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ABSTRACTS

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- Solid State Methods: Laser Ablation and Related Applications

and

KN 05

THE IMPORTANCE OF AEROSOL TRANSPORT IN LASER ABLATION-INDUCTIVELY COUPLED PLASMA –MASS SPECTROMETRY

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The capabilities of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) have been significantly improved within the last couple of years and the increasing number of applications demonstrate its importance for elemental analysis and isotope ratio determinations in geology, material science, forensics or gemology.

Besides the success of this technique, a number of processes are still unknown, which includes the transport efficiency of aerosols, the vaporization and ionization properties of particles within the ICP and the ion extraction yield into the MS. All these parameters have a significant influence on non-matrix matched calibration capabilities, precision, accuracy and limits of detection.

This presentation will focus on aerosol formation and aerosol distribution when using femtosecond and nanosecond laser ablation for aerosol generation. In collaboration with ISAS in Dortmund, aerosol extraction and transportation efficiencies and preliminary results addressing mass balance in LA-ICP-MS will be presented.

In addition, mass load induced matrix effects have been previously reported for a single glass matrix using single hole drilling. These studies were extended to scanning/raster ablation, where the amount of material and the particle size distribution remain more constant over time. Mass load effects for these two types of sampling will be compared. Furthermore, the role of the gas composition of the plasma to reduce the degree of such matrix effects will also be discussed.

Tu01

DETECTION OF TRACE IMPURITIES IN CIGS-SOLAR CELLS BY LASER-ABLATION-ICP-MS

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With the increasing world-wide demand for energy, conventional energy sources running short and the limited capacity of the ecosystem for greenhouse gases photovoltaics is widely regarded as one of the key technologies for future power generation. Currently over 85 percent of the current production of solar cells base on silicium technology. However, due to limited silicium resources and thus increasing prices thin film solar cells have gained considerable attention. Their functional layers are only a few microns thick, which combines lower weight with potentially lower manufacturing costs. Among thin film cells those based on $Cu_{1-x}(In,Ga)_xSe_2$ absorbers yield the highest efficiencies with 19,2%. A novel approach utilizes substrates made of flexible and light fibre glass fabrics rather than rigid and comparably heavy glass substrates, which allows the utilization in several new applications such as the installation on curved walls and less sturdy roofs, for example on sheeted storage halls. The extreme waviness of this material however requires an additional layer of varnish to reduce the surface roughness and ensure homogenous thicknesses of the functional layers.

This varnish layer however bears the risk of introducing possible contaminants into the CIGS-layer by diffusion. As the efficiency of the solar cell depends largely on the purity and stoichiometry of the absorber layer, investigation of possible contaminants with analytical techniques providing sufficient sensitivity is crucial.

We employed Laser-Ablation-ICP-MS in depth-profiling mode to investigate the elemental composition of the CIGS-layer. Due to its high sensitivity this technique is suitable for the analysis of trace elements in sub-ppm concentrations. The depth resolution proved to be sufficient to distinguish the individual layers and determine the distribution of the varnish elements. Migration of several elements into the molybdenum electrode layer was demonstrated, which proved to be an efficient diffusion barrier, as these elements were not detected within the absorber layer. Additionally, in-depth variations of the CIGS-stoichiometry could be shown, which provides vital information about the deposition process. Solid state spectroscopy techniques like electron probe microanalysis, micro-X-ray fluorescence (micro-XRF) and proton-induced-X-ray-emission (PIXE) were used to validate the results.

Tu02

MASS TRANSPORT EFFICIENCY IN FEMTOSECOND-LA-ICP-MS APPLYING ABLATION CELLS FOR BULK AND SINGLE-SHOT ANALYSES

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Relative mass transport efficiencies of near infrared femtosecond (fs) laser generated aerosols in helium have been measured applying ICP-MS and different ablation cells with short and long washout times. Within the mutual experimental uncertainties, the transport efficiencies were found to be *independent* of the cells used. This was confirmed by measurements of the absolute transport efficiencies of fs-LA in helium. Here, the transport efficiency was determined by weighing the samples before and after ablation with a micro-balance, collecting the particles by low-pressure impaction, and evaluating the impacted masses by total reflection X-ray fluorescence. Within the experimental uncertainties, the same absolute transport efficiency (near to 80 %) was found for all cells applied. This efficiency value can be regarded as a *lower limit of the absolute mass transport efficiency in fs-LA-ICP-MS* since particle losses in the impactor system were difficult to quantify.

The present paper also presents ablation cells for bulk and single-shot analysis. E.g., long particle wash-out times are obtained if nozzles at the gas inlet creating strong turbulent flows. This improves the signal statistics and averages over sample inhomogeneities in bulk analysis because the particles from successive shots are accumulated and mixed in the ablation cell. On the other hand, particle wash-out times are very short if the laser directly ablates into the transport tube. An ablation arrangement will be presented which is particularly suited for single shot analyses. It maintains spatial analytical information from the sample from shot to shot without decreasing the pulse frequency to an unacceptable level. The sampling tube cell should be applied, for example, in microanalysis, depth profiling, and 2-dimensional imaging applying LA-ICP-MS.

Tu03

HIGH PRECISION ISOTOPIC ANALYSIS BY LA-MC-ICP-MS: THE ROLE OF ULTRA SHORT PULSE WIDTH (Fs) LASERS.

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LA-MC-ICP-MS shows great promise for expanding the role of in-situ isotopic studies of natural materials and allowing high spatial resolution analyses with precision and accuracy

approaching TIMS methods. To achieve high precision and accuracy with LA-MC-ICP-MS requires the ability to consistently control mass bias and chemical fractionation in the ablation, transport and analysis of the sample and simultaneously to create the large ion beams in the MC-ICP-MS, required for high precision analyses with Faraday detectors.

Ultra short pulse width (Fs) lasers have been shown to minimize fractionation during ablation and produce the uniform and small particle size distributions required for high transport efficiencies and efficient and quantitative atomization and ionization in the ICP. To create large ion beams requires high laser power to ensure that the energy density over a significant area of the sample surface is well above the ablation threshold. We utilize the Quantronix Integra C$^{®}$ Fs laser at both the fundamental (785 nm) and 2nd Harmonic (393 nm) wavelengths to investigate sampling efficiencies and mass bias issues in the production of high precision Sr isotopic analyses of Ca-rich natural materials (otoliths, bones, teeth). Preliminary results indicate that mass fractionation corrections for complete in-situ analyses are very similar to solution nebulization analyses of pure solutions and with comparable precisions on the isotopic ratios.

Tu04

ELEMENTAL RESPONSE IN LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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The influence of the individual operating parameters of the ICP-ion source on ion signals obtained with laser ablation sampling has been studied in detail.

Sample aerosols that contain a significant fraction of large particles are prone to incomplete vaporization within the ICP leading to sample-dependent variations in the respective ion yields and systematic errors during quantification.

Addition of helium to the ICP did not affect the estimated plasma temperatures in a similar fashion as argon. Comparing helium and argon as carrier gases, the addition of 0.3 L/min of helium causes a similar change in plasma temperatures as 0.1 L/min of argon. Furthermore there is evidence for increased diffusion rates of vaporized material in the ICP and away from the particle surface when helium is used. The mass bias of the ICPMS is thus not only affected by processes in the vacuum interface and ion optics but also related to element and mass dependent diffusion rates in the ion source directly.

These results indicate that elemental fractionation in LA-ICPMS is not related to the ablation process(es) alone but also caused by element-specific and matrix dependent effects like vaporization efficiency, diffusion and ionization within the ICP.

KN 06

LASER ABLATION AND SAMPLE TRANSPORT: THE HEARTBEAT AND BLOOD CIRCUIT OF LA-ICPMS

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In this talk, we will present an overview of our modeling efforts for laser ablation, as sample introduction method for ICP spectrometry. Different aspects of the laser ablation process, starting from laser heating, melting and vaporization, over plume expansion and plasma formation, until laser ablated aerosol evacuation out of the ablation cell and transport towards the ICP, will be highlighted.

The laser solid interaction is treated with a thermal conduction model, which describes the target heating, melting and vaporization. Results are, among others, the temperature distribution inside the target, the melt depth and the evaporation rate.

Based on the evaporation rate, the expansion of the evaporated plume in a background gas, is simulated with fluid dynamics, i.e. partial differential equations describing conservation of total mass, momentum and energy, as well as conservation of metal vapor mass in the background gas. This model is applied to a range of different metals (i.e., Cu, Fe, Al, Zn, Mo and Mn) and background gases (i.e., He, Ne, Ar, Kr, Xe, N_2). Typical results include the density spatial profiles of metal vapor and background gas, the plume velocity and temperature.

Because of the high plume temperature, a plasma will be formed. This plasma can be considered in local thermal equilibrium (LTE) so that the ionization degree is calculated with the Saha equation. Hence, beside the total density of metal vapor and background gas, also the number densities of individual metal and background gas ions and atoms, as well as the electron number densities, are obtained. Moreover, the laser beam interaction with the plasma is also calculated, based on inverse Bremsstrahuling and photo-ionization. This plasma absorption, or plasma shielding, yields a much lower laser intensity reaching the target, compared to the original laser intensity.

Beside the processes taking place during and immediately after the laser solid interaction, we have also studied the behavior of the laser ablated aerosol. Both the evacuation of the aerosol out of the laser ablation cell, and the transport through the transport tube towards the ICP, are modeled with a computational fluid dynamics program, FLUENT. Various cell designs and tube configurations have been evaluated, in order to predict the most efficient setup.

Tu05

INFLUENCE OF LASER WAVELENGTH AND LASER PULSE DURATION ON PARTICLE SIZE DISTRIBUTIONS

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The understanding and modelling of particle production mechanism is crucial for the improvement of laser-based analytical techniques as laser-induced breakdown spectroscopy (LIBS) or laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Very early it has been recognized that particles constitute the link between ICP and laser ablation. They form the material that is transported and subsequently evaporated in the ICP. It is also clear that their chemical composition, form, morphology, and size influence transportability and response to the ICP. Therefore, the generation of an appropriate aerosol with regard to a specific detection system (i.e., transport, evaporation, excitation/ ionization) has significant impact on the total analytical method. The question arises how aerosol conditioning can be accomplished and how laser parameters like energy, wavelength and pulse duration influences the particle size distributions. In addition, the surrounding atmosphere has also some impact.

This presentation is aimed to answer these questions. Experimental results will be compared with theoretical considerations to establish a relation between accessible laser parameters, given sample properties and desired analytical performance. In terms of these relations the versatility of different laser systems is discussed.

Tu06

COMPARISON OF EFFICIENCY AND PERFORMANCE OF LASER ABLATION SYSTEMS - WHICH SYSTEM FOR WHICH APPLICATION?

