu), and therefore the measurement of plutonium isotopes in sediments at such concentration level requires the use of very sensitive techniques. Moreover, sediment matrix contains huge amounts of mineral species, uranium and organic substances that must be removed before the determination of plutonium isotopes using ICP-MS. Hence, an efficient sample preparation step is necessary prior to analysis.

Plutonium in environmental samples has been efficiently determined in the past by alpha-spectrometry, liquid scintillation counter, and thermal ionization mass-spectrometry (TIMS). Using ICP-MS, different Pu isotopes were successfully analysed in different environmental samples, including sediments. Recently, the use of sector-field ICP-MS instruments provided better sensitivity, good accuracy and precision. Nowadays, ICP-MS could achieve detection limits within the sub-femtogram level. As a consequence, all types of interferences must receive additional consideration.

In this work we demonstrate different analytical approaches for the multi-isotopic determination of Pu in sediments. The methodology developed for the quadrupole ICP-MS detection (Varian) uses microwave acid leaching of sediments and on-line flow-injection ion-chromatography with possibility of detection ^{239}Pu and ^{240}Pu isotopes. The methodology developed for sector-field ICP-MS detection (PlasmaTrace2) removes uranium from the sample very efficiently and uses microwave mineralization, liquid-liquid extraction and two steps of ion-chromatography with possibility of detection ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{242}Pu and ^{244}Pu isotopes. Concentrations of Pu isotopes in sediments from English Channel, Okhotsk sea (Japan), Lake Baikal (Russia) and Lake Hovsgol (Mongolia) were determined. Results were validated using spiking and measurements of Pu isotopes in sediment reference materials, i.e. IAEA-135 (Irish Sea sediment) and IAEA-368 (Mururoa Atoll sediment), IAEA-375 (Radionuclides in Soil) and NIST-SRM 4354 (Freshwater Lake Sediment).

ThPo32. ICP-MS MEASUREMENTS TO CONTROL IRON CONCENTRATION IN ANCIENT POTTERIES

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Most of ancient potteries are made of local clay material, which contains relatively high concentration of iron. The powdered samples are usually quite black, due to iron compounds, and, although they can be dated by thermoluminescence with minimal sample pre-treatment, making them much clearer one eliminates some interference and TL measurements became more accurate. For ESR measurements, the huge signal due to spin-spin interaction, any other signal becomes completely hidden. As consequence, ESR dating can not be used, since iron signal do not depend on radiation dose. A chemical process to eliminate iron compounds was developed. A sample of powdered ancient pottery was treated in five different combinations of acid mixture and hydrogen peroxide, kept at room temperature. After the leaching treatment, the sample was washed several times in distilled

water to remove all acid matrixes. The original black sample becomes quite white. The resulting material, of each one of the five leaching process, was analyzed in a quadrupole ICP-MS system. The proposed procedure is not chemically selective so, a series of geological standard reference materials (GSJ) was also analyzed to determine precisely the remaining concentration of all elements. The chemical leaching process is useful to eliminate ca. 90% of iron compounds and consequently for ESR dating.

ThPo33. DETERMINATION OF BURN-UP IN FUELS FOR USE IN NUCLEAR FORENSICS

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The use of a burn-up monitor or fission product, typically ^{148}Nd , has been routinely used to characterize the performance of a nuclear fuel, i.e. the number of fissions. The inductively coupled plasma mass spectrometer is able to monitor a variety of other burn-up monitors accurately and precisely, without additional work. These additional elements include ^{99}Tc , ^{139}La , ^{141}Pr , ^{142}Ce , ^{143}Nd , ^{145}Nd and ^{148}Nd . This presentation will detail the determination of the burn-up monitors given above in a variety of nuclear fuels. A comparison of the fission products will then be used to interpolate vital nuclear forensic information such as original enrichment based on the estimated number of fissions the fuel has produced. This is particularly important for mixed (U, Pu) oxide (MOX) fuel and advanced fuels containing Am-241, Np-237 and Pu-239 as major constituents.

ThPo34. ^{234}U AND ^{230}Th DETERMINATION BY FIAS-ICP-MS AND APPLICATION TO URANIUM-SERIES DISEQUILIBRIUM IN MARINE SAMPLES

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A ^{234}U and ^{230}Th determination method based on an extraction chromatographic separation on a flow injection system coupled to a quadrupole ICP-MS was developed. Two milliliters TRU (Eichrom Company) cartridges were applied as separation tool and ^{236}U and ^{229}Th as spikes. Loading and washing steps were carried out in 3M HNO_3 solution and 0.05M ammonium oxalate applied to elute both uranium and thorium. The method was applied initially to the IAEA-327 soil and NIST-SRM-4357 ocean sediment reference samples and the obtained ^{234}U and ^{230}Th concentrations were in agreement with the reference levels. Samples from a deep-sea sediment core (2450 m water depth) were analyzed and, based on $^{230}\text{Th}/^{234}\text{U}$ dating, a mean sedimentation rate of 3.3 cm ky^{-1} was calculated. Samples from two sediment layers were also dated by ^{14}C -AMS and the observed ages agree with the $^{230}\text{Th}/^{234}\text{U}$ results. The developed method was also applied to deep-sea fossil corals and the obtained ages compared to those obtained by ^{14}C -AMS.

ThPo35. APPLICATION OF ICP-QMS FOR THE DETERMINATION OF PLUTONIUM IN ENVIRONMENTAL SAMPLES FOR SAFEGUARDS PURPOSES

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Aiming the determination of the plutonium amount as well as its isotopic composition, in particular, in swipe samples for safeguards purposes, it was developed an analytical method with a plutonium separation based on extraction chromatography using 2 cm TEVA columns and detection with quadrupole ICP-MS applying an ultra-sonic nebulizer coupled with membrane desolvation system. The method was successfully applied to New Brunswick plutonium certified materials as well as to round robin samples, prepared by the Lawrence Livermore National Laboratory, based on the round robin samples provided by the Institute for Reference Materials and Measurements (Belgium), as part of the Regular European Interlaboratory Measurement Evaluation Programme (REIMEP), campaign 16 (isotopic abundances of plutonium in plutonium nitrate samples), with total plutonium amount between 1 and 0.25 ng per sample. After the introduction of an additional separation step, it was also possible to carry out precise and accurate total plutonium, ²⁴⁰Pu/²³⁹Pu, ²⁴¹Pu/²³⁹Pu and ²⁴²Pu/²³⁹Pu atom ratios determination in sediment samples showing its applicability to environmental samples in general, reaching a detection limit equivalent to 5 mBq ²³⁹Pu kg⁻¹.

ThPo36. MEASUREMENT OF HIGH-PRECISION ISOTOPE RATIOS FOR MERCURY FROM NORWEGIAN LAKE SEDIMENTS USING COLD-VAPOR GENERATION MULTI-COLLECTOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Precise and accurate analysis of Hg isotope ratio in lake sediments samples can be invaluable tool in investigating Hg cycles in the environment. An on-line Hg reduction technique using stannous chloride as reductant was applied for Hg isotope ratio determination by multi-collector inductively coupled mass spectrometry (MC-ICP-MS). Special attention has been paid to ensure optimal conditions (such as acquisition time and mercury concentration) allowing the precision of the measurements to be good enough to detect the anticipated small differences in Hg isotope ratios in nature. Typically, internal precision was better than 0.002% (1 RSE) on all Hg ratios investigated as long as approximate 20 ng of Hg was measured with a 10-min acquisition time. The instrumental mass bias was corrected using ²⁰⁵Tl/²⁰³Tl correction coupled to a standard-sample bracketing approach. The large number of data acquired allowed us to validate the consistency of our measurements over a one year period. On average, the short-term uncertainty determined by repeated runs of NIST SRM 1641d Hg standard during a single day was <0.005% (1RSD) for all isotopes pairs investigated (¹⁹⁸Hg/²⁰²Hg, ¹⁹⁹Hg/²⁰²Hg, ²⁰⁰Hg/²⁰²Hg, and ²⁰¹Hg/²⁰²Hg). The precision fell over a year (over 100 measurements were considered). The ratio ¹⁹⁸Hg/²⁰²Hg expressed as δ values (per mil deviations relative to NIST SRM 1641d Hg standard solution) displayed differences from +0.74 to -4.0%. This study confirmed that analytical techniques have reached a level of long-term precision and accuracy that is sufficiently sensitive to detect even small differences in Hg isotope ratios that occur within one type of samples. Thus, the determination of Hg isotope signatures in environmental studies is potentially a very powerful tool to better understand its geochemical cycling in the environment and anthropogenic impacts.

ThPo37. FRACTIONATION OF MERCURY ISOTOPES IN THE ENVIRONMENT AND PRECISE MEASUREMENT OF MERCURY ISOTOPE RATIOS BY MC-ICP/MSH.

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This paper discusses techniques for measuring precise isotope ratios of mercury using a continuous-flow cold-vapor technique coupled to MC-ICP/MS. The optimized method achieved a precision of better than 0.001 % RSD for mercury isotope ratios at concentrations of ~10 ng/mL. To correct for instrumental mass bias during the measurement, a thallium solution with known $^{203}\text{Tl}/^{205}\text{Tl}$ ratio was measured simultaneously. The method was applied to measure natural variations of mercury isotope ratios in sediments. Variations in mercury isotope ratios were confirmed in the uppermost horizon of long sediment cores (representing modern time mercury). The newly deposited mercury appeared to be enriched with heavier isotopes compared to the mercury down core (representing background mercury). A fractionation of close to 0.60 ‰ between surface and deeper sediments was observed. Precise mercury isotope ratio measurements were further applied to track sources of mercury at contaminated sites. The fractionation that occurs during reduction of Hg(II) to Hg(0) and subsequent evaporation of Hg(0) was systematically investigated and Raleigh fractionation factors calculated.