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Laser Ablation ICP-MS has come a long way since its introduction in the mid-eighties. Whereas the first generation of laser systems used infrared lasers - mainly the fundamental wavelength of an Nd:YAG laser (1064 nm) - modern systems are using UV-lasers at different wavelengths. Most common commercial systems are using 266 nm, 213 nm or 193 nm. Laser energy in the deeper UV is more efficient at delivering the laser energy to a wider variety of samples, allowing uniform sampling of even transparent materials. However, a system designed to deliver 193 nm is more expensive than laser systems based on 213 nm or 266 nm making the choice of the right laser system for the anticipated applications important. This talk will compare laser systems with different wavelengths and energy-outputs and will discuss the suitability for different applications and sample-types, such as metals, industrial materials, plastics, biological materials as well as geological applications.

The first laser system investigated uses a high power laser operating at 266 nm. The LSX-500 delivers a > 9 mJ, 6 nanosecond laser pulses to produce small particles of uniform dimension from a wide range of sample types. Applications where a high power 266nm-system is well suited are metals (ferrous and nonferrous, steels, aerospace alloys, precious metals, semiconductor and pressed metal powders), plastics, soils and other opaque solids as well as biological materials such as tissues, bones and teeth.

Operating at the shorter wavelength of 213 nm is the LSX-213 Laser Ablation system. It is optimised to deliver homogenized "flat-top" energy profile with > 4mJ, 5 ns laser pulses with repetition rates of 1-20 Hz. The use of Helium as a carrier gas improves sample transport efficiency and reduces fractionation. The 213 nm wavelength is better suited than 266 nm for ablating hard and transparent solids, such as gemstones, calcite, fluorite, natural and synthetic quartz and other transparent materials. It finds its application in the analysis of several types of geological samples. Other application areas are forensic glass, plastic analysis, and ceramic analysis.

For the most challenging and highly transparent samples it may be necessary to use even shorter wavelengths, such as 193 nm. The concept of an excimer-laser based system the GeoLas Pro is discussed with particular applications in Geochemistry. Due to its high energy density of up to 45J/cm² at 193 nm and its homogenized beam profile, the GeoLas Pro has advantages for very precise Geochronology and fluid inclusion analysis, especially for very small craters down to 4 μm in diameter. The use of a petrographic microscope enables the identification of even very small features of a few micrometers. Features and Applications for the GeoLas Pro are discussed.

Tu07
LASER-INDUCED PLASMAS FROM METALLIC SAMPLES INVESTIGATED USING TIME-OF-FLIGHT SPECTROMETRY AND SIMULATIONS.

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Laser-induced plasmas (LIP) have both *laser*-specific and *sample*-specific characteristics that are transient and rapidly decaying in the very first ns of plasma evolution. Time-of-flight (TOF) spectrometry is a non-invasive technique, which allows studying LIP characteristics in an angle-resolved way (2D distributions) based on the early stage plasma conditions. Metals were ablated using a KrF excimer laser at 1.3 GW/cm².

Experimentally obtained Maxwell-Boltzmann ion velocity distributions could be derived theoretically in the framework of a collisional model, with formation of a layer of translational instability above the sample surface, called Knudsen layer (KL).

Within the KL, with thickness around 10 μm (apart for the case of Al which showed different characteristics from the other metals) the ablated ions exchange energy by means of collisions until a condition of translational equilibrium is attained, with formation of a plume *drift velocity*. This complicates the extraction of temperatures from the TOF signals. The obtained plume temperatures are significantly higher that those reported using traditional optical spectroscopy approaches, in the range 4 – 25 eV depending on the ablated sample, and can be considered as *truly initial*.

The plasma angular spreads were found to be an element-dependent function in the range 16°- 37° from the normal (e.g., smaller for Fe, higher for Al). This suggests that *(i)* laser-induced plumes are in the transient state of plasma for a few ns, which is too short to be highlighted with spectroscopic techniques; *(ii)* the ablation of ions from the surface is highly collimated, though the 2D spread is a function of element; *(iii)* the LIP temperature is discontinuous to the sample surface temperature; *(iv)* the treatment of LIP with fluid models can be questionable for certain elements like Al due to the weak particle-particle coupling.

Tu08

CALIBRATION OF LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY USING ABSORPTION COEFFICIENT MODIFIED PRESSED POWDERS

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Recent work in this laboratory has focused on establishing fit-for-purpose calibration strategies for LA-ICP-MS that can be used in a routine environment where perfectly matrix matched solid standards and internal standards might not be available. To this end we have investigated the use of highly absorbing chromophores, e.g. those used in MALDI-MS, with which the powdered samples are pressed (10 ton KBr press) to form 13 mm disks. Chromophores such as vanillic acid, used for 213 nm laser radiation, form very stable disks that ablate to give clean tracks or craters. It has been demonstrated that the highly absorbing chromophore dominates the absorption process providing matrix matching in terms of absorptivity and constant mass flow to the plasma. Thus external calibration with non-matched standards provided recoveries that are close to 100% for a variety of reference materials with precisions of the order of 10%. Unlike non-absorbing binders, the chromophore enhances signal strength by providing greater energy density in the sample leading to smaller particles with better transport and processing. Data employing isotope dilution calibration will also be presented.

KN 07

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY: A VERSATILE TOOL FOR DETECTION OF HETERO-ELEMENTS IN PROTEINS

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For the detection of metal and hetero-element concentrations in proteins increasingly ICP-MS is applied as a sensitive multi-element detector. The interest in such studies is rapidly growing so that even a new discipline of "metallomics" and hetero-element tagging is already

established. In most of the related studies in literature on-line coupling with various separation techniques has been applied to pre-fractionate the complex biological or medical sample and to identify the protein of interest by use of standards or antibodies if available. A quite new technology in proteomics, first applied by Cameron Mc Leod´s group, is the application of laser ablation for sample introduction into an ICP-MS and measurement of the metal content of proteins in one or two dimensional separations.

We are using ICP-MS for detection of metallo-proteins and plan to determine their post-translational modification by application of various techniques all based on ICP-MS detection. For this purpose we have developed and characterised a new laser ablation system for sample introduction into ICP-MS to measure hetero-elements directly in protein spots. The proteins of interest are separated by sodium dodecyl polyacrylamide gel electrophoresis. Protein spots are either directly detected in the gel or after blotting onto a membrane. Different membrane materials will be compared concerning best signal to noise ratios.
 Recently, we also have developed new technologies for labelling, tagging and staining of proteins. By these new technologies we can make all proteins detectable by ICP-MS even if they do not contain a useful hetero-element for ICP-MS detection. Different quantification schemes will be discussed. Examples will be shown where we have applied the new technology for investigations of iron-chelating proteins and in particular cytochromes.

Tu09
 IDENTIFICATION AND CHARACTERISATION OF METALLOPROTEINS SEPARATED BY NON-DENATURATING GEL ELECTROPHORESIS USING A COMBINATION OF LA-ICP-MS AND MALDI/ESI-MS

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The identification and structure determination of proteins, including the determination of post-translational modifications such as glycosylation, fatty acylation and phosphorylation, is a challenging task in analytical chemistry. Besides the structure analysis of proteins by MALDI- or ESI-MS (matrix assisted laser desorption ionization or electrospray ionisation mass spectrometry) the quantitative determination of selenium and metal concentration (e.g, of Fe, Cu, Zn) in tissues and fluids is required. The combination of atomic and molecular mass spectrometric methods was developed for the characterization and identification of several metalloproteins.

Rat tissue protein mixtures were separated non-denaturating gel electrophoresis and the protein bands/spots were fast screened by microlocal analysis using LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) in respect to several elements, such as S, Se Cu, Zn and Fe. Selected protein bands/spots in the non-denaturating gels containing these elements were identified after tryptic digestion by MALDI/ESI-MS. Results of structure analysis of proteins by MALDI/ESI-MS were combined with those of the direct element determination in protein spots with LA-ICP-MS in order to characterize proteins in respect to their structure, sequence, selenium state and metal content as well.

IMAGING LA-ICP-MS AND IT'S APPLICATION IN BRAIN RESEARCH

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Determination of elements concentration as well as their distribution (imaging) in different kind of biological tissues (e.g. brain, liver, etc) is a challenging task in analytical chemistry and is of interest in different areas of biological research. Of particular interest, nowadays, is the characterization of element distribution in different regions of the brain samples (e.g. hippocampus, cortex, *etc*) as well as analysis of brain cancer tissues (Glioblastoma Multiforme [GBM] [1]).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [2] was used to produce images of element distribution in 20 μm thin sections of brain tissues. The different regions of the brain were analyzed. The sample surface was scanned (raster area ~1 cm^2) with a focused laser beam (wavelength 266 nm, diameter of laser crater 50 μm, and laser power density 1×10^9 W cm^{-2}). In order to study reproducibility of the method the 5 neighboring cross section (20 μm thickness) of the same region of human brain tissue were measured and compared in respect to the $^{13}C^+$, $^{63}Cu^+$ and $^{64}Zn^+$ distributions. The accuracy and the precision of these measurements were evaluated.

Furthermore, the quantitative determination of copper and zinc distribution in thin slices of the measured tissues was performed using matrix matched laboratory standards. The comparison of element distribution images as well as the concentration of selected elements between the control and affected with the GBM tissues will be also discussed.

[1]   P. Kleihues, D.N. Louis, B.W. Scheithauer, L.B. Rorke, G. Reifenberger, P. Burger, W.K. Cavenee, J. Neropathol. Exp. Neurol., 61 (2002) 215.

[2]   J.S. Becker, J. Anal. At. Spectrom., 17 (2002) 1172.

MONITORING THE CELL SIGNALING EVENTS USING ICP-MS

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In recent years inductively coupled plasma mass spectrometry (ICP-MS) has often been used for biological applications especially for determining the phosphorylation status of proteins. For this purpose it has been coupled to laser ablation (LA) to detect hetero-elements on membranes or directly on 1D and 2D polyacrylamide gels. We have explored here the possibility of determining one of the cell signaling processes, phosphorylation using LA-ICP-MS for detection of proteins blotted onto nitrocellulose membranes.

We focus on the phosphorylation of proteins in the human urothelial carcinoma cell line 5637 after treatment with epidermal growth factor (EGF) and hydrogen peroxide. EGF stimulates phosphorylation of its receptor and in turn activates a cascade of cytoplasmic protein kinases which phosphorylate several transcription factors and down-stream cell cycle regulators controlling G1/S transition. Hydrogen peroxide is used to see the variable protein expression under oxidative stress conditions. The treated cell cultures then will be analyzed to identify differences in their phosphorylated protein status.

Proteins of treated and control cell culture samples are separated by SDS PAGE and detected by staining and blotting techniques. We use LA-ICP-MS for detection of phosphorylated proteins. For this purpose a new LA cell has been designed specifically for detection of hetero-elements on membranes. The optimization of the laser ablation hyphenated to ICP-MS

for this specific approach will be discussed. The phosphorus signal pattern of treated cell culture samples will be compared with that of non-treated control cells. A calibration strategy to quantify the phosphorylated proteins will be presented. To validate our results two different approaches will be compared; phosphatase treatment and immuno-blotting using monoclonal antibodies which specifically react with the phosphorylated forms of particular proteins. The presence of phosphorylated residues in a protein can be obtained from altered gel mobility after incubation of the protein with a phosphatase in the first approach. In the second approach an immunoblot which could show signals for a set of primary antibodies targeted against the phospho-serine/threonine residues of the targeted protein will be presented.

Tu12
QUANTIFICATION OF FISSION GASES IN HIGH BURNUP FUEL WITH LASER ABLATION ICP-MS

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Approximately 20% of all fission products in nuclear fuel for power plants are gaseous. Most important gases are Xenon, Krypton and Helium. Upon reaching a burnup of 60-75 GWd/t_{HM}, a so called High Burnup Structure (HBS) is formed within the rim of the fuel. In this region a depletion of the noble fission gases (FG) in the matrix and an enrichment of FG in μm-sized pores can be observed. Calculations show that in these pores the pressure at room temperature can be as large as 30 MPa. The knowledge of the FG pressure in pores is important to understand the high burnup fuel behavior in case of an accident.

With analytical methods routinely used for the characterization of spent nuclear fuel samples, i.e. EPMA, SIMS, the quantification of gaseous inclusions is not straight forward.

The combination of a laser ablation system (LA) with an inductively coupled plasma mass spectrometer (ICP-MS) offers a powerful tool for quantification of the gaseous pore inventory. This method offers the advantages of high spatial resolution with laser spot sizes down to 10 μm, low detection limits and isotope measurement capability. The development of a suitable calibration technique for gases allows the quantification of xenon amounts in the HBS. Two different calibration strategies were evaluated and the analytical performance is compared.

The pressures in the pores can be calculated by using the pore sizes found with scanning electron microscopy (SEM) and the amount of gas released from pores wit LA-ICP-MS.

Pressurized water reactor (PWR) fuel samples with a rod average burnup of 80 and 105 GWd/t_{HM} were investigated applying this technique. The local FG distribution and the pressure in individual inclusions were determined. The quantification approach, the pressure calculation and the results found in the HBS structure will be discussed in detail.

Tu13
APPLICATION OF LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (LA-ICP-MS) FOR THE INVESTIGATION OF ANCIENT SILVER COINS

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During the last ten years, the interest for Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) in the field of archaeometry steadily increased. The relevant results obtained on homogeneous materials, whether siliceous (glass, obsidian) or metallic (such as gold coins) made of LA-ICP-MS a leading method for the analysis of ancient objects. Its application to the heterogeneous materials that are ancient silver coins was not a simple transposition: an original analytical process had to be developed to take into account the specificities of this kind of artefacts.

Ancient silver coins are silver-copper alloys containing five minor elements whose content might reach or exceed 1 % (Zn, Sn, Au, Pb, Bi), and many trace elements that might be helpful for provenance studies. All these elements have to be determined accurately for a reliable numismatic interpretation.

The near surface of the coins does not reflect the composition of the safe alloy: several phenomena such as segregation during the cooling or the hammering of the blanks, and even more the depletion of copper caused by the corrosion after the burying entail a non-negligible silver surface enrichment. The main innovation of the analytical protocol we developed consists in the real-time acquisition of the signal all along the laser ablation, allowing the obtaining of concentration depth profiles for Ag, Cu and the five main minor elements. By this way, the contents rendered by LA-ICP-MS reflect the composition of the inside of the objects that is unaffected by segregation and corrosion phenomena. This constitutes a main improvement as the techniques that have been used until now, either surface methods (XRF, PIXE) or global methods (Fast Neutron Activation Analysis) don't take into account the compositional variations between the surface and the interior of the coins, and might overestimate their silver content.

The number of elements that can be determined by LA-ICP-MS and its low detection limits constitute another advantage. The analytical process we developed involves reference materials whose content is similar to the one of the ancient coins to analyze, and whose reliability has been checked. The calculation of the concentrations is based on the use of an internal standard, in order to correct the fluctuations of the signal.

The results obtained by this way have been compared to the ones rendered by Fast Neutron Activation Analysis, and the good agreement between the two methods confirmed the relevance of the analytical protocol proposed. LA-ICP-MS is nowadays the only method that allows the obtaining of concentration profiles from the surface to the interior in a nearly non-destructive way for ancient silver coins.

Tu14
ICPMS AS A TOOL IN IDENTIFYING THE COUNTRY OF ORIGIN OF TEA AND CANNABIS SAMPLES

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In a forensic situation the aim of the chemist is often to provide information on the likelihood of two samples having the same point of origin (co-provenance) or determining where a sample may have come from (origin). With the increased requirement to identify country of origin of foodstuffs and drugs, the ability to provenance plant materials has gained considerable importance. Consequently, there is significant pressure on the forensic chemist

to develop new analytical and investigational methodology to achieve both provenance and origin identification for plant materials.

This paper details a study into the development of laser ablation and solution ICP-MS protocols, to be used in association with isotope ratio mass spectrometry data for carbon, hydrogen and nitrogen isotopes, to establish both co-provenance and origin of tea and cannabis samples. Chemometrical analysis was initially undertaken on the data for tea to successfully identify its growing region. Following the successful application of methodology in this area a further application to establish the growing area of cannabis seizures was also successfully undertaken. Having established the uniqueness of spectral-fingerprint data in determining origin of both materials it was also then possible to use this data to establish co-provenance of equivalent material.

Tu15

IMAGING OF PHARMACEUTICALS IN TISSUE VIA LA-ICP-MS AND MALDI-MS

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Over the past few years laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) and matrix-assisted laser desorption ionisation mass spectrometry (MALDI-MS) have been utilised as imaging tools to provide spatially resolved information on elements and molecules in a diverse range of samples. This work explores the use of both techniques for imaging pharmaceuticals in a single tissue sample. Ebselen (a Se containing drug) was selected as a test compound and preliminary analyses via MALDI were shown to be semi-quantitative. Multiple laser interrogations of samples, in both MS and MS/MS modes, allowed detailed molecular information to be acquired. In contrast to MALDI, which is relatively non-destructive, LA-ICP-MS is destructive but yielded full quantitative images of Se. Liver and kidney sections from mice dosed with Ebselen were studied in an attempt to locate and identify Se-containing species. LA-ICP-MS showed elevated Se levels in comparison to control samples, however identification of the Se-species (parent compound, metabolites, elemental Se etc) proved to be problematic. The presentation will address aspects of method development including tissue preparation and laser desorption/ablation strategies for tissue interrogation. Emphasis will also be given to data reduction and image computation procedures. Results indicate the possibility of combining data from both experiments, to provide comprehensive chemical images.

Poster Session Tuesday 20 Feb 2007

TuPo1.   SULFUR ANALYSIS IN FLUID INCLUSIONS BY LASER ABLATION ICP-MS

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Many ore deposits are formed by hydrothermal fluid circulation in large magmatic systems. To investigate the geological processes leading to this metal enrichment, analytical techniques for fluid-inclusion microanalysis are of fundamental importance. This work presents and discusses improvements in fluid inclusion analysis with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The opening of a single quartz hosted inclusion with a laser is delicate due to stress in the mineral and the low absorbance of the laser light even at 193 nm. Therefore, the possibility of cracking resulting in a so called catastrophic ablation is high. An established strategy is to start with a small crater and stepwise increase the crater diameter as shown before by Günther et al.. Our new strategy includes an iris diaphragm with a minimal opening in the range of 0.1 mm (resulting in a minimal crater size of 4 μm) and a continuous opening to the desired crater size.

To characterize hydrothermal fluids, trace elements like Au, Cu, Mo, Fe and main components like Na, K need to be quantified within individual inclusions. The quality of inclusions varies widely, and to analyze very small inclusions in the range of 10 micrometers dedicated optimization procedures on the ICP-MS are inevitable. Several aspects to improve the limits of detection and extend the available size range to smaller inclusions, like polyatomic gas addition to the Helium carrier and the influence of signal dispersion will be discussed.

Sulfur is arguably the most critical chemical element in hydrothermal ore formation, but difficult to measure in microscopic fluid inclusions. Isobaric interferences with O and N-based polyatomic ions, the high first ionization potential and the relatively high gas blank are limiting factors. The use of a double focusing sector field-based ICP-MS is one possibility to separate the polyatomic interferences from the S^+ signals. A limiting factor for inclusion analysis seems to be the surprisingly high sulfur concentration in the range of 100 to 300 μg/g within the host mineral quartz as determined with LA-ICP-MS and EPMA. For sulfur quantification, we used NIST SRM 610 standard reference material and validated the sulfur content therein with Scapolite minerals characterized by electron microprobe. The possibilities and limitations of sulfur determination in fluid inclusions will be discussed in the presentation.

TuPo2. CAPABILITIES OF NON-METRIX MATCHED CALIBRATION FOR RICE SAMPLES USING LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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In this work the capabilities of laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) of quantitative analysis of powder samples using non-matrix matched calibration was studied. Therefore, different powder samples were pressed as pellets without using binder materials. Glass standards and various reference powder samples were quantified and precision and accuracy as well as limits of detection will be reported. Based on this evaluation, optimized parameters were applied to rice powder samples and whole grains. A representative selection of rice samples (different origins, different colors and different types) were analyzed as bulk powders. The "fingerprints" were statistically evaluated (principle component analysis) for the determination of the origin of the samples. Furthermore, local analyses of the grains were carried out to provide information about the element distribution within individual grains.

TuPo3. A SIMPLE LASER ICP-MS CELL WITH WASH-OUT TIME LESS THAN 100 ms.

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More and more analytical applications in biology, geology or material sciences are in demand for better spatial resolution without loss in detection limits. LA-ICP-MS has the potential to accomplish the idea of elemental mass spectrometry imaging. In conventional laser ablation the diameter of the laser spot focused on the sample with a lens is limited by diffraction and therefore by the wavelength of the laser radiation. However, a sub-micrometer size can be reached by near-field (NF) ablation, which is a combination of laser-ablation and AFM (Atomic Force Microscopy) distance control techniques. In this case, the laser radiation is focused into a waveguide which is held several nm above the sample surface by a shear force control loop. The size of the laser spot is defined by the geometry of the waveguide tip. However, the analytical useful spatial resolution is given by the heat affected zone. To minimize this zone and to deliver enough energy to surpass the ablation threshold the application of fs-laser pulses is advantageous.

Here we report our preliminary experiments on the NF-fs-LA-ICP-MS of solid samples. Helium gas flow is used to transport the ablated material to the quadrupole ICP-MS. The size of the crater is controlled by means of an electron microscope.