ThPo38. DETERMINATION OF CADMIUM IN STAPLE FOODS BY ISOTOPE DILUTION ICP-MS WITH A CO-PRECIPIRATE SEPARATION USING SAMPLE CONSTITUENTS AS A PRECIPITANT

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Inductively coupled plasma mass spectrometry (ICP-MS) is one of the powerful techniques for determination of trace elements in foodstuff. In combination with an isotope dilution (ID) technique, it can provide highly accurate and precise determinations. However, the ID-ICP-MS measurement of Cd is subject to spectra interferences from concomitant elements in the sample. In the case of staple food samples such as rice, wheat and beans, the interferences of MoO^+ seriously affects on the Cd isotope ratio measurement. The concentration range of Mo in staple foods is commonly ca. 50 -200 fold higher than that of Cd, though the formation ratio of MoO^+ in ICP-MS is typically 0.1-0.2%. Therefore, a correction for the interferences or a selective separation of Cd from Mo must be performed in the determination of Cd in staple food samples by ID-ICP-MS.

We propose a unique coprecipitate separation method using sample constituents as a precipitant. By the addition of NaOH solution to the sample digested solution, colloidal suspension, mainly magnesium hydroxide, is generated upon hydrolysis. Cadmium also forms hydroxides, occludes in and/or adsorbs on the colloid, while Mo neither forms the colloid nor absorbs on the hydrolysis colloid. As a result, Cd can effectively be separated from Mo. This proposed method was applied to two certified reference materials, NIST SRM1568a rice flour and SRM1567a wheat flour, and CCQM-P64 soybean powder. Good analytical results with small uncertainties were obtained for all the samples. Now, we are employing this method for developing new rice flour certified reference materials.

ThPo39. DETERMINATION OF THE CAESIUM DISTRIBUTION IN HIGH BURNUP FUEL SAMPLES WITH DIFFERENT ANALYTICAL TECHNIQUES

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The determination of the migration of volatile fission products like caesium and thus an estimation of the rates of release are important criteria for the integrity of irradiated fuel rods from nuclear power plants. Different analytical methods are used in post-irradiation examinations to ensure the product quality of reactor core components and to provide data for nuclear safety approval procedures.

The non-destructive technique of computerized tomography (CT) was applied on high burnup fuel rods for the determination of the within-pin distribution of fission products like caesium and europium. To perform such investigations, a high resolution gamma-ray spectrometry measurement station, allowing transmission and emission tomography, has been built. The results of this technique indicated a large depression in the caesium distributions at the centre of the pin, with higher concentrations in the peripheral region. In order to support these data, other analytical techniques were applied on samples from the same fuel rod.

EPMA analyses have been performed to gain information about the elemental distribution of caesium and other elements (actinides and fission products). In order to achieve information about the isotopic composition the combination of a laser ablation system with an inductively coupled plasma mass spectrometer was used as complementary analytical method. The interpretation of the measured data on the solid fuel samples was supplemented by HPLC-MC-ICP-MS measurements on fuel solution from the same fuel rods.

The presentation aims to compare the results from the different analytical techniques and to discuss the advantages and limitations of each of them.

ThPo40. SYNTHESIS AND CHARACTERISATION OF SULFUR ISOTOPICALLY-LABELLED COMPOUNDS.

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Isotopically-labelled compounds have been extensively used for the improvement of analytical techniques, for both environmental and clinical analysis. However, till now, most of the commercially available Isotopically-labelled compounds are ^{13}C or deuterated species. Our group has been working for several years now, in the synthesis of heteroatom-labelled compounds which can be detected by ICP-MS or GC-MS with electron impact ionization. This opens the way to new quantification methodologies, as different species can be labelled with alternative stable isotopes of the elements (Hg, Sn, Se, etc.) providing full control of chemical degradation processes occurring during sample pre-treatment. Previously, the biosynthesis of ^{77}Se -enriched selenomethionine (SeMet) was developed in our laboratory by yeast growth on a ^{77}Se -rich culture medium and it was applied to the determination of SeMet in nutritional supplements based on selenized yeasts using IDA-HPLC-ICP-MS.

The current communication focuses on the synthesis and characterisation of aminoacids and small peptides labelled with 34-sulfur, which are not available commercially and should offer significant analytical advantages over similar compounds labelled with ^{13}C or deuterium. These new sulfur compounds will be used for the determination of natural species in biological materials by Isotope Dilution Analysis (IDA) using HPLC-ICP-MS or GC-ICP-MS.

ThPo41. CERTIFYING MERCURY CONCENTRATIONS IN CONCENTRATED ACIDS BY ICP-MS

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Seastar Chemicals manufactures high purity acids, water and ammonia for trace element analysis. The use of concentrated hydrochloric, nitric and sulphuric acids for mercury determinations are very common. We have developed ICP-MS methods to determine the amount (or the maximum possible amount) of mercury in these reagents. We will present data from our high resolution ICP-MS (Thermo Element2) on optimizing mercury sensitivity, reducing instrument backgrounds and reducing memory effects.

ThPo42. ULTRATRACE ANALYSIS OF BIOFLUIDS BY FLOW INJECTION-ICP-MS

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Analysis of clinical samples cause is problematic due to either low volume, complex matrix and/or low level of analyte. A preferred method of sample presentation is simple dilution and direct introduction of aliquot to the ICP-MS. This minimises contamination of the sample and possible loss of analyte during the digestion procedure. The approach does require enhanced sensitivity to determine lower levels of analyte and a means for minimising the effects of protein and/or salt deposition on the torch injector tip/MS cones. The Apex is a high efficiency sample introduction system which gives enhanced sensitivity for ICP-MS measurement. This unit has been configured with a fully automated flow injection system (SC-FAST) for high throughput analysis. Application to the determination of metallodrugs in pre-clinical and clinical samples is evaluated.

ThPo43. REMOVAL OF SPECTRAL INTERFERENCE IN ISOTOPE DILUTION ANALYSIS WITH ICP-SFMS AND DRC-ICP-MS

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NMIJ is developing certified reference materials of non-oxide fine ceramics such as silicon carbide and silicon nitride, and isotope dilution mass spectrometry (IDMS) is used as one of the key analytical methods for the determination of metal impurities in CRMs. IDMS essentially requires two isotopes free from spectral interference, however, it is quite difficult to find such isotopes especially in the determination of first transition metals. Therefore specific measurement techniques are necessary to exclude the effect of the spectral interference.

Spectral interferences due to matrix and/or acid solvent can be removed by ICP-SFMS under the medium resolution. However, the peak shapes measured under the medium resolution do not have the flat top, so the mass axis fluctuates in the range of m amu to lead less precision of isotope ratio measurements. In order to avoid deterioration of measurement precision, highly frequent corrections of mass axis and mass bias were adopted. As a result, it was found that the 0.05 - 0.2 % of precision was realized for isotope ratio measurement with ICP-SFMS under the medium resolution, when the signal profile assay was carried out every eight sample solution measurements and when the mass discrimination correction was carried out every four measurements.

On the other hand, it is impossible to remove isobaric interferences even with ICP-SFMS. In the case of V measurement in fine ceramics by ICP-MS, the isobaric interference of Ti and Cr is very serious because one of the two V isotopes is overlapped by ^{50}Ti and ^{50}Cr . We proposed

a new selective determination of V in their presence using DRC-ICP-MS with CH₃F - NH₃ mixed reaction gas. We found the formation efficiency of [MF₂(NH₃)₄]⁺ (M=V, Cr, Ti) were significantly different to elements, and the optimum condition for selective formation of [VF₂(NH₃)₄]⁺ was found by controlling gas flow rates of CH₃F and NH₃. The IDMS analytical result of V in fine ceramics with the present system agreed well with that obtained by matrix matching calibration method within the expanded uncertainty.

It can be concluded that the reduction of spectral interference in ICP-SFMS and DRC-ICP-MS expands application fields of IDMS.

ThPo44. INFLUENCE OF SAMPLE TREATMENT AND STORAGE FOR THE STUDY OF SELENIUM UPTAKE BY FRESHWATER PHYTOPLANKTONIC ALGAE BY HPLC-ICP-CRC-MS COUPLING

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Selenium is an essential micronutrient for living animal organisms, but becomes toxic at high doses. The concentration range between its indispensable role and its toxicity is very narrow. The toxicity of Se in aquatic ecosystems is mainly linked to its bioaccumulation by microorganisms and subsequent transfer upwards the food chain. The knowledge of Se uptake and transformation at low trophic level, by organisms such as algae, plays therefore a crucial role to investigate its behaviour in freshwater ecosystems. The phytoplanktonic alga *Chlamydomonas reinhardtii* was chosen for the study as a potential vector of Se from water to filter-feeders organisms. Toxicity of Se for this alga has already been assessed but speciation studies are lacking to investigate deeply the role of biotransformations. In this work, the speciation analysis of Se is carried out by ion exchange HPLC coupled to ICP-MS equipped with a collision/reaction cell.