TuPo4. CHARACTERIZATION OF 213 NM LASER ABLATION-GENERATED AEROSOLS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY AND TOTAL REFLECTION X-RAY-FLUORESCENCE SPECTROMETRY

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become a powerful technique for direct elemental analysis. Nonetheless, it still suffers from elemental fractionation, caused e.g. by boiling point-correlated sequential vaporization of the sample components during the ablation process or during the evaporation of resulting particles within the ICP. This effect can be minimized to some extend by reducing the laser wavelength and/or the duration of the laser pulse, used for the ablation of the sample. Otherwise the achievable accuracy suffers from this effect, which can be compensated for if a calibration strategy is selected, based on the use of standards with virtually identical matrix composition, i.e. matrix-matched calibration.

This study focuses on the characterization of aerosols, generated by 213 nm laser ablation. The aerosol, obtained under varying conditions regarding gas-flow rate, laser energy, type of carrier gas and laser spot size, is directly sampled on quartz plates by a cascade impactor prior to the analysis by total reflection X-ray-fluorescence spectrometry. The influence of the particle size on elemental fractionation will be outlined through the comparison of such data with the certified values of the ablated sample, with data obtained by TXRF and ICP-MS analysis of the digested samples and those data resulting from electron microprobe analysis of the ablation craters and adjacent areas.

TuPo5. VISUALIZATION OF AEROSOL PARTICLES GENERATED BY NEAR INFRARED NANO- AND FEMTOSECOND LASER ABLATION

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Even though the exploratory focus related to laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has recently shifted to the fundamental characteristics of aerosol particles as the actual information carrier less attention has been paid to their expansion dynamics. However, knowledge about the kinetic properties of laser-produced aerosols appears to be crucial for the understanding of processes such as particle dispersion or material losses during the analysis which are assumed to currently restrict the versatility of LA-ICP-MS.

In the present study, the expansion of aerosols generated by near infrared (NIR) nanosecond (ns) and femtosecond (fs) LA of metals at atmospheric pressures is being examined by high-resolution, laser-induced Rayleigh scattering. It could, for instance, be shown that NIR-ns-LA under argon atmosphere provokes the formation of a dense aerosol confined within a radially propagating vortex ring. The expansion dynamics achieved under these conditions was found to be fairly small whereas the degree of aerosol dispersion for NIR-ns-LA using helium drastically increased due to its lower viscosity. The trajectories of aerosol particles generated by NIR-ns-LA using argon could, furthermore, be simulated on the basis of computational fluid dynamics (CFD).

In contrast, NIR-fs-LA generally resulted in extremely dynamic expansion patterns. Our results, moreover, indicate that fs-LA carried out under helium atmosphere favours a chaotic aerosol expansion. Analytical implications concerning, e.g. dispersion phenomena or the choice of the LA protocol and physical dimensions of future ablation cell designs will be discussed.

TuPo6. DETERMINATION OF ARSENIC IN SINGLE STRANDS OF HUMAN HAIR BY LASER ABLATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (LA-ICP-MS)

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Hair is rich with disulfide bonds and sulfhydryl (-SH) functional groups in its keratin structure. These functional groups are sites where trace elements can be complexed. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is ideally suited for the analysis of trace metals in hair since small samples can be used, no digestion is required, and analysis is rapid. Arsenic concentrations in single strands of hair from individuals who were chronically exposed to arsenic contaminated drinking water from a village in the Atacama Desert in Chile were determined by LA-ICP-MS. For the arsenic determination in hair 800 μm long single line scans were more suitable than spot analyses. Applicability of ^{13}C and ^{32}S as internal standards was evaluated. Our experience with hair sample preparation, sample mounting, and optimized laser ablation conditions for LA-ICP-MS analysis of hair will be presented. The sample throughput is high and it takes ~ 3 minutes per each hair sample including mounting, focusing and analysis. They were satisfactorily correlated with total As concentration measured previously by hydride generation (HG)-ICP-MS. This method can be used for the rapid identification and screening of chronically exposed individuals for environmental arsenic.

TuPo7. POSSIBILITIES AND APPLICATIONS OF A DUAL-SOLUTION LOADING PNEUMATIC NEBULIZER IN ICP-OES

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The use of a modified cross-flow pneumatic nebulizer with dual solution loading for ICP-OES was evaluated for several applications. In this nebulizer the liquids from both channels are mixed during the aerosol generation step. It was shown in the determination of Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb to be possible to perform internal standardization and calibration by standard addition in an on-line way to correct for matrix effects induced by 40 mmol.L^{-1} Na, K, Rb and Ba. The calibration by standard addition has also been applied for elemental trace determinations in steel and alumina samples. This nebulizer furthermore could be used for the determination of Hg using the cold vapor technique with $SnCl_2$ or $NaBH_4$ as reductants. The multielement capability of ICP-OES here could be maintained so as to determine other elements simultaneously. The detection limits for Hg were improved by a factor of 20 as compared to conventional pneumatic nebulization and are down to 100 ng.L^{-1}. As a further field of application of this nebulizer, the possibility to directly analyse oil samples applying an on-line calibration by standard addition using aqueous standards will be discussed.

TuPo8. ANALYSIS OF TTHIN PLATINUM LAYERS analysis BY LASER ABLATION ICP-MS

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The life time management of boiling water reactors has to consider intergranular stress corrosion cracking (SCC) of internals and pipings. To mitigate this SCC the water chemistry can be changed in order to lower the electrochemical corrosion potential. This is normally achieved by adding hydrogen or by the NobleChem™ technology. During this process noble metals are added to the feed water of the reactor either offline during annual shutdown (classical NobleChem™, CNC, with Pt and Rh) or during the power production phase (online NobleChem™, OLNC, with only Pt). The added noble metals are deposited on the reactor inner surfaces and act as electrocatalysts that efficiently recombine O_2 and H_2O_2 with H_2 on metal surfaces.

In order to understand the distribution and the deposition behavior of the noble metals an analytical tool for local determination of the Pt and Rh concentrations is crucial. The tool has to be capable of secure handling of highly radioactive deposition and crack monitors or reactor internals. Because of the low amounts of Pt and Rh deposited on the metal surfaces the analytical technique should offer very low detection limits and if possible a low sample preparation need.

The presented study shows that a shielded Laser Ablation Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS) is feasible for this purpose. For the calibration of the instrument a set of Pt coated stainless steel coupons was used. These coupons are prepared by the means of physical vapor deposition and cover a range from 0.003 – 3 μg/cm^2. It could be shown that the presented setup can achieve detection limits lower then 0.003 μg/cm^2.

TuPo9. PLANT PHYSIOLOGICAL ANALYSIS AT NORWAY SPRUCE DRILL CORES USING LA-HR-ICP-MS

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Investigations on the distribution of macronutrients such as sulphur, phosphorous, potassium or calcium in trees are of high interest in plant physiological research. Especially information about seasonal element variations within single tree rings could improve metabolism studies but were so far not accessible. Thus, a micro-analytical method involving LASER ablation coupled to a double-focusing magnetic sector field inductively coupled plasma mass spectrometry has been developed for this task. Method development is especially challenging because of the difficult sample consistency, the relatively low P and S concentrations in wood, a relatively high sulphur background levels in ICP-MS and the unavailability of appropriate calibration standards. Thus, careful optimization and suitable quantification strategies for direct micro-analysis were required.

Critical aspects in method development and possible strategies to reduce background levels will be discussed. Different calibration strategies will be compared.

The method was applied to investigations in Norway spruce drill cores from different sampling sites. Results of analyses in distinct zones within single tree rings for selected elements will be presented and interpreted.

TuPo10. ELEMENTAL ANALYSIS OF ANCIENT BRONZE AND SILVER OBJECTS BY LA-ICP-MS: AN OPTIMIZED METHODOLOGY USING A NEW MOUNTABLE CELL DESIGN

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Element patterns are important criteria for dating, origin determination and authenticity verification in archeometallurgy and evident to define appropriate restoration methods. The chemical characterisation requires an exact quantification in concentration ranges of lower ppm levels (impurities) to % levels of the main alloy element components. Non- or low-destructive methods are preferable especially with regard to preserve antique objects.

LASER ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a sensitive micro-analytical method with high detection power. A mountable LASER cell design provides the advantages of low destruction because no sampling is necessary as required for LA-ICP-MS with conventional cells or for usually applied techniques such as NAA or digestion methods prior AAS, ICP-OES or ICP-MS analysis.

Some years ago, EMPA developed a mountable cell for the analysis of artificial antique silver objects. However, problems in positioning, especially at uneven surface areas, and a reduced transport efficiency due to the large cell volume compared to a small inlet orifice lead to development of a novel cell design. The evolution in cell design and improvements will be presented as well as examples in application to antique silver and bronze objects. Moreover, methods and calibration strategies for the analysis of bronze and silver objects have been developed and validated by comparison to established methods such as NAA and acid digestions prior ICP-OES or ICP-MS analysis. Potential and limitations of LA-ICP-MS for the analysis of antique metal objects will be discussed.

TuPo11. DIFFERENT APPROACHES FOR SAMPLE PREPARATION TO IDENTIFY AL_2O_3 INCLUSIONS IN STEEL SAMPLES BY LA-ICP-MS.
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There is a clear need for microanalysis techniques with high sensitivity and good spatial resolution, since trace elements present in the form of segregates may be of considerable importance for material properties. Focusing on Low Carbon Al-Killed steel (LCAK steel), Al_2O_3 inclusions can generate many defects in the steel product. The mentioned segregations will change in size from nanometers up to millimeters, presenting different geometry. The analytical technique based on laser ablation of the sample followed by Argon plasma excitation and mass spectrometry detection (LA-ICP-MS), was used to identify Al_2O_3 segregations in steels. Reliable reference samples will be of paramount importance for the characterization of segregations, giving the size, distribution and chemical composition. The main aim of the work is to evaluate different approaches for samples preparation. Samples were prepared from pure Fe powder and Al_2O_3 with different particles size, using the four following procedures: pressed pellets, sintering (after pressing, sintering at 1050ºC for 8 h), melting (in a Induction furnace under Ar atmosphere) and fused glass (melting with lithium metaborate).The study includes the optimization of LA-ICP-MS operating parameters and rastering of heterogeneous areas, monitoring the time resolved signals to identify and to establish the size of the inclusion.