The aim of this study was to evaluate the influence of sample treatment and storage on the determination of selenium species in the algae *Chlamydomonas reinhardtii* exposed to different forms and concentrations of Se. After culture in appropriate media, low amount of algae is obtained by filtration. Due to the few sample available, and the low levels of Se expected, special attention was paid to sample treatment to maximise Se extraction. Cells lysis was evaluated for Se recovery after exposure of algae either to selenite or selenomethionine. As it may also be necessary to store the samples before analysis, a study was conducted to evidence any possible transformations or losses before and after lysis during storage at different temperatures.

ThPo45. DETERMINATION OF CARBOXYLIC ACIDS, CARBOHYDRATES AND METALS IN DIFFERENT TOMATO CULTIVARS BY HPLC-ICP-AES IN A SINGLE CHROMATOGRAPHIC RUN

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The determination of carbohydrates, carboxylic acids and metals in foods is important because of their influence on food quality. Moreover, the study of the profiles of these compounds in foods such as tomatoes can be employed to discriminate between different varieties.

The determination of carbohydrates by coupling HPLC to ICP-AES has been carried out in previous works. These compounds are detected by means of the measurement of the carbon emission signal at 193,090 nm. In our laboratory we have demonstrated that HPLC-ICP-AES can be employed to determine carbohydrates, carboxylic acids, alcohols and metals in a single chromatographic run. In the present work the influence of several variables, related to the sample introduction system in ICP-AES, on the sensitivity of carbon emission signal and chromatographic resolution have been studied. These variables include the nebulizer and the spray chamber design and the temperature used to heat the spray chamber. A combination High Efficiency Nebulizer and cyclonic spray demonstrated to be the best choice.

In addition, the calibration procedure has been also studied. ICP-AES is characterized by its universality with regard to non-volatile species. In a previous work, we have demonstrated that a full calibration curve can be constructed with a single injection^{Error! Bookmark not defined.}. This can be achieved by injecting a solution containing different concentrations of a set of non-volatile organic compounds and then plotting peak area obtained for a given compound against its carbon concentration. This procedure has been applied in the present work to determine the carbon concentration of several identified and unidentified organic compounds in a set of native varieties of tomato. The comparison of the profiles of these organic compounds as well as metals in tomatoes allows the discrimination between the different varieties studied in the present work.

ThPo46. TUNING OF A COLLISION/REACTION CELL-BASED Q-ICP-MS FOR SUPERIOR URANIUM ISOTOPE RATIO ANALYSIS

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Exceptional detection power and high analytical speed have been the driving forces for ICP-MS over the past 20 years. Consequently, ICP-MS has evolved into the most powerful and versatile technique in inorganic analytical chemistry. With the development of collision/reaction cell technology, spectral interferences caused by molecular ions can be widely overcome and quadrupole-based ICP-MS opens the applications window even further. Apart from routine quantitative analysis, ICP-MS has the intrinsic ability of performing isotope ratio determinations. Although a variety of dedicated instruments have been developed for that kind of application with excellent performance, it is important to many analytical laboratories in the nuclear business to use their quadrupole-based ICP-MS equipment for that purpose on a part-time scale.

In the nuclear industries the determination of Uranium isotope ratios – especially the $^{235}\text{U}/^{238}\text{U}$ ratio - is extremely important because of technical, economic and safety reasons; high-quality data is mandatory.

This work describes the tuning steps for a quadrupole-based ICP-MS equipped with a 3rd generation collision/reaction cell required to meet the demands of the nuclear industry with respect to $^{235}\text{U}/^{238}\text{U}$ ratio measurement in both enriched and natural Uranium samples.

ThPo47. ASSESSMENT OF THE ACCURACY OF URANIUM ISOTOPE RATIO MEASUREMENTS PERFORMED BY QUADRUPOLE AND MULTI-COLLECTOR MAGNETIC SECTOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETERS

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The $n(^{235}\text{U})/n(^{238}\text{U})$ isotope amount ratio measurements in a group of samples in the range of 0.5 to 3.5% ^{235}U were performed by two types of inductively coupled plasma mass spectrometers. The first one was assembled with a quadrupole analyser and single electron multiplier while the second one had a magnetic sector analyser and multi Faraday collectors. The most important sources of uncertainty in both instruments were identified and their contribution to the combined standard uncertainty was evaluated using the ISO-GUM procedure. The correction of the mass discrimination effect was carried out using the single and the double standard methods enabling a comparison between these two approaches. The expanded uncertainties associated to the measurements results provided by the quadrupole ICPMS was around 1.0 % while the values for the multi-collector instrument was lower than 0.05%.

ThPo48. SPACE CHARGE AND MASS DISCRIMINATION EFFECTS ON LEAD ISOTOPE RATIO MEASUREMENTS BY ICP-QMS IN ENVIRONMENTAL SAMPLES WITH HIGH URANIUM CONTENT

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In this work the accuracy of lead isotope ratio determinations by ICP-QMS in the presence of different uranium concentrations was investigated.

The influence of uranium concentration on the measurement of lead isotope ratios is very severe due to space charge and mass discrimination effects, which play important role during the process of signal acquisition.

For the purpose of this research, solutions of the isotope reference material NBS SRM 981 spiked with different amounts of uranium were analyzed for lead isotope ratios evaluation using a ICP-QMS and a HR-ICP-MS. The obtained results demonstrate the existence of a strong interference of uranium content in the analytical process, being the same behaviour exhibited by both equipments.

In order to optimize an analytical procedure to perform with a ICP-QMS, a new method with external standardization and matrix match has been developed. This method produced results that show excellent agreement with data obtained by Thermal Ionization Mass Spectrometry ($r = 0.9995$).

As conclusion, it can be stressed that the developed methodology offers the adequate analytical quality for lead isotope data when they are used for identification of lead different sources in environmental studies and applications.

ThPo49. MATHEMATICAL CORRECTION FOR TUNGSTEN OXIDE INTERFERENCE ON MERCURY ISOTOPE RATIO MEASUREMENT BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR SAMPLES CONTAINING LARGER AMOUNTS OF TUNGSTEN

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A mathematical correction scheme was devised for the isobaric overlap of tungsten oxide, WO, on mercury, Hg, isotope ratio measurement using inductively coupled plasma (quadrupole) mass spectrometry, ICP-MS, for detection. This allowed Hg determination by isotope dilution, ID, in samples of a material that contained greater amounts of tungsten, W, by a direct ICP-MS based method with simple sample preparation and conventional sample

introduction. Tungsten forms oxides in an ICP that isobarically overlap with all Hg isotopes except 201 and 204, and the latter is isobarically overlapped by Pb. Isobaric overlap can be corrected by measuring the interfering species at an m/z for which the analyte does not have a natural isotope, and calculating the level of interference using the known relative isotopic abundances of the interfering element. However, no such isotope pair exists for the W + Hg combination, so it was necessary to devise an alternative scheme to assess the influence of WO on Hg. Prior measurement of a simple-matrix W solution established the rate of oxide formation. Simultaneous measurement of W and Hg isotopes in samples was used to calculate the level of W influence, and to correct for differences in mass discrimination between the samples and the simple-matrix W solution.

The calculation scheme allowed calculation of WO corrected results, together with a full uncertainty budget, which allowed the identification of uncertainty contributions from individual parameters. It was necessary to apply correction for the difference in mass discrimination between samples and the simple-matrix W solution as neglecting this effect could lead to error in the result greater than the uncertainty of measurement. Use of ^{201}Hg as reference isotope instead of the more abundant ^{200}Hg reduced uncertainty on measurement, as this isotope is not isobarically overlapped by WO, and the correction scheme could be simplified. The most suitable spike isotope was ^{202}Hg as the naturally high abundance with the increase in Hg content by spike addition reduced the relative effect of WO. It was important to measure the WO formation rate with the greatest possible reproducibility, as this gave a critical contribution to the combined uncertainty budget. Comparison of ID measurement of samples with ^{200}Hg or with ^{201}Hg as reference isotope, (with appropriate modification of the scheme for WO correction) showed no difference in the result and tests made by spiking natural Hg to samples showed that Hg recovery was complete.

This poster presents the experimental method and calculation scheme for the result and its uncertainty, and demonstrates additional validation through successful participation in a laboratory inter-comparison.

ThPo50. ISOTOPE RATIO MEASUREMENT BY MULTI-COLLECTOR ICP-MS FOR SOURCE APPORTIONMENT OF MERCURY

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Mercury, Hg, emissions to the atmosphere in Europe are largely given by coal-fired power stations, metal and metal ore refining, the production of bulk inorganic chemicals and fertiliser and by other industrial processes such as cement production. As these industries also produce the bulk emissions of fine particulate matter, there is the potential that measurement of Hg in air particulates could give local information on sources of mercury pollution. Such information would be of use to European Union member states in implementing the requirements of the Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC). When Hg emissions are identified, compliance with licenses may be tested and remediation strategies implemented. The isotopic composition of Hg in a sample might provide insight into the either natural or anthropogenic origin of the Hg, and may even give information on the process by which the sample material was produced. Multi collector - Inductively Coupled Plasma – Mass Spectrometry, MC-ICP-MS, has the potential to measure Hg isotope ratios with levels of combined uncertainty lower than those proposed for isotopic fractionation of Hg in nature (δ values for ^{198}Hg , ^{199}Hg , ^{200}Hg , ^{201}Hg or ^{204}Hg of the order of 1 ‰).