TuPo12. ISOTOPE DILUTION LASER ABLATION ICP-MS FOR DIRECT AND ACCURATE ANALYSES OF CHLORINE, SULFUR AND TRACE METALS IN COAL SAMPLES

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Determination of concentrations of chlorine, sulfur, mercury and other heavy metals in coal is required to control the emission of these toxic substances into the atmosphere from fuel burning. The development of fast, sensitive and accurate analytical techniques on a routine basis is therefore necessary to determine these potential pollutants. Accurate determinations of volatile elements like sulfur and halogens at trace levels are always a critical task in analytical chemistry. The most common problems of "classical" analytical methods with wet digestion are caused by time-consuming sample preparation procedures, by a high risk of contamination but also by the risk for possible loss of the volatile analytes.
The direct introduction of solid samples into an ICP-MS by laser ablation has many advantages but there is still a lack of accurate calibration methods. Since a couple of years the group at the University of Mainz therefore developed isotope dilution techniques for accurate determinations of trace elements in powdered samples using LA-ICP-MS. This work presents the application of this technique for coal analyses and discusses merits of different laser ablation and ICP-MS systems. Relatively short analysis times, low detection limits and precise results qualify LA-ICP-IDMS as a routine method for accurate analysis of chlorine, sulfur and trace metals in coal samples.

TuPo13. TITANIUM PARTICLES IN ORAL TISSUE IDENTIFIED BY LASER ABLATION ICP-MS

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Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP MS) is a new analytical method that quantifies elements in the evaporated gases caused by a laser beam of about 55 µm diameter. In the present study the technique was used to identify metal particles

in biopsies of non-perforated oral mucosa. In otherwise healthy patients without previous implants of any type, the bone crest areas destined for implant placement were exposed and dental implants of commercially pure titanium (Nobel Biocare) were inserted. Prior to wound closure, a full mucosal tissue biopsy was cut from the edge of the mucoperiosteal flap (baseline). At abutment connection after 6 months, biopsies were taken by a 6 mm punch. Haematoxylin and eosin stained 5µm sections were analysed by light microscopy, and portrayed gingival tissue with intact oral epithelium and underlying connective tissue with variable accumulation of inflammatory cells. Metal particles were seen in all 6 month biopsies by both light- and scanning electron microscopy. The particles observed were from 470 nm to 80 µm in diameter. The 5µm thick sections were then analysed by LA ICP-MS. Multiple parallel line scans of 4 mm length each were made for both the baseline and 6 months biopsies. Titanium signals of varying intensity were detected in all sections indicating titanium particles of different sizes. The laser ablation technique offers sensitive and specific multielement microanalyses of tissue that has been in contact with implants. This method is time efficient and gives a spatial localisation of metal debris.

TuPo14. THE APPLICATION OF LASER ABLATION ICP-oTOF-MS TO THE ANALYSIS OF ARCHEOLOGICAL ARTIFACTS

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This poster will explore the analysis of archeological artifacts by LA-ICP-TOFMS advantages in terms of speed, cost, and volume of data collected (e.g. 1-260 amu in approximately 30µs) when compared to traditional techniques (such as TIMS). Using the LA-ICP-TOFMS technique, sample volume requirements are minimal (<1mm3), and the non-destructive nature of analysis makes this technology particularly desirable for unique or valuable specimens. Preliminary LA-ICP-TOFMS results for Sr and Pb isotopic ratios from a dataset of archaeological materials previously analyzed by TIMS demonstrate the promise of the technique for generating high precision isotopic data.

TuPo15. ABLATION AND IONIZATION RELATED STUDIES ON QUANTIFICATION OF PHASE CHANGE MATERIALS (PCM) USING LA-ICP-MS

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Phase change materials are based on the reversible transition between a crystalline and an amorphous state. Phase change materials are widely used in commercial rewriteable optical data storage devices such as CD-RW and DVD-RW. The fast and accurate determination of stoichiometry, homogeneity and purity is an important task in industrial quality control. In LA-ICP-MS minimum sample preparation is required and high spatial resolution is accessible, which favours this technique for such routine analysis.

In this study, AgInSbTe samples with different stoichiometry were quantified for major elements using an in-house AgInSbTe standard material as external standard. Furthermore a 100% normalization approach was used to correct for differences in the amount of ablated material and the ionization process within the plasma.

The experiments were carried out using a 193nm Geolas Pro ArF Excimer laser system in combination with an Agilent 7500ce quadrupole ICP-MS. The ablation behaviour of these phase change materials was studied in detail under different fluence conditions using raster and drilling mode. It will be shown that the raster ablation mode provides significantly improved accuracies in comparison to single hole drilling. Furthermore the influence of the laser generated aerosol in terms of particle size distribution on precision and accuracy of the results will be discussed in detail.

TuPo16.   2D-GEL PROTEIN MAPPING BY LA-ICP-SF-MS

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Modern drug discovery strategies for transition metal-based anticancer complexes continue to focus largely on the classical approach of screening using specific *in vitro* or *in vivo* models. Such tests are "result-oriented", especially those based on the effect of the drug on cell viability but it is not trivial to establish the drug mechanism directly even if a structural lead is established.

The key is to identify the target proteins within the cell that binds to the transition-metal. One possible way is to combine the advantages of established proteomic techniques for protein separation and LA-ICP-SF-MS for the detection of metal ions in higher mass resolution that are not endogenous to the biological systems as previously shown by Becker et al..

Protein separation by PAGE/IEF allows for the visualisation of protein "spots" on a proteome map while LA-ICP-MS can be used to identify the "spots" of interest as successfully shown by McLeod et al. The protein "spots" can then be retroactively excised and identified using mass spectrometric techniques such as peptide mass fingerprinting (PMF).

The "ultimate" goal is to create a map of drug-protein interactions in the proteome of a cancer cell line after treatment with transition-metal drugs. Besides establishing the mechanism of drug activity, it is also a potential way of identifying areas in the proteome on which transition metal drugs could target, and hence towards a more systematic way of drug development.

As a first phase in the development of this technique, drug candidates based on ruthenium (Ru) and platinum (Pt) were used to establish the sensitivity levels of the method and its application to the A549 lung carcinoma cell model will be discussed. A challenging goal of this study is to establish accurate quantification strategies by using modified gels to on-line quantify the amount of transition metals in the target proteins.

TuPo17.   MULTIELEMENTAL SPECIATION OF METAL-HUMIC SUBSTANCES IN NATURAL ORGANIC MATTER (NOM) BY POLYACRYLAMIDE GEL ELECTROPHORESIS – LASER ABLATION –ICP- MASS SPECTROMETRY (PAGE-LA-ICP-MS)

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We have used (1) Size Exclusion Chromatography (SEC) with spectrophotometric (UV/visible) and ICP-MS detection for the characterization of elements binding to humic substances derived from municipal compost (1). In a second step we studied (2), the effect of metal ions (Co, Cu, Ni, Pb, Zn) upon the molecular weight distribution of humic substances from the same source. The results indicate that coupling a chromatographic separation with

element-specific detection is a promising analytical tool for studying the aggregation of humic substances in the presence of metal ions. Recently (3) we used three different separation techniques , Ultrafiltration (UF), High Performance Size Exclusion Chromatography (HPSEC) and Asymmetrical Flow Field-Flow Fractionation (AsFlFFF), for the characterization of a compost leachate. In this case, we described the possible interaction of about 30 elements with different size fractions of humic substances (HS) coupling these separation techniques with UV–Vis Absorption Spectrophotometry and ICP-MS as detection techniques. The number-average molecular weight (Mn), the weight-average molecular weight (Mw) and the polydispersity (ρ) parameters were calculated both from AsFlFFF and HPSEC experiments and compared for HS and some metal-HS species.

We are going to present now the first results on the off-line use of Polyacrylamide Gel Electrophoresis coupled off-line to Laser Ablation and ICP-Mass Spectrometry to know the distribution of several metals in the fractions of Natural Organic Matter separated and characterized by the travelling distance.

The PAGE separation process is strongly influenced by the kind of Gel Electrophoresis (NATIVE or SDS-PAGE), composition of resolving gel, composition of stacking gel, composition of sample buffer, sample/buffer ratio, running buffer, Humic and Fulvic concentration, sample loading volume, staining solution, destaining solution, and maintenance solution. Every parameters have been optimized.

A serious problem when using PAGE and LA-ICP-MS is the quantification of the obtained signal. Different calibration modes have been tested by casting standards gels enriched with analyte elements, hydrating dry gels with aqueous standard solutions, loading gels with standard fulvic acids or aspirating standard solutions through the LA chamber. In this work, a very simple and fast calibration method for PAGE and LA-ICP-MS is proposed. This method is based on the dried-droplet ablation of known amounts of standards superficially applied on dry gels. Good linear correlation coefficients have been obtained for Cd, Co, Cu , Fe, Hg, Mn, Ni, Pb, Se and Zn,

1.- Baki B. M. Sadi, Kazimierz Wrobel, Katarzyna Wrobel, Sasi S. Kannamkumarath, J. R. Castillo and J. A. Caruso. *J.Environ. Monit.2002, 4,1010-1016*

2.- K. Wrobel , Baki B. M. Sadi, Kat. Wrobel,, J.R Castillo, and J.A. Caruso. *Anal.Chem.2003,(75),761-767*

3.-E. Bolea a*, , M.P. Gorriz a, M. Boubyb, F. Laborda a, J.R. Castillo a, H. Geckeis *Journal of Chromatography A, 1129,(2006)236-246*

TuPo18. LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR THE CHARACTERIZATION OF PIGMENTS FROM PREHISTORIC PAINTINGS

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In prehistoric times, the human being learnt to represent in paintings important aspects of his life. These paintings were made using Fe oxides (red-yellow colour), Mn oxides (black colour) or carbon (black colour) as pigments, but there is little more data available on the composition of these materials. This information can provide relevant hints about the technological level as well as on the social structure of early societies. Ideally, analysis of these kinds of samples should be carried out using techniques that offer sufficient sensitivity, multi-element possibilities and minimum sample damage. The potential for depth profiling analysis can also be welcome owing to the depositions found on the surface of the paintings through the years. Laser ablation-Inductively Coupled Plasma Mass Spectrometry seems

capable of fulfilling these requirements but no work to date has reported on the use of this technique for this particular application.

The goal of the present work is investigating the possibilities of this technique for determining the elemental composition of pigments from different prehistoric paintings found in the vicinity of the Vero River, in Northern Spain, in an attempt to discriminate the between the possible origins of these pigments. Additional analysis of the materials by means of Scanning Electron Microscopy provides a concentration value for Ca for its use as internal standard in the LA-ICPMS measurements. Raman Spectroscopy analysis of the pigments will provide further information on the molecular composition of the samples, thus complementing the LA-ICPMS data.

TuPo19. STUDY LASER ABLATED MATTER: APPLICATION TO LA-ICP-AES ANALYSIS OF ALUMINA POWDERS

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Elemental analysis of refractory materials such as alumina-based catalyst is being facilitated by the use of LA-ICP-AES. One of the most used supports for catalysts is Alumina and, there are few reports in the literature concerning the analysis this matrix by laser ablation. Different crystalline phases impregnated with platinum or tin are studied to evaluate if the nature of the phase modifies the ablation process (yield, nature of ablated matter …).