An analytical setup was developed specifically for Hg isotope ratio measurement with a Nu Instruments MC-ICP-MS. It combined sample Hg introduction as cold vapour in a stream of argon, mixed with dried aerosols originating from the simultaneous aspiration of a thallium

solution through a Nu Instruments Desolvation Nebuliser System (DSN-100). The system was optimised to record isotope ratios for Hg with greatest repeatability and to record the $n(^{203}\text{Tl})/n(^{205}\text{Tl})$ ratio for use as an internal standard for instrumental mass discrimination, at the time of measurement. Delta measurements to a reference material of Hg (ERM[®]-AE639) were carried out. As the smallest observable changes in isotope composition could lead to differing conclusions on source apportionment, all sources of uncertainty on the isotope ratio measurements were identified and quantified, and a calculation scheme was devised that included all parameters affecting the measurement. Validation of the measurement method demonstrated that δ values could be measured with uncertainty of $< 1 \%$.

ThPo51. LEAD ISOTOPIC ANALYSIS OF CORAL SAMPLES BY MULTIPLE COLLECTOR ICPMS

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Anthropogenic lead has been emitted to the atmosphere over the past three millennia through activities such as mining and smelting. After 1920s, Pb pollution has been accelerated with the introduction of alkyl Pb. Temporal variations of the Pb source have been reported using Pb isotopic compositions of geological samples, such as lake sediments and ice cores. In addition, it is suggested that coral samples are useful to assess Pb pollution, which is easily transported to the ocean via atmosphere, in the sea surface. In this study, we established the method for precise determination of Pb isotope ratios of coral skeletons using carbonate standard material, JCp-1 and Jct-1 and several coral samples collected from the western Pacific. Then the spatial distribution of Pb and their sources in the western Pacific were discussed.

Sample powders (100 mg) were dissolved in 1M HBr, and pure Pb fractions were collected after removal of matrix elements through an anion exchange resin. Procedural Pb blank was 5 pg. Pb isotope ratios were determined with multiple collector ICP-MS using Tl doping technique. Pb transmission of NEPTUNE (Thermo Electron, Bremen, Germany) was more than 70×10^{-11} A/ppm, and 5 ng Pb was consumed in one analysis for 5 mins. Isobaric interference of Hg-204 and Tl peak tailings on Pb-204 were correctly estimated, and on peak subtraction method were applied. One day repeatability of a Pb isotopic standard was Pb-206/Pb-204: 0.25%, Pb-207/Pb-204: 0.24%, Pb-208/Pb-204: 0.26%, Pb-208/Pb-207: 0.04%, and Pb-206/Pb-207: 0.06%, respectively (2xSD, n=11) (5 ppb Pb + 0.5 ppb Tl solution).

The results of determination of Pb isotopic compositions of JCp-1 and Jct-1 showed that the method proposed in this study were effective for analysis of Pb isotopic compositions of coral samples. Additionally, Pb isotope ratios obtained from coral samples were compared with reported values of those of the aerosols, suggesting the surface of the western Pacific has been affected by anthropogenic Pb emitted from East Asia, mainly China.

ThPo52. URANIUM ANALYSIS IN BLOOD BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Depleted uranium (DU) is a byproduct of the uranium enrichment process for nuclear fuel. Natural uranium in the environment contains 0.72% ^{235}U , and 99.27% ^{238}U , whereas DU contains 0.2% ^{235}U , and 99.8% ^{238}U . Because of DU's high density and low relative cost, it has been incorporated into projectiles and armor for military applications. As a result, soldiers in battle can be exposed to DU by inhaling airborne DU particles, ingesting DU particles, and/or experiencing wound contamination by DU particles. Because of the toxicological (chemical) properties of uranium, the long-term health effects of DU exposure are of concern.

In this study we report a simple robust method for the determination of total uranium levels in blood specimens followed by isotopic analysis. The isotopic measurements allow us to determine the nature of uranium exposure. Exposure to DU causes a decreased percentage of ^{235}U in blood samples, resulting in measurements that vary between natural environmental uranium 0.72% ^{235}U , and depleted uranium 0.2% ^{235}U . Blood specimens were digested in an open vessel microwave digestion system using a nitric acid / peroxide mixture. A quadrupole ICP-MS was used for the subsequent analysis of all uranium isotopes. In the total uranium determinations, enriched ^{233}U was used as an internal standard to correct for biological matrix effects. Interferences at m/z 235 were minimized by the use of a dynamic reaction cell ICP-MS.

ThPo53. THE COUPLING OF THE ICP-MS TO CHROMATOGRAPHY: FIT FOR PURPOSE IN THE INDUSTRIAL ROUTINE ANALYSIS?

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Hyphenated techniques involving ICP-MS (inductively coupled plasma mass spectrometry) are among the fastest growing research and application areas in atomic spectroscopy. This trend is driven by the need to determine not just the total amount of an element, but also its chemical form, since this can have a dramatic impact on the element's bioavailability, mobility, toxicity and other chemical properties. Hyphenated ICP-MS is the coupling of the ICP-MS to a separation technique – normally a chromatographic separation. In this way, target analytes are separated into their constituent chemical forms or oxidation states before elemental analysis [1]. Gas chromatography (GC), liquid chromatography (LC), ion chromatography (IC) and capillary electrophoresis (CE) are commonly used in the combination with the ICP-MS for speciation analysis.

Apart from academic research, these techniques are finding increasing application in commercial uses as well. Elemental speciation analysis in biological, environmental and clinical sample matrices are important applications of several new hyphenated techniques including the GC-ICP-MS. With integrated equipment such the HPLC-ICP-MS or the GC-ICP-MS, sample preparation prior to analysis is minimized and “on-line” species separation is much faster. These techniques are becoming increasingly popular in applications where analyses of complex matrices with low detection limits and high specificity are expected [2].

One of the industry analysts Kiran Unni said: “Hyphenated Techniques Breathing New Life into the Analytical Instrumentation Industry”.

And what about other branches of industry?

Examples of GC-ICP-MS application at the Competence Center Analytics of BASF AG will be presented. Advantages and disadvantages of this approach will be discussed in consideration of a routine application.

¹ <http://www.chem.agilent.com/Scripts/Generic.ASP?IPage=41743&indcol=Y&prodcol=Y>

² Kiran Unni at <http://www.frost.com/prod/servlet/market-insight-top.pag?docid=9298168>

ThPo54. METHOD PERFORMANCE STUDY OF ON-LINE INTERNAL STANDARD ADDITION IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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The use of an internal standard plays an essential role in correcting analytical signal suppression (or enhancement) due to matrix effects; signal fluctuations due to temporal variations in the plasma and potential variability within sample introduction system due to intra-sample variability in nebulization efficiency (viscosity effects). Traditionally, internal standardisation is achieved by adding an identical aliquot of the internal standard solution to all samples, blanks and calibration standard solutions to be measured. This can be very time-consuming, especially when using the gravimetric approach and when there are a large number of samples to be measured.

In our work, we have evaluated the concept of adding the internal standard to all solutions at a constant level by on-line merging of the internal standard (steady state) and the sample solution streams. This on-line addition is faster; however the outcome strongly depends on the effectiveness of the mixing of sample with the internal standard. To this end, an internal standard introduction system was developed using a knotted reactor, a mixing T-piece and two peristaltic pump channels. The length of the knotted reactor, the sample flow rate and the wash out time were optimized for best mixing performance (i.e. highest possible precision of the analyte count rates corrected by the appropriate internal standard for 5 replicate determinations across the whole mass range). For the optimization and measurement, a multiple internal standard containing 20 ng/ml Sc, Rh and Tl was used in order to provide full coverage of the mass range of the analytes of interest.

Both internal standard addition methods were used for determination of Mg, Ca, Ti, Mn, Fe, Zn, As, Se, Cd, Ba, Pb, Th and U mass fractions in an IAEA candidate biological reference material (whole egg powder). Additionally, the uncertainty components of the internal standard addition and these of the calibration function were evaluated and compared. No significant difference was found in terms of accuracy and precision between the two methods underpinning the advantage of the more practical on-line internal standard addition technique.

ThPo55. ACHIEVING LESS THAN 3% UNCERTAINTY ON THE SULFUR CONTENT DETERMINATION IN LOW SULFUR PETROL SAMPLES CONTRIBUTION TO THE CERTIFICATION OF ERM-EF211, - EF212, - EF213

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Sulfur in transport fuels is a significant source of atmospheric pollution. Sulfur, present in the fuel as an impurity, is converted during the combustion mainly to SO₂ causing respiratory diseases, stratospheric ozone depletion or “acid rains”. In addition, sulfur in the fuel limits the development of cleaner engine technology. During the past decades the sulfur content in fuels was progressively reduced. Since the 1st of January 2005, petrol with maximum sulfur content of 10 mg/kg shall be available on the market in the EU.

Following the administrative decision, suitable reference materials with certified value (CRM) on the sulfur content have to become available. Such internationally recognized CRM's, with small uncertainty statements, are needed both in the petroleum industry and in the laboratories of the regulatory body controlling the fuel on the market.

In response to these regulations a set of three new candidate low-level sulfur petrol CMRs (50, 20 and 10 mg kg⁻¹; respectively ERM-EF211, ERM-EF212 and ERM-EF213) was produced, for which IRMM contributed with certified values using two-way isotope dilution applied as a primary method of measurement.

The difficulty of such measurements results from a combination of factors including the volatility of the material and the characteristics of the analyte (e.g. very low contents and complex speciation of sulfur compounds). The whole analytical protocol was extensively validated, including estimation of combined uncertainties on measurement results according to ISO guidelines. Maintaining the petrol at - 78°C during sample preparation was found to be necessary to achieve complete recovery of the S content (more than 5% difference otherwise). Samples were acid digested under high pressure conditions (optimum sample size ~ 0.5 g). Isotope ratio measurements were carried out by inductively coupled plasma mass spectrometry at medium mass resolution. The repeatability on the S content determination was excellent – between 0.6 % – 0.8 % (n = 6) and, overall, combined uncertainties of 2.7–2.8% (k = 2) were achieved for all three candidate CRMs.

ThPo56. DIRECT DETERMINATION OF Te AND REE IN SEA-ICE USING AN ICP-SFMS COUPLED WITH A DESOLVATION SYSTEM

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Sea ice represent a complex matrix to analyse because its variability in salinity (from like-distilled water up to 25‰ depending on age of sea-ice) and particulate matter content. The different response of ICP-SFMS to the different salinity of sample is well known; the tuning on measured matrix is necessary to maximize the signal intensity and stability and minimize the interferences and the use of an internal standard is required to compare the samples with different salinity and quantify the element contents using a single matched calibration curve. We present here the results of the analyses performed on sea-ice samples from Mc-Murdo sound and on certified reference materials (SLEW 3 and NASS5) to determine trace element (TE) and rare earth element (REE) contents. The use of a desolvation unit has allowed us to minimize the problem of oxide and hydroxide interferences. The relationship between an added internal standard (indium) and a like-internal standard (xenon, argon-argon, nitrogen-nitrogen) response is also shown to highlight the possibility of using Xe, Ar-Ar, and/or N-N (from added gas, i.e. argon and nitrogen) as internal standard avoiding the addition of a real internal standard (In).

ThPo57. ULTRA-TRACE LEVEL Ra-226 ANALYSIS BY ISOTOPE DILUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Radium-226 ($T_{1/2} = 1620$ years) is one of the most frequently analysed long-lived radionuclides. Its concentration is measured in foodstuff, mineral water and drinking water because of radiation protection purposes and in environmental matrices to assess geological or oceanographic processes applying radium-226 as a tracer. However, as the half-life of this

radionuclide is rather long, traditional radiochemical techniques require long measurement time. Moreover, meticulous and labor-intensive sample preparation is necessary to obtain accurate results.

The aim of the study was to develop a novel and rapid analytical procedure using isotope dilution inductively coupled plasma sector-field mass spectrometry (ID-ICP-SFMS) for the measurement of Ra-226 from various matrices at ultra-trace level. To improve the accuracy and precision of the method isotope dilution with radium-228 ($T_{1/2} = 5.75$ years) was applied. The sample preparation involves a pre-concentration step with MnO₂-impregnated resin and a cation-exchange chromatographic separation. The achieved detection limit of the procedure is 0.084 fg g⁻¹ (3.0·10⁻³ mBq g⁻¹), which is comparable to that of the radon-emanation method, but less tedious and more rapid. The sample preparation, elimination of possible interferences and figures of merit of the ID-ICP-SFMS method is discussed.

ThPo58. DIRECT ELEMENTAL ANALYSIS OF BIODIESEL BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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With growing concern regarding greenhouse gas emissions, particularly carbon dioxide as a combustion product of fossil fuels, “carbon neutral” fuels are gaining popularity as a means of reducing the carbon footprint on the environment. One such area where carbon emissions can be reduced is through transportation; biodiesel (typically manufactured from a mixture of petro-diesel and naturally-sourced esters) can be run on most modern diesel engines without modification. Typically the “bio” content of diesel will come from vegetable oil of some form (Rapeseed, Palm, Tallow, Soy, etc.) after a simple transesterification using methanol and a basic catalyst. The resulting material is then typically blended 70:30 bio:petro in essence reducing the greenhouse emissions by up to 70%.

Although biodiesel is in essence a natural product, inorganic contaminants need to be determined in order to fall within legislation or to ensure correct burn characteristics. Additionally, certain contaminants have a negative effect on engine life causing corrosion or “sludging” depending upon the element present, reducing the effective lifetime of the engine. Traditional analytical approaches include ICP-OES or AAS. ICP-MS offers a viable alternative to these techniques and can provide a much wider elemental and concentration coverage for less overhead in terms of analysis time. The direct determination of organic matrices is routine on modern ICP-MS systems due to intelligent generator and sample introduction system designs; any interferences resulting from the carbon matrix are essentially filtered out with Collision-Reaction-Cell (CRC) equipped instruments. In this paper, an instrument fitted with an Octopole Reaction System (ORS) is used to directly measure the inorganic content of several biodiesel materials. The ORS operates primarily in an inert collision mode using energy rather than reaction processes to remove interferences, simplifying operation and improving data quality for unknown matrices/interferences.

ThPo59. DETERMINATION OF GLOBAL FALLOUT PLUTONIUM ISOTOPES USING SECTOR-FIELD ICP-MS FOR RAPID DATING OF RECENT SEDIMENTS IN HONGFENG AND CHENGHAI LAKES, SW CHINA

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Accurate dating of lake sediments is important for many studies, such as the reconstruction of pollution history of organic pollutants and heavy metals, and the historical variation of lake biological productivity and/or carbon preservation. The most commonly used radionuclides for radiometric sediment dating are ²¹⁰Pb and ¹³⁷Cs. Recently, the potential of using Pu isotopes for the dating of recent aquatic sediments (<100 years age) has been considered. Taking into account the long half-lives of Pu isotopes (²³⁹Pu, $t_{2/1} = 2.44 \times 10^4$ yr; ²⁴⁰Pu, $t_{2/1} = 6.58 \times 10^3$ yr), this dating technique established in our current generation could be a great legacy for next generations to study the history of anthropogenic pollutants in the environment.

We applied a sector-field ICP-MS to establish the chronology of recent lake sediments in Chenghai and Hongfeng Lakes, SW China via measurements of Pu isotopes. The Pu activity profile obtained with SF-ICP-MS was in agreement with a γ spectrometric ¹³⁷Cs profile, indicating that the ¹³⁷Cs and Pu activities convey essentially the same information about sedimentation processes in the investigated lakes. The inventory of ²³⁹⁺²⁴⁰Pu in sediment cores ranged from 35.4 to 50.7 Bq/m², close to the expected global fallout inventory (36-42 Bq/m²) at this latitude band (20⁰-40⁰N). The average ²⁴⁰Pu/²³⁹Pu atom ratios in these two sediment cores are 0.195 ± 0.021 for Chenghai Lake and 0.185 ± 0.009 for Hongfeng Lake. The sources of Pu isotopes and the potential application of Pu isotopes for sediment dating will be discussed.

ThPo60. ELEMENTAL AND ISOTOPIC STUDIES ON URANIUM-CONTAMINATED SOILS -USE OF FLOW INJECTION AND FIELD FLOW FRACTIONATION TECHNIQUES.

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Flow field flow fractionation (FFF) in combination with ICP-MS represents a powerful strategy for gaining physicochemical information on environmental samples. In this work we apply FFF for the study of uranium in contaminated soils. Specifically we are interested in clarifying the chemical and physical speciation of uranium (and associated chemistry) in soils contaminated with depleted uranium derived from weapons testing. Chemical and sequential extraction procedures, similar to that used for trace metal characterisation of sediments, are applied to two dissimilar sample types i.e. a sandy loam and a clay-rich soil. The presentation will report fractograms (U, Al, Cd, Cr, Cu, Fe, Mg, Mn, Pb, Sr, Ti, Zn) for chemical/sequential extracts in order to characterise soils in terms of uranium/trace metal mobility. Isotopic measurements (²³⁵U/²³⁸U) are also used to distinguish between naturally derived and military sourced uranium.

ThPo61. ANALYSIS OF SULFUR BY ICP-QMS: QUANTITATIVE EVALUATION OF HETEROATOM-PROTEIN STOICHIOMETRY.

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The quantitative determination of heteroatom - protein stoichiometry is an important challenge in the metalloproteomics field and constitute an emerging issue. Even if several works describe the complementarity of the elemental and molecular mass spectrometry in the qualitative detection of metalloproteins only few studies were focused on the quantitative evaluation of stoichiometry. In fact, proteins contain only one element suitable for protein quantification by elemental analysis, sulfur. Sulfur is of particular usefull because it is present in two amino acids, cysteine and methionine, that occur with a cumulative abundance of 5% in natural proteins. Unfortunately the determination of sulfur by ICP-MS is complicated by important polyatomic interferences that can be removed only by using of high resolution mass spectrometer or collision/reaction cell coupled to a quadrupole mass spectrometer. Although ICP-Quadrupole-Mass Spectrometers (ICP-QMS) are the most commonly employed instruments. Unfortunately, their analytical performances for quantitative sulfur analysis are not still completely defined. In this work we revalued the potentialities of low resolution ICP-MS without collision/reaction cell in the quantitative determination of sulfur and describe the full validation of two methods based on the detection of the minor isotope of Sulfur, ^{34}S and the oxide ion of the most abundant isotope, $^{32}\text{S}^{18}\text{O}^+$. Validation was performed according to the Eurachem guidelines. These methods were also applied to quantitatively define the metal and non metal stoichiometric ratio on commercially available protein standard.