The system used for ablation is a Lina Spark[(TM)] atomiser (Nd:YAG laser –1064nm) associated to a simultaneous ICP-AES (Varian-Vista). The hyphenation is realized using a modified Scott double-pass spray chamber, allowing the simultaneous introduction to the plasma of both the laser produced aerosol and a nebulized solution. As the spray chamber implies a filtration of the laser produced aerosol, yields of the system were evaluated by solution ICP-AES to search for fractionation effects during ablation, particle transport and filtration.

Furthermore, the shape and size of filtered and non-filtered particles were also investigated for different alumina crystalline phases and irradiances. Collected particles and craters were imaged by optical microscopy and SEM. Chemical repartition of Pt and Sn around the crater was also studied by XRF and electron microprobe.

TuPo20. NEAR-FIELD FEMTOSECOND LA-ICP-MS OF SOLID SAMPLES.

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More and more analytical applications in biology, geology or material sciences are in demand for better spatial resolution without loss in detection limits. LA-ICP-MS has the potential to accomplish the idea of elemental mass spectrometry imaging. In conventional laser ablation the diameter of the laser spot focused on the sample with a lens is limited by diffraction and therefore by the wavelength of the laser radiation. However, a sub-micrometer size can be reached by near-field (NF) ablation, which is a combination of laser-ablation and AFM (Atomic Force Microscopy) distance control techniques. In this case, the laser radiation is focused into a waveguide which is held several nm above the sample surface by a shear force control loop. The size of the laser spot is defined by the geometry of the waveguide tip. However, the analytical useful spatial resolution is given by the heat affected zone. To

minimize this zone and to deliver enough energy to surpass the ablation threshold the application of fs-laser pulses is advantageous.

Here we report our preliminary experiments on the NF-fs-LA-ICP-MS of solid samples. Helium gas flow is used to transport the ablated material to the quadrupole ICP-MS. The size of the crater is controlled by means of an electron microscope.

TuPo21. FEMTOSECOND-LA-ICP-MS IN-DEPTH PROFILING OF ORGANIC AND INORGANIC COATINGS ON STEEL SUBSTRATES

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Ultra-short laser pulses (< 1 ps) add a new dimension in versatility to LA-ICP-MS. They allow new applications as high resolution, mass spectrometry imaging or in depth profiling of multilayered samples. Currently, cost and complexity of fs-laser prevent a widespread application of these new tools. However, the potential of the new applications and the possibility to overcome current limitation with ns-lasers will promote the acceptance of ultra short lasers.

We will demonstrate how the well known minimal energy dissipation mechanism of fs-lasers ablation allows the analysis of thin films and polymeric multilayer systems as they are currently used in commercial steel products. The results are compared with GD-OES measurements and it is shown that good agreement can be found. Current limitation in terms of analysis speed and quantification are discussed and new strategies to overcome the problems are proposed.

TuPo22. MASS LOAD INDUCED MATRIX EFFECTS IN LA-ICP-MS.

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In this study various experimental set-ups were used to investigate mass load induced matrix effects within the ICP when using laser ablation for sample introduction. Previously it has been reported that under dry plasma conditions low melting point elements undergo a significant ICP-induced matrix effect. For example, the Zn/Ca ratios changed in dependence of the mass introduced into the ICP by up to 25% when ablating a glassy matrix in single hole drilling mode by 193 nm ArF excimer laser. Since these effects have not been found to be related to particles size distribution changes, raster or scanning laser ablation mode was used as a sampling technique. Such an approach allows maintaining the amount of material entering the plasma constant over time. However, the amount of the ablated sample was modified by applying different ablation crater diameters and scanning speeds for ablation. 50 elements in single matrix NIST SRM 610 were measured and the results compared with those obtained for single hole drilling. In addition, the operating conditions of the ICP were changed by introducing different amounts of mix gases. Their influence on mass load induced matrix effects will be discussed.

TuPo23. THE ROLE OF LASER ABLATION IN ISOTOPIC FRACTIONATION OF COPPER DURING LASER ABLATION MC-ICP-MS.

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Studies about isotopic fractionation in laser ablation MC-ICP-MS of metals showed that the laser ablation process significantly influences the analytical outcome. Energy densities close to ablation threshold have been shown for copper to lead to an enrichment of the lighter

isotopes in the aerosol. For iron, differences as large as 4 ‰ have been reported for the composition of different aerosol particle size fractions. Particles >100 nm have been reported to be isotopically heavier compared to the total aerosol. The data on iron, however, base on experiments where the aerosol has been introduced directly into the ICP, and isotopic fractionation due to incomplete particle vaporization could not be excluded.

For the results presented here, various particle size fractions of a copper aerosol have been collected separately on filters. This allowed digesting and measuring them independently in solution. Results show that particles smaller than 200 nm are enriched in the lighter ^{63}Cu by up to 0.7 ‰ compared to the ablated sample. These particles are predominantly agglomerates of sub-10 nm particles formed by vapor condensation in the laser plume. The amount of the isotopic fractionation, furthermore, is changing with ongoing ablation, which can be explained by a crater effect. Mechanisms leading to isotopic fractionation will be discussed in detail.

TuPo24. RAPID SCREENING METHOD FOR ARSENIC SPECIATION BY THIN LAYER CHROMATOGRAPHY AND LASER ABLATION-INDUCTIVELY COUPLED PLASMA-DYNAMIC REACTION CELL-MASS SPECTROMETRY

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There is a growing need for the development of rapid and sensitive screening methods for arsenic speciation in order to comply with present regulations in the European Community (e.g., the strict water quality regulations). In this regard, thin layer chromatography (TLC) may be capable of offering a fast and low cost separation procedure. On the other hand, for the detection of As at the low ng level, the use of laser ablation (LA)-inductively coupled plasma mass spectrometry (ICPMS) can be a suitable tool, providing a high sample throughput and sufficient sensitivity. Thus, the aim of this study was the development of an arsenic speciation method combining the advantages offered by these two techniques. In order to prevent the possible influence of ArCl polyatomic ions on the As signal, the use of a dynamic reaction cell pressurized with hydrogen was evaluated. Amounts of 25 ng of each of the following four arsenic species: arsenite [As(III)], arsenate [As(V)], dimethylarsenic acid (DMA) and monomethyl arsenic acid (MMA) were separated in less then 10 minutes on PEI cellulose TLC plates by using an acetone : acetic acid : water mixture (2 : 1 : 1 V/V) and a development distance of 8 cm. Organoarsenicals, like arsenobetaine and arsenocholine, remained on the application point of the samples. The air-dried plates were ablated into the plasma with a 193 nm ArF excimer laser ablation unit in rastering mode. The arsenic species of the extract resulting from a NIST SRM 1568a rice sample, subjected to enzyme-assisted microprobe focused sonication prior to analysis, were also separated using the proposed method. The results suggest that this technique may be a powerful low-cost tool for rapid identification of arsenic species in biological and environmental samples**.**

TuPo25. TREE RING ANALYSIS BY LA-ICP-MS FOR ENVIRONMENTAL MONITORING: VALIDATION OR REFUTATION?

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The use of dendrochemistry, i.e. chemical analysis of tree rings, as an environmental archive for pollution has been proposed since more than ten years. In particular, laser ablation sampling coupled to ICP-MS detection is perfectly suited for elemental analysis in this field as it combines the high spatial resolution required for tree ring analysis with the elevated sensitivity typical of ICP-MS. Anyhow, in spite of their potentiality, the validation of tree rings as a reliable environmental record is far from being accomplished. In fact, notwithstanding the substantial development laser ablation sampling has undergone, making it a fully consistent method, what tree rings really record, i.e. soil chemistry and/or atmospheric depositions, and which mechanisms are active in the mobility and fixation of chemicals inside wood are a matter of debate. In this presentation, case studies of tree ring analysis by LA-ICP-MS are presented. Both point source emissions (i.e. mining areas) and diffuse atmospheric pollution are tentatively investigated by tree ring analysis: tree species selection, chemical proxy choice and quantification strategy have been addressed. Elemental temporal profiles in tree rings and nearby lake sediments were compared in an attempt to validate the former: anyhow, a strong correlation was established only for sites where soil composition was strongly affected by direct input of the pollutant, e.g. mass transport of contaminated sediments. Use of dendrochemistry for atmospheric pollution monitoring resulted instead questionable.

TuPo26. CAPABILITIES OF FEMTOSECOND LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR DEPTH PROFILING OF THIN METAL COATINGS.

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The capabilities of ultraviolet femtosecond laser ablation inductively coupled plasma mass spectrometry (UV-fs-LA-ICP-MS) for depth profile analysis of thin metal coatings was evaluated. A standard sample (Kocour, USA) consisting of a single Cr thin layer of 500 nm ± 5% on a Ni substrate was used. The fast wash out obtained with a high efficiency aerosol dispersion ablation cell (V ~ 1cm^3) allowed single-shot analysis to increase the depth resolution. The ablation was performed in He at atmospheric pressure. A laser repetition rate of 1 Hz and laser fluence close to the threshold value of the metal sample (< 0.5 J/cm^2) were used. Very low ablation rates (< 10 nm/pulse), which are important for nm-depth resolution, were determined by atomic force microscopy (AFM). The UV-fs laser beam was passed through an aperture (diaphragm) for beam shaping and resulted in a well-defined laser spot size of about Ø 25 μm. Information about the crater geometry and morphology was investigated using the optical microscopy (OM), scanning electron microscopy (SEM) and AFM. The depth resolution, calculated by means of the slope of tangent in the layer interface region, was smaller than 300 nm. Our data indicate, that UV-fs-LA-ICPMS provides a combination of high lateral and depth resolution for the analysis of thin metal coatings.

TuPo27. MOZART AND HIS CONTEMPORARIES – HISTORY STORED IN BONES, TEETH AND HAIR ANALYZED BY LA-ICP-MS

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Skeletal remains of Mozart and suspected relatives have been subject to scientific investigations to solve the question of authenticity of the skull. A film project by the Austrian television ORF was broadcasted at the beginning of the 'Mozart year 2006'. In our work, the skull and excavated skeletal remains of relatives and contemporary citizens have been quantified for the elemental content of Pb, Cr, Hg, As and Sb to retrieve additional information about the living conditions of these individuals. A small splinter of Mozart's tooth enamel was available for investigation, as well. Above that, several hair samples of Mozart have been investigated in comparison to hair samples of contemporary citizens. LA-ICP-MS has been applied for all investigations to minimize damage of valuable historical relicts.

Pb concentrations up to about 16 µg g^{-1} could be found in the samples of 18th century individuals reflecting elevated Pb levels in food or beverages. The Sb level in the enamel sample of Mozart was significantly higher than all other tooth samples indicating a possible ingestion in early childhood. Elevated elemental concentrations in single hair samples gave additional information about possible exposure of heavy metals of the individuals at a certain point of their life.