ThPo62. MULTI-ELEMENT ANALYSIS OF HUNGARIAN WINES BY COLLISION CELL ICP-MS AND THEIR CLASSIFICATION ACCORDING TO GEOGRAPHICAL ORIGIN

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Wine is one among those agricultural products whose proved authenticity could be a factor that is able to command a higher price on the markets. Authenticity is a complex feature of foodstuffs that affects both compositional purity, processing technology, geographical origin and age. Since the element suit present in grape and consequently in must and finally in wine can be coupled to that of the soil, therefore elemental analysis of wines might be able to provide information of the provenance of the given wine. When an elemental fingerprinting method is used for wine authentication it should be considered that beyond the fact that numerous soil-chemical, physiological etc. factors have leading role in determining the actual element pattern of grape, technological and other contaminations would further deform the picture.

In this study the development of a routine method for obtaining multi-elemental information suitable for multivariate statistical evaluation of the elemental fingerprint of wines was carried out. For the experiments 30 Hungarian white and red wines from 7 regions were used. Considerations on variable selection and comparison of sample preparation methods such as digestion and the simple dilution, along with different quantification techniques will be presented.

ThPo63. MC-ICPMS DELTA-SCALE MEASUREMENTS DOWN TO 0.005%. VALIDATION USING GRAVIMETRIC REFERENCE VALUES FOR CANDIDATE IRMM Pb δ -iCRM

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δ -scale calculations, i.e. the establishment of the relative difference between two isotope ratios, originally developed for applications involving light elements (C, H, O, N, S), are now

used for isotope ratios of a different range of elements (B, Li, Mg, Fe or Zn among others) measured by MC-ICPMS (Multiple Collector Inductively Coupled Plasma Mass Spectrometry).

A major potential advantage of such approach is the reduction of the uncertainty associated to measurements results, as compared to absolutely calibrated isotope ratio values. However, this advantage is realised only if measurement biases in both measured isotope ratio values of the δ expression are identical and neutralise each other mutually.

Thus, short term variations of mass discrimination during MC-ICPMS measurements can be seen as a limitation in the application of the δ method, and a validation is necessary.

In this context, IRMM produced a series of four pairs of candidate Pb δ -iCRM (isotopic Certified Reference Materials) available as ampouled solutions (a natural Pb material and the same natural Pb slightly enriched in ^{207}Pb , with $\delta^{207}\text{Pb}$ ranging $\sim 0.01 - 0.001\%$). Natural Pb was enriched gravimetrically, using substitution weighing (0.0025% standard uncertainties, no impact from the non-linearity of the analytical balance) against operational mass standards traceable to the Kg in the shortest possible comparative way. Certification at less than 1% ($k=2$) level of the relative degree of enrichment depended essentially from the quality of the weighing measurements.

This presentation will introduce a method to obtain accurate $\delta^{207}\text{Pb}$ results by MC-ICPMS down to 0.005%. Validation using the aforementioned produced Pb δ -iCRM series as well as the way meaningful uncertainties below 0.005% were achieved will also be described.

ThPo64. NOVEL APPROACH FOR DETERMINATION OF TRACE METALS IN SUSPENDED SOLIDS OF SURFACE WATER BY ICP-SFMS

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The new EU Water Framework Directive (2000/60/EC) suggests suspended solids as additional compartment for monitoring of Environmental Quality Standards (EQS) for priority substances in surface water. Conventional methods for determination of compounds bound to suspended solids comprise on-site collection and isolation of sufficient amounts of suspended solids followed by sample preparation. All of these steps are tedious, expensive, time consuming and prone to various sources of contamination.

We have developed and validated a new, fast and contamination free sample preparation scheme for studying the partition of As, Cd, Cr, Cu, Hg, Ni, Pb and Zn between suspended solids and the water phase.

Sample preparation is very simple and straight-forward: The dissolved metal content is determined from centrifuged and subsequently acidified river water, while the total metal content is measured by introduction of the acidified river water sample via slurry-type nebulization (“V-Groove”-nebulizer). In order to avoid any form of contamination sample preparation and measurement are performed under clean room conditions (class 100,000 and 10,000 respectively). The particle bound metal fraction is calculated via subtraction of the two fractions and division by the concentration of suspended solids (gravimetric determination).

The method was applied to samples stemming from three Austrian rivers covering the typical range of suspended solids concentration. Results of a campaign performed in summer/autumn 2006 are presented.

Acknowledgement:

Financial support from the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management (BMLFUW, Project Title: “Determination of trace metals in water phase and suspended solids of river water by ICP-SFMS”) is gratefully acknowledged.

ThPo65. CHARACTERISATION OF COPPER STRESS IN *ARABIDOPSIS THALIANA* BY ICP MS & ESI MS COUPLED TO HPLC

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Heavy metals like Cd, Cu and Pb are highly reactive and toxic to living cells. Plants have developed complex mechanism by which they control the uptake and accumulation of heavy metals. These mechanisms involve chelation and sequestering of metals ions mainly by glutathione (GSH), phytochelatins (PCs) and metallothioneins (MTs).

The role of PCs in regulation of copper toxicity was investigated in *Arabidopsis thaliana* by RPLC – ESI-MS in comparison to plants treated with cadmium. Only glutathione was found to be involved in copper detoxification mechanism. The lack of phytochelatins response to copper presence allowed to suspect, that glutathione acted rather as a reducing agent than a species taking part in synthesis of PCs. This hypothesis was proved by study concerning copper complexes with glutathione by ESI-MS. Speciation of the metal was investigated by SEC – ICP MS in order to demonstrate the translocated metal forms in individual organelles. The main part of copper was found in buffer extract (10 mM Tris – HCl, pH 7.4) containing water soluble peptides and small proteins. RPLC – ESI MS and PAGE experiments indicated the activity of metallothioneins in copper deactivation.

ThPo66. HIGH-PRECISION CALCIUM ISOTOPE RATIO MEASUREMENT FOR BIOLOGICAL MATERIALS USING MULTIPLE COLLECTOR-ICP-MS

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Calcium is one of the most abundant elements for animals, and the Ca deficiency can cause serious diseases including osteoporosis. In this study, in order to investigate the Ca intake efficiency or metabolism, we have measured Ca isotope ratios ($^{44}\text{Ca}/^{42}\text{Ca}$, $^{43}\text{Ca}/^{42}\text{Ca}$) on series of bone and plasma samples collected from experimental mice of various ages by means of a multiple collector-ICP-MS (MC-ICP-MS). The combination of microwave digestion and cation-exchange chromatography was adopted to collect Ca from the biological samples. Interfering signals such as $^{40}\text{Ar}^{1}\text{H}_2^+$ and $^{12}\text{C}^{16}\text{O}_2^+$ were successfully minimized by employing a dissolving nebulizer device, and residual interfering signals were corrected by an on-peak baseline subtraction technique. The $^{44}\text{Ca}/^{42}\text{Ca}$ ratios for adults' plasma samples were 0~0.3‰ heavier than that of their food source, whereas the $^{44}\text{Ca}/^{42}\text{Ca}$ ratio for adults' bone samples were 0.5~0.2‰ lighter than that of their food source, suggesting the presence of isotopic fractionation through the formation of bone. Moreover, the $^{44}\text{Ca}/^{42}\text{Ca}$ ratios for newborns' and infants' bone samples showed slightly higher than that of adults', indicating the $^{44}\text{Ca}/^{42}\text{Ca}$ ratios of bones can vary with age. These results indicate that Ca isotope ratios can become a new tool to evaluate Ca metabolism in animals.

ThPo67. A NEW ENZYME-ASSAY FOR PLA₂ ACTIVITY IN JELLYFISH VENOM BASED ON PHOSPHORUS DETECTION USING HPLC-CC-ICP-MS

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Although their function in the marine ecosystem is not yet fully understood, jellyfish seem to become important key species in the environment due to the limited number of natural enemies, global warming effects and environmental pollution especially with micro nutrients. Mass occurrences in some regions indicate a strong impact on the local food webs with negative effects on all trophic levels due to their continuous ingestion of different prey species. Fishing tentacles and mesenteric tentacles, which are equipped with specialized cells harboring venom containing capsules (nematocysts) are used for prey capture and self defence.

Up to now only little is known about the chemical composition of the jellyfish toxin cocktail, the chemical structures and the biochemical effects. To understand their role in the environment it is essential to gather more information about the mechanisms and the compounds especially, which are mainly responsible for the toxic effects. The complexity of the venom cocktail requires an effect orientated fractionation strategy in order to distinguish toxicologically active and inactive fractions and to reduce the complexity of the sample.

In several reptile and insect venoms Phospholipase A₂ (PLA₂) is known as a major compound. The Phospholipase A₂ family is an enzyme class, which catalyze the hydrolysis of phospholipids at the *sn*-2 position to release the corresponding fatty acid and lysophospholipid. PLA₂-activity of the jellyfish venom may be responsible for some typical inflammation reactions like pain or oedema and toxic effects such as myo- or neurotoxicity in the affected organism. Additionally PLA₂ can destabilize the cell membranes and alter the cell permeability. The responses caused by a fatty acid activated cascade reaction whose products are responsible for the inflammation reactions.

This contribution will present first results on the development of an enzyme assay for the investigation of the venom of Lion's Mane jellyfish with respect to PLA₂-activity. The main goal is to separate and simultaneously determine the phosphorus containing enzyme substrate and the reaction products caused by the PLA₂ activity by using high performance liquid chromatography (HPLC) on-line hyphenated to collision cell inductively coupled plasma mass spectrometry (CC-ICP-MS). Changes of the enzyme substrate and the product quantity directly indicate an PLA₂-activity of the sample fraction under investigation. Sonicated vesicles consisting of phospholipids are applied as enzyme substrate. Reversed phase liquid chromatography (RP-HPLC) has been used to separate the lipid and the lysophospholipid. Molecule ions formed and interfered with the sensitive phosphorus specific detection, are minimized by using helium as cell gas. The established assay should allow effective indication of PLA₂-active compounds in different fractions of nematocyst extracts to guide their final identification during a multidimensional separation process.

ThPo68. THE POTENTIAL OF GEL ELECTROPHORESIS COUPLED TO ICP-MS FOR THE DETERMINATION OF CISPLATIN-OLIGONUCLEOTIDE ADDUCTS

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The use of elemental mass spectrometry was successfully applied to different questions in biological and medical research in the last few years. Particularly, the online coupling of powerful separation methods like liquid chromatography (LC) or capillary electrophoresis (CE) to inductively coupled plasma-mass spectrometry (ICP-MS) with its excellent multi-element detection and quantification capabilities gained great importance to the determination of biopolymers and their interaction with metals. Different methods were developed for the separation and detection of metalloproteins or DNA metal adducts in various samples³. However, the most popular and powerful separation method for biopolymers, gel electrophoresis (GE), was not coupled online to ICP-MS for such studies at this time. Several approaches have been developed on the basis of laser ablation^{4,5}, but this technique is quite laborious and time-consuming, so easier approaches are highly desirable.

In this paper we describe the technical realisation of an online coupling of GE to ICP-MS for the direct determination of cisplatin-oligonucleotide adducts.

The system bases on the principle of preparative GE, which uses a continuous elution of the separated compounds from the gel. The eluted compounds are directly transferred into the elution buffer, which accomplishes the transport to the nebulisation system of the ICP-MS⁶.

Gel electrophoresis enables to separate large biopolymers like oligonucleotides and DNA fragments without further sample pre-treatment like an enzymatic digest. For this reason it is possible to determine the formation of cis-Platin-oligonucleotide adducts nearly in “real-time” with the consequence that kinetically unstable compounds can be detected and monitored.

For these studies, different 8-mer oligonucleotides, e.g. 5'-TCCGGTCC-3' and 5'-TCCTGTCC-3', are incubated with cisplatin under physiological conditions and the reaction products are monitored via ³¹P and ¹⁹⁵Pt with the GE-ICP-MS system. It is well known that the preferred binding site of cisplatin to DNA is a GG sequence, which can be verified in this study. Additionally, intermediate adducts can be monitored. The use of ESI-MS as a complementary mass spectrometric method could identify the cisplatin DNA adducts.

ThPo69. PROVENANCE DETERMINATION OF METALLIC OBJECTS FROM THE ARCHAEOLOGICAL SITE ED-DUR (UMM AL-QAIWAIN, U.A.E.) BY MEANS OF LEAD ISOTOPE RATIO ANALYSIS USING SINGLE COLLECTOR – ICP – DYNAMIC REACTION CELL – MASS SPECTROMETRY

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Ed-Dur is a large coastal archaeological site on the Arabian side of the Persian Gulf. The main occupation phase at this site dates from the 1st century BC until the 2nd century AD. International sea-trade between the Roman Empire and the Indian sub-continent peaked during this period and the many imported products (Roman glass-work, Indian ceramics, Parthian coins,...) excavated at ed-Dur show that also this region was involved in the trade system.

In this work, several metallic objects from ed-Dur with a lead content ranging from trace up to main element level (local coins made from copper/silver alloys, copper base alloy objects and lead fragments), have been subjected to lead isotope ratio analysis. The results were compared

³ J. Szpunar: *Analyst* (2005) **130**, 442-465

⁴ J.L. Nielsen, A. Abildtrup, J. Christensen, P. Watson, A. Cox, C.W. McLeod: *Spectrochim. Acta* (1998) **53B**, 339-345

⁵ M. Wind, I. Feldmann, N. Jakubowski, W.D. Lehmann: *Electrophoresis* (2003) **24**, 1276-1280

⁶ W. Bröchert, J. Bettmer: *Anal. Chem.* (2005) **77**, 5072-5075

to an extended database concerning lead isotopic compositions from mines and objects from all over the old world, in order to determine the provenance of the investigated objects. This study will help to obtain insight into trade relations in the region at that time, and is useful to reconstruct commercial routes in the past.

After complete sample digestion with quantitative lead recovery, lead was isolated quantitatively or purified using an extraction chromatographic separation based on a lead selective crown ether (Pb specTM, Eichrom Technologies Inc.). Isotope ratio measurements were carried out using a Perkin Elmer SCIEX Elan DRC*plus*. The results will be presented, along with conclusions about the provenance of the investigated objects.

ThPo70. PLAYING WITH IRON ISOTOPES TO OBTAIN ANALYTICAL INFORMATION OF CLINICAL RELEVANCE IN SERA SAMPLES

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Carbohydrate deficient transferrin (CDT) measurements are considered a reliable marker for chronic alcohol consumption and its use is becoming extensive in forensic medicine. However, CDT is not a single molecular entity but refers to a group of sialic acid-deficient transferrin isoforms from mono to tri-sialotransferrin. Thus, the development of methods to analyze accurately and precisely individual transferrin isoforms in biological fluids such as serum is of increasing importance.

The present work illustrates the use of ICP-MS isotope dilution analysis for the quantification of transferrin isoforms once saturated with iron and separated by anion exchange chromatography (Mono Q 5/50) using a mobile phase consisting of a gradient of ammonium acetate (0 to 250 mM) in 25 mM Tris-acetic acid (pH= 6.5). Species-specific and species unspecific spike have been explored. Also, we have investigated the use of enriched ⁵⁷Fe as tracer to study how much natural Fe was presented initially in each isoform by using Isotope Pattern Deconvolution Mass Spectrometry. The aim of this study is to calculate total iron binding capacity (TIBC), unsaturated iron binding capacity (UIBC) and serum iron by Isotope Dilution Analysis.

In the first part of the study, the use of post-column addition of a solution of 200 ng mL⁻¹ of isotopically labeled iron (⁵⁷Fe, 95%) in 25 mM sodium citrate/citric acid (pH=4) permitted the quantification of individual sialo-forms of transferrin (from S₂ to S₅) in human serum samples of healthy individuals as well as alcoholic patients. Secondly, the use of a species-specific-spike method was performed by synthesizing an isotopically labeled standard of saturated transferrin (saturated with ⁵⁷Fe). The characterization of the spike was performed by reverse isotope dilution analysis (this is, by post-column addition of a solution of 200 ng mL⁻¹ of natural iron in sodium citrate/citric acid of pH=4). Also the stability of the transferrin spike was tested during one week with negligible species transformation. Finally, the enriched transferrin was used to quantify the individual isoforms in the same sera samples obtaining comparative results to those of post-column isotope dilution and to those previously published in the literature, demonstrating the suitability of both strategies for quantitative transferrin isoforms determination in real samples.

ThPo71. MEASUREMENT OF STRONTIUM ISOTOPE RATIOS BY ON-LINE Rb-Sr ION CHROMATOGRAPHY SEPARATION COUPLED TO MC-ICP-MS

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Strontium isotope ratios have been widely employed for Rb-Sr dating and as tracer for provenance studies in many geological, archaeological and authenticity studies.

High precise isotope ratio measurements are required for the measurement of Sr isotope variations in nature. TIMS and MC-ICP-MS analysis often require a previous Sr separation from sample matrix due to the spectral interference of ^{87}Rb on the ^{87}Sr signal. This separation has been traditionally achieved using ion-exchange resins resulting in tedious and time-consuming off-line procedures. The on-line coupling of a separation technique to the MC-ICP-MS instrument has been attempted providing short transient signals that lead to lower precision measurements compared to continuous sample introduction (steady state signal).

In this presentation an on-line procedure for the chromatographic separation of Rb and Sr before MC-ICP-MS measurement of isotope ratios has been developed. Chromatographic separation conditions were optimized so that high sample injection volumes (about 3 mL) and similar composition in the sample solution matrix and the HPLC eluent lead to flat topped transient signals with several minutes of stable plateau. On-line IC-MC-ICP-MS data acquisition during several minutes at the maximum of Sr chromatographic signal provided similar precisions for Sr isotope ratios to continuous sample introduction MC-ICP-MS. Moreover, $^{85}\text{Rb}/^{87}\text{Rb}$ isotope ratio could be measured in the same chromatographic run and this ratio could be employed for internal mass bias correction of Sr isotope ratios.

The developed procedure was applied to the measurement of Sr isotope ratio in ciders from different geographical origin. Similar chromatographic separations for samples and standards were obtained by addition of an excess of 18-crown-6 ether in samples and eluent. Sample preparation consisted of a simple 1:10 dilution of the cider samples after adding HNO_3 and 18-crown-6 ether to obtain similar concentration in the sample solution and the HPLC eluent. Minor sample pretreatment and relatively short times of analysis (15 min for the on-line determination) allowed high sample throughput. This procedure may be also applied for high precision strontium isotope ratio measurement in acid sample solutions resulting from acid digestion of solid or liquid samples

ThPo72. INITIAL STUDIES ON ISOELECTRIC FOCUSING GEL ELECTROPHORESIS COUPLED ONLINE TO ICP-MS

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Gel electrophoresis (GE) has shown to be a powerful separation technique for biopolymers. Its variety of separation mechanisms includes isoelectric focussing (IEF) which is regularly applied as the first separation step for proteins during two-dimensional GE. The aim of this work is to combine the separation efficiency of IEF and the excellent detection capabilities of ICP-MS for the analysis of proteins.