TuPo28. DIRECT MEASUREMENT OF TRACE ELEMENTS IN AIRBORNE PARTICULATE MATTER BY USING LA-ICP-MS.

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A conventional analytical method of airborne particulate matter (APM) is time-consuming because the sample must be completely digested by inorganic acid followed by determination using ICP-MS. Therefore, the conventional method does not enable to achieve high frequent analysis. On the other hand, LA-ICP-MS can analyze the APM sample without any pre-treatment, which may expect to shorten the analysis time. In this study, the alternative analytical method of APM by using LA-ICP-MS was developed.

Using a cellulose acetate membrane filter immersed in an aqueous standard solution, some analytical parameters of LA-ICP-MS (laser pulse number, laser pulse frequency and defocusing distance) were optimized. Next, the suitability of the calibration was investigated for the cellulose acetate membrane filter on which a certain amount of an aqueous standard solution was dropped (Calibration Filter A) and for the cellulose acetate membrane filter on which a certain amount of APM was collected (Calibration Filter B). The ablation efficiencies of the Calibration Filter A and the Calibration Filter B were ca. 40% and ca. 100%, respectively. Consequently, it becomes clear that the Calibration Filter B is more suitable for the determination of trace elements in APM.

Finally, the diurnal variation of the concentrations of trace elements in APM was investigated by the developed method and the conventional method, simultaneously. From the intercomparison of both results, the feasibility of the measurement of APM was evaluated.

TuPo29. ANALYTICAL EFFICIENCY OF IN TORCH LA-ICP-MS

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Laser ablation from samples placed inside the torch of ICP-MS instruments offers unique analytical possibilities. 10 Hz laser pulse repetition rate leads to baseline resolved signal peaks. Signal to background ratios (S/N) of these single signals surpass the values of the transient signals after ablation inside an ablation cell, even if taken into account the higher number of evaluated data points per time interval in the case of conventional LA.

In torch LA-ICP-MS therefore increases the information gain from single laser shots significantly. Up to now it is not clear whether the increase in signal intensity is due to

shortening of signal duration only or whether the amount of material removed from the sample and transported to the ICP is higher compared to conventional ablation inside an ablation cell.

Two main approaches to determine the transport efficiency in LA-ICP-MS are described in literature, measuring of the crater volume or weighing of the sample before and after LA in combination with the determination of the amount of material transported to a collector system. In this study we investigated single laser pulses in torch and in an ablation cell. Based on the total ion transmission the in torch transport efficiency will be discussed.

TuPo30. LASER ABLATION-ICP-MS: QUANTIFICATION OF FEMTOSECOND LASER ABLATION GENERATED AEROSOLS USING SOLUTIONS FOR CALIBRATION

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The quantification of laser generated aerosols using solution nebulization for calibration has been successfully applied for a number of applications. Therefore, solutions have been introduced into the plasma as desolvated solutions, as wet solutions or have been directly ablated out of a solution. The quantification is based on the assumption that a solution behaves similar to a laser-generated aerosol. Quantitative analysis of solids reported using solution based calibration show excellent results for selected elements, but also significant deviations in dependence on the matrix ablated and the determined elements.

Femtosecond laser ablation is suitable as a sampling tool to generate particles small enough to vaporize and ionize completely within the ICP. Furthermore it has been reported that the ablated material represents the stoichiometric composition of the original sample when entering the ICP.

Recently it has been shown that matrix effects in LA-ICP-MS for dry plasma conditions are induced by different mass loads of the plasma (e.g. Cd up to 25 %, Zn 16%). Therefore, the existence of mass load dependent matrix effects should question the capabilities of solution based calibration strategies for LA-ICP-MS. However it might be possible that already a very small amount of water could significantly influence the plasma conditions and might contribute to a reduction in matrix effects. First indications for such an effect have already been given in the literature.

This study focus on the quantification of femtosecond laser (265 nm) generated aerosols using solution based calibration. The influence of the solvent on the quantification of various elements was studied. Furthermore, the behavior of different matrices such as glass and brass will be discussed in detail.

TuPo31. IMPROVED TIME RESOLVED ANALYSIS (TRA) SOFTWARE FOR LA-ICP-MS.

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A new TRA software package has been introduced in the latest version of the PlasmaLab software for XSeries ICP-MS instruments. This package is designed for the quantification of transient signals in both chromatography applications (LC, GC etc) as well as in LA-ICP-MS and, with the range of powerful quantification techniques possible, removes any need for external software packages. All calculations can be made inside PlasmaLab.

This poster will highlight some of the new features in this release:

- Individual time slices in a single TRA acquisition can be defined as blanks, standards and samples – full flexibility in quantification in a single analysis!
- Intuitive, mouse controlled definition makes TRA quantification as easy as continuous quantification.

With the unique bidirectional control available with the XSeries[II] hardware, a complete, fully automated, flexible LA-ICP-MS solution is now available

TuPo32. TRACE ELEMENT IMAGING OF 6-OHDA INDUCED PARKINSON'S DISEASE IN RAT BRAINS USING LASER ABLATION ICP-MS

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Parkinson's disease (PD) is suspected to be associated with neurotoxic elements that cause oxidative stress along the dopaminergic pathway in two structures of the brain known as the substantia nigra and the striatum. Therefore, isotope-specific mapping of trace elements in neurological tissue may provide specific information on the role of various elements in neuronal degradation. This presentation details a method utilising laser ablation inductively coupled mass spectrometry (LA-ICP-MS) for the two-dimensional mapping of Mg, Al, P, Ca, V, Mn, Fe, Co, Ni, Cu, Zn and Se in neurological tissues. Rats were lesioned on one side of the brain with 6-hydroxydopamine to induce Parkinson's disease. The other side of brain remained unaffected. 10 μm thick transverse sections of the brain containing either the substantia nigra or the striatum were ablated and the elemental content measured by the ICP-MS. Two-dimensional contour maps were constructed that show isotopic concentration across the entire section. Resolution of the images was equivalent to a 40 μm pixel size. Preliminary results demonstrated a decrease in zinc expression and a corresponding increase in copper expression around the site of the lesion in the striatum. This is consistent with previous reports. Increased levels of phosphorus were also noted in the lesioned hemisphere.

TuPo33. AERODYNAMIC LENS SYSTEMS FOR LASER ABLATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) is a versatile tool in atomic spectroscopy; however, one great disadvantage is elemental fractionation. The three main areas where this occurs are: 1) at the ablation site, 2) during transport to the ICP and 3) in the ICP.

Transport- and plasma-induced fractionation arise due to particle size. As large particles are transported to the ICP, they become enriched in low volatility elements. Some large particles can be lost by impaction in the transport process, whilst those that reach the ICP are incompletely atomised. Both stages lead to a false low concentration for the low volatility elements. The aerodynamic lens system is proposed as a solution for the latter two stages.

Originally developed for aerosol measurements, aerodynamic lenses are used to concentrate particles in a gas flow field into a collimated beam. The implicit properties of this collimation means that only a small range of particle sizes are focused, determined by the particle Stokes' number and the particle Reynolds' number. Those particles smaller than this range maintain their entrainment in gas streamlines, whilst those particles larger than this size range are lost by impaction.

The work presented shows the design and use of different lenses in conjunction with LA-ICP-MS. By using an aerodynamic lens immediately after the ablation chamber, larger particles are filtered out and do not have the opportunity to contribute to transport or plasma based fractionation processes.

TuPo34. SPECIFIC DETECTION OF SELENOPROTEINS IN GEL ELECTROPHORESIS BY FEMTOSECOND LASER-ICP-MS PRIOR TO IDENTIFICATION BY NANOHPLC-ICP-MS AND NANOHPLC-ESI-MS

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Since the discovery of the beneficial effects of selenium in bacterial and mammalian cells, the detection and identification of selenoproteins have been of great interest. Selenoproteins contain genetically encoded amino acid selenocysteine (ex. Glutathione peroxidase, thioredoxine reductase, selenoproteins P and W) and are in low abundance in living organisms. The present work discusses multimode detection (femtosecond laser ablation ICP-MS, nanoHPLC-ICP-MS and nanoHPLC-ESI MS/MS) in 1D gel electrophoresis for selenoproteins analysis. The approach is based (i) the specific detection of Se-proteins in the gel by femtosecond laser ablation ICP-MS, and the specific detection of Se-containing peptides in tryptic digests of the proteins from the gel to focus on the sequence analysis on Se-containing peptides. The potential of the techniques is demonstrated on the example of thioredoxine reductase, a selenoprotein with one selenocysteine residue.

The application examples discussed include the comparison of Se-incorporation in proteins by *Escherichia coli* in the presence of selenomethionine and selenite and specific detection of selenoproteins in *Desulfococcus multivorans* bacteria.

TuPo35. DEVELOPMENTS OF AN ONLINE QUANTIFICATION METHOD TO CHARACTERISE CeO_2 NANOPARTICLE UPTAKE INTO LUNG CELLS

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The production and the use of Nanoparticles (NP) is an increasing research topic due to the manifold applications of such materials. However, together with the production of these materials a number of health risks have been reported. Most of these reports are based on high concentration responses, which do not reflect "real case" studies. Therefore, NP-Uptake experiments with physiologically relevant concentration of NP were carried out with human lung cells. The quantification of the NP-transfer into cells was realized by using solution nebulisation inductively coupled plasma mass spectrometry (ICP-MS).

Cells were exposed to various suspensions of NP. Afterwards, cells were extracted, digested and analysed. It was evaluated that the sample preparation procedure (digestion) is the most time-consuming step. Therefore, direct introduction of cell cultures into the ICP-MS is a major aim to provide fast technique for their analysis. To provide a suitable quantification

procedure, different suspensions (slurries) of different size fractions of NP were prepared and introduced into the ICP-MS. The concentration of the NP was determined using external solution calibration. The 'completeness' of particle vaporization within the ICP is a prerequisite to apply such a quantification procedure. The critical size and concentration of NP for complete vaporization and ionisation in the ICP was investigated and will be discussed in detail.

TuPo36.   APPLICATION OF A HIGH REPETITION RATE FEMTOSECOND LASER ABLATION - ICPMS FOR GEMSTONES CERTIFICATION AND HIGH RESOLUTION IN-DEPTH ANALYSIS**.**

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The recent applications of femtosecond laser sources in analytical chemistry have demonstrated a huge potential in terms of signal stability, sensitivity enhancement and suppression of elemental fractionation. We have developed a compact and integrated femtosecond laser ablation device specifically designed for ICPAES and ICPMS coupling. The femtosecond laser source used in this instrument operates at low energy (100µJ/pulse) and high repetition rate (1 Hz - 10 KHz) which represents a new approach in analytical laser ablation where high energy (>1mJ/pulse) and low repetition rate (< 20 Hz) were used so far. The analytical strategy is consequently significantly modified in order to obtain the best performances and will be presented in details.

Two original applications will then be presented to illustrate the analytical potential of this system.

The certification of blue sapphires is of growing interest because of the recent discovery of a new beryllium treatment which is not detectable by conventional gemmological instrumentations. This treatment permits to improve the colour of the gem and so distorts the precious stone. Beryllium occurs in the treated gems in concentrations in the low ppm level. A high sensitive and non destructive microanalysis method is then required to identify Be-treated sapphires. We will present a micro scale (<20µm) fs LA/ICPMS method that was used to discriminate Be-treated gems among a series of 50 sapphires.

Investigation of high resolution in-depth analysis will also be presented. We evaluate the best resolution achievable in fsLA/ICPMS as a function of laser fluency, pulse energy, and repetition rate. Certified multi layer materials were used in order to quantify the in-depth pulse resolution. Our results show that resolution better than 20 nm can be obtained in a routine basis on pure metals (Cr/Ni) which opens new field in surface analysis of materials.

TuPo37.   DIRECT DETERMINATION OF TRACE ELEMENTS IN SOILS USING ISOTOPE-DILUTION FEMTOSECOND LASER ABLATION ICP-MS

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Soils and sediments store key information about metal distribution and speciation in the environment. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been widely investigated as a powerful analytical technique for the direct analysis of different types of solid samples and offers the spatial resolution, detection limits, and element range required by biogeochemical studies [1]. Nevertheless, LA-ICP-MS technique suffers from various non-stoichiometric effects through ablation, aerosol transport, ionization, and transmission processes which can induce changes in signal intensity of the analytes, defined as elemental fractionation. The recent applications of femtosecond laser sources in analytical chemistry have demonstrated a huge potential in terms of signal stability, sensitivity enhancement, spatial resolution, and suppression of elemental fractionation comparing to the nanosecond and picosecond lasers [2].

On the other hand, isotope dilution mass spectrometry (IDMS) is internationally regarded as an absolute or reference calibration technique for trace element determinations. The application of isotope dilution in LA-ICP-MS can correct for some common fractionation effects in LA-ICP-MS arising during the laser ablation process [3,4]. If a homogeneous distribution of both isotope-enriched spike and analyte is achieved, all fractionation effects can be eliminated by the measurement of isotope ratios in the isotope-diluted sample. A combination of LA-ICP-MS with the isotope dilution technique is, therefore, a promising strategy for the direct determination of trace elements in solid materials.

In this communication, high repetition femtosecond LA-ICP-IDMS has been investigated in detail to determine the concentrations of trace elements in soil samples (Cr, Cu, Zn, Cd, Sn, Hg, and Pb). For this purpose, the soil powders were incorporated into a pellet and matrix-matched multi-element isotopically enriched calibration standards for femtosecond LA-ICP-MS analysis will be employed. The influences of laser operating conditions (especially repetition rate of 10 kHz and fluence), pellet preparation, isotope equilibration, and fractionation effect were carefully studied. Finally, the proposed methodology will be evaluated by the direct analysis of several certified reference materials.

[1] D. Günther and B. Hattendorf, Trends Anal. Chem. 24 (2005) 255.
[2] C. Liu, X. L. Mao, S. S. Mao, X. Zeng, R. Greif and R. E. Russo, Anal. Chem. 76 (2004) 379.
[3] S. F. Boulyga, M. Tibi and K. G. Heumann, Anal. Bioanal. Chem. 378 (2004) 342.
[4] S. F. Boulyga and K. G. Heumann, Anal. Bioanal. Chem. 383 (2005) 442.

TuPo38. CATCHING THE DUST - STUDY OF PLASMA-INDUCED ELEMENTAL FRACTONATION BY COLLECTING SOLID PARTICLES IN THE ICP REGION

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Elemental fractionation poses a serious problem in laser ablation ICP mass and optical spectrometry and represents a limiting factor in improving the precision and accuracy of in-situ trace element and isotopic analysis. It has been demonstrated that (1) laser beam – sample interaction, (2) transport of ablated aerosol and (3) incomplete vaporization of solid particles in the ICP are the main sources of decoupling of chemical elements observed as elemental fractionation in spectral analysis. Fractionation during laser ablation and aerosol transport can be studied directly by comparing the chemical and phase properties of the target material of the sample with the ablated particles in the aerosol. However, elemental fractionation due to incomplete atomization of ablated aerosol in the ICP has so far only been inferred on the basis of indirect evidence.

We will present results of chemical and phase analysis of aerosol particles captured on a silica-based aerogel placed directly above the plasma in an ICP-OES instrument. Particles of

known size and composition can be introduced to the ICP either as dry aerosol (powder) or dispersed in a liquid. Alternatively, the particle size distribution of aerosol generated by laser ablation can be modified in particle sizers and/or monitored prior to the introduction to the ICP to ensure a good reproducibility of the experiment. This experimental setup allows for simultaneous analysis of optical spectra of aerosol by ICP-OES and for the SEM/TEM study of captured particles, including measurement of the critical particle size for complete evaporation in the ICP. We will present results of analysis of silicate particles, such as NIST-series glasses and zircon. Our preliminary data suggest that synthetic particles of TiO_2 undergo a partial melting and evaporation in the ICP that is associated with changes in their volume and phase composition.

TuPo39. MEASUREMENT AND MAPPING OF PROTEIN BIOMARKERS VIA LA-ICP-MS

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Immunohistochemical procedures are in widespread use to reveal the presence of protein biomarkers implicated in cancer. Current strategies for imaging tissue sections are based on chromogenic or fluorogenic measurement. LA-ICP-MS can provide an alternative strategy for mapping protein distribution provided the antibody used for immunochemical reactions is suitably labelled, e.g. rare earth element or colloidal gold. In this work labelled sections are examined for over-expression of proteins implicated in breast cancer. The presentation will discuss measurement opportunities for this newly emerging approach and address key performance characteristics, i.e. sensitivity, specificity, resolution and 'scoring' with respect to measurement and mapping of HER-2 in biopsy sections. The scope for simultaneous multiple biomarker measurement via suitably tagged antibodies will be addressed.

TuPo40. CHARACTERIZATION OF HISTORICAL ARTEFACTS BY (LA)-(MC)-ICPMS

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Several studies have shown that elemental pattern and isotope ratios are good markers for provenance and authenticity in archaeological research. Laser ablation-ICPMS is a sensitive technique generating minimal damage to highly valuable samples. This technique will be presented on two selected examples:

The central question of the first study was whether three glazed putti made of terracotta belong to the same ensemble. Visual judgement suggests that one does not belong to the ensemble created by Andrea della Robbia in the 15th century. He enhanced a pottery glaze which had been developed by his uncle and manufactured altarpieces, supraporten and small figures made of terracotta in an almost industrial way. Pb isotope ratios and elemental data have been mass bias corrected and quantified using glass standards as reference material. Finally, the possible provenance of the artefacts could be assigned.

The second application was the analysis of a number of bronze fibulas from different origin of the La Tène period to study the potential to assess the provenance via the alloy composition. Elements in the fibulas have been quantified using a solid copper reference material. Provenance authentication was difficult due to numerous trade routes and remelt of the originals at different places.

TuPo41. LA-ICP MS AND NANO HPLC-ICP MS FOR THE DETECTION AND IDENTIFICATION OF SELENIUM-CONTAINING PROTEINS IN SELENIUM-RICH YEAST

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The recognition of the essentiality of selenium in human nutrition and the indication of its putative role in prevention of some types of cancer have resulted in the proliferation of food supplements fortified in this element in recent years. The most popular of these products is yeast grown in selenium rich media which leads to the incorporation of selenium into proteins and other species. Despite a rich analytical literature on the characterization of selenium-rich yeast, the speciation of this element in yeast is amazingly poorly understood. Only few work, and only recently, appeared to allow an insight into the Se-containing protein fraction.

A new analytical strategy was developed combining a classical proteomic approach with LA-ICP MS and nanoHPLC-ICP MS. This allowed the analysis of the complete selenium-containing proteome in selenium-rich yeast. First, 2D gel electrophoresis was applied to the total protein extract (~ 45 % of the total Se content) and resulted in about 50 protein spots. The selenium-specific analysis of the gel by laser ablation – ICP MS revealed 14 selenium containing spots. These spots were excised and enzymatically digested. NanoHPLC-ICP MS of the tryptic digest served for a sensitive and specific selenopeptide mapping. Indeed, a remarkable part of peptides could have been lost during sample preparation. Hence, nanoHPLC-ICP MS is required to show the existence of selenium-containing peptides in the digests before their identification by nanoHPLC-ESI MS/MS. This novel approach allowed a deeper insight into the identity of 16 selenium-containing proteins and revealed, for example, the existence of selenium-containing glyceraldehyde-3-phosphate dehydrogenase 3 in yeast.

TuPo42. PROVENANCE DETERMINATION OF FLINT TOOLS FROM THE STONE AGE BY MEANS OF LA-ICPMS

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Before the widespread diffusion of metallurgy during the Bronze Age, flint was one of the most important raw materials for the production of tools with sharp, durable edges. As such, its use during the Stone Age was widespread, making it, combined with its virtual indestructibility, one of the most frequent finds from the earlier periods of prehistory. Flint as a natural resource though, is distributed quite unevenly, being mostly linked to the (former) presence of carbonate rocks. This situation necessitated from the very beginnings of human culture a widespread transport of raw materials from their source to the sites where they were used. Characterisation and sourcing of the raw materials can thus uncover lines and directions

of prehistoric contact and mobility, revealing socioeconomic networks hardly traceable by any other means.

The fast, (semi-) nondestructive characteristics of LA-ICPMS and its ability to determine trace elements constitute important advantages of this technique for the analysis of chert. The immobile elements such as the lanthanides, Zr, Hf, Nb, and Ta are measured and the ratio between different elements is compared between different pieces of chert from different quarries, but also between different pieces of chert coming from different locations in one quarry. The use of Si as an internal standard might enable us to obtain quantitative results enabling to distinguish chert coming from different locations even better. In a further stage, archaeological flint tools will be analysed and compared to the data of the different chert quarries.

TuPo43. TRACE ELEMENT MAPPING IN BIOLOGICAL SAMPLES WITH LASER ABLATION-ICPMS

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Laser Ablation-ICPMS is successfully employed for the determination of major and minor elements in geological samples. This elegant sample introduction technique is scarcely used for trace element analysis in biological samples, most probably because of quantification difficulties. Nevertheless, LA-ICPMS has many advantages compared to conventional nebulization of mineralized samples. The spatial resolution and the possibility of element profiling are outstanding advantages of the method. LA-ICPMS is more or less non-destructive, which makes it attractive when only limited amount of sample is available.

In the present work we used a UP-213 LA