In this study we present the set-up and initial results of IEF-GE coupled online to ICP-MS. In order to separate common proteins a pH-gradient (e.g. pH range 4 - 10) is stabilised between the electrodes with the aid of ampholytes. After sample injection IEF allows the protein separation in terms of their isoelectric points. As second step the elution from the gel is necessary. This can be realised by changing the electrode buffer to a lower pH. As a result the proteins can be eluted with decreasing isoelectric points. Finally, the detection of the separated biopolymers is carried out via $^{32}\text{S}/^{34}\text{S}$ and in the case of phosphorylated proteins via ^{31}P using the ELEMENT 2 in the medium resolution mode ($m/\Delta m = 4,000$).

ThPo73. APPLICATION OF SPECIES-SPECIFIC ISOTOPIC DILUTION ANALYSIS ON THE CORRECTION OF SELENOMETHIONINE OXIDATION IN Se-ENRICHED YEAST SAMPLE EXTRACTS

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The inherent difficulties to provide accurate results on Se methionine and other Se species in complex matrices such as yeast are very well known.

In this presentation we provide information on the determination of selenomethionine content by specific Se-species Isotopic Dilution Analysis (IDA) in a selenium enriched yeast reference material. The advantages of this specific species mode were exploited on the correction of selenomethionine oxidation on hydrolysed yeast extracts. Enzymatic hydrolysis were performed under two different conditions: by using ultrasound probe sonication and incubating at 37⁰C during 24 hours. [⁷⁶Se]SeMet isotopically labelled spike was added to the sample after extraction, and ⁸⁰Se/⁷⁶Se and ⁷⁸Se/⁷⁶Se isotope ratios were measured as peak area ratios after HPLC-ICP-MS. In order to evaluate Se-species stability, the obtained extracts, using enzymatic hidrolisis by both USP and control temperaure bath, were splited in several fractions. One was immediately analysed, meanwhile other portions were stored for 24 hours at different temperatures (4, 25 and -20⁰C). Selenomethionine oxidation process showed a strong dependence with the extraction method used and the storage temperature. In general, the degree of SeMet transformation into SeMetO on extracts obtained by probe sonication were more remarcable that in those obtained at control temperature. This interconversion provides erroneous results on selenomethionine content. However, since natural selenomethionine and [⁷⁶Se]SeMet spike are degraded in the same extent, determination of initial SeMet concentration on the extracts was not affected by this transformation.

In this presentation we will illustrate and discussed the advantages provided by the specific species isotopic dilution analysis on selenium speciation in this kind of matrix.

ThPo74. INVESTIGATION OF ISOTOPE FRACTIONATION AND COMPOSITION VARIATION EFFECT IN DEFORMED DOUBLE CHAMBER HUNTING MUNITION BY ICP-MS

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Twin-core projectiles belong to the recent generation of high performance cartridge hunting munitions. They usually consist of two lead cores with different hardness coated by a Tombak or steel jacket. Sometimes the harder tail core has an additional tough jacket separating it from the softer tip core. The core weight ratio is mostly 50:50. A tail groove at the rear end of the projectile reliably bonds the tail core with the external jacket. The shooting velocity as an important ballistic characteristic of projectiles is relatively high and varies for twin-core types between 800 and 900 m/s at shooting start with an average decrease by 10- 15 m/s.

Due to friction and collision energy the lead is exposed to relatively high temperature which can reach even melting temperature. Thus, transformations or enrichment effects are suspected which could effect or change composition in fragments and residuals. In this study, trace element patterns and lead isotope ratios have been compared for new and fired projectiles of the same munitions type and the same manufacturing lot. Sample preparation

using acid digestion and analysis using ICP-MS have been developed especially for this task. The results should enlighten if isotope fractionation or composition variation occur due to melting processes during shooting or collision.

ThPo75. COUPLING OF GC AND LC TO MULTICollectOR ICPMS TO DETECT ISOTOPIC VARIATIONS IN COMPLEX MIXTURES

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Stable isotopes, such as C, N and O are successfully used as classical environmental tracers. During the last few years, heavy stable isotopes are getting more and more attention as tracers and proxies in biogeochemical and environmental studies. Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) has enabled scientists to obtain high precision isotopic analyses of heavy stable elements such as S, Cl, Ca, Fe, Cu, Zn, Hg and Pb. These isotopic systems can be used as important tracers in studying metal contaminants, biomedical processes and pollution of aquatic environments.

The advantage of the ICP source is that it can ionize all elements with very high sensitivity. Various separation technologies can be combined with mass spectrometry, like gas chromatography (GC) and liquid chromatography (LC) to analyze isotopic variations in complex biomedical, biogeochemical and environmental samples. These chromatographic techniques separate complex matrices into their constituents and the elemental species of interest. Additionally, these techniques allow the analysis of small samples (down to a few ng) and since these are on-line techniques, the amount of sample preparation is significantly reduced. This study discusses applications of GC- and LC-coupling to the NEPTUNE MC-ICPMS.

ThPo76. COMPLEMENTARY SPECIATION OF OXALIPLATIN IN HUMAN URINE

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Among the currently approved cancerostatic platinum compounds (CPC), Oxaliplatin shows the highest degree of biotransformation. As a matter of fact the origin of unwanted side effects (e.g. neurotoxicity) is possibly linked to the metabolization of this drug. Accordingly, investigation of metabolization pattern in human urine is necessary.

We will present first data obtained by complementary speciation strategies using ICP-MS and ESI-MS detection. Novel rapid separation schemes employing sub 2 µm – particles will be presented.

ThPo77. DETERMINATION OF PLATINUM GROUP ELEMENTS IN ENVIRONMENTAL MATERIALS BY ISOTOPE DILUTION ICP-MS USING ON-LINE MATRIX SEPARATION

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The increased use of platinum group elements (PGE) in automobile catalysts has led to concern over potential environmental and biological accumulation. The contamination of the environment occurs mainly in the form of dust from the abrasion of the catalysts.

Soils and Grass were collected from roadside near a highway located close to a PGE bearing serpentinite mine (Kraubath, Styria). The samples were spiked with enriched isotopes and digested in a HNO₃/HCl (5+2) acid mixture at 300°C and 125 bar pressure in a high pressure asher (HPA-S, Anton Paar) for 8 hours. The PGEs were then measured with an ICP-MS (HP4500) after a simple on-line matrix removal. Through this technique it is possible to monitor in every sample the isotopes of the analytes as well as of those elements that cause isobaric interferences or that potentially cause interferences through molecular species. The concentrations were determined via the isotope ratio through isotope dilution and external calibration (Rh).

The results indicate that the PGE concentrations in roadside soils and grass are directly influenced by coarse grained traffic condition and not by PGE dust from the mine. The PGEs concentrations ranged between 0.1-6.3 Rh, 0.8-6.7 Pd and 1.1-35 ng/g Pt. Since the site was sampled in 2002 and 2005 it was possible to detect a significant increase of Pt and Rh due to automobile traffic in roadside soils.

ThPo78 LASER ABLATION ICP OPTICAL EMISSION SPECTROMETRY ANALYSIS OF SEMICONDUCTOR COMPONENTS AS SPECIFIED BY WEEE AND ROHS COMPLIANCE

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Starting in August 2005, companies selling a broad range of electrical goods in Europe will need to conform to WEEE (Waste Electrical and Electronic Equipment Directive) and as of July 2006, those same companies will also need to conform to RoHS (Restriction of use of certain Hazardous Substances Directive).

The WEEE and RoHS Directive 2002/95/EC are having an enormous impact on anyone who produces or distributes electronics or electrical goods. Manufacturers of products from computers to IT equipment to clock radios to toasters could find themselves banned from selling their products in the European Market if they do not comply with these new directives by the specific dates.

From 1 July 2006, new electrical and electronic products that contain more than the agreed levels of lead, cadmium, mercury, hexavalent chromium (or chromium IV), polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants will be banned from the EU. A wide range of goods is affected, from computers and telecommunications equipment, to domestic appliances and electronic tools, toys and automatic dispensers. Recent improvements in both optical spectrometer technology and laser ablation system design have helped to improve accuracy and precision. We will be presenting data describing a Laser Ablation ICP Optical Emission Spectrometry (LA-ICP-OES) technique for the analysis of Pb, Cd, Hg and Cr, in various semiconductor components integrating a large spot, ultraviolet, Nd: YAG laser ablation system with a simultaneous ICP-OES, incorporating a large format detector. This solid sampling technique has a number of advantages over traditional dissolution techniques. These include, but are not limited to, high sample throughput and the elimination of additional mixed waste typically generated by aqueous analysis methods. Both bulk and microstructure chemical analysis will be performed and the data presented.

ThPo79 THE DETERMINATION OF HALOGENS BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY IN ULTRALOW UV WAVELENGTH RANGE

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Interest in determining halogens, along with other elements more commonly measured by ICP-OES, has grown significantly in the last ten years. The most sensitive emission wavelengths for the halogen elements are below 160 nm, a region which presents different challenges in optical design from most commercial plasma spectrometers to achieve good light transmission and signal detection.

Results for halogens and other elements for several matrices will be shown. Elements determined will demonstrate performance across a wavelength range of 134 – 900 nm.

Instrumental figures of merit including optical configuration, wavelength coverage and resolution will be presented. Optimal plasma operating conditions, wavelength selection and background correction will be discussed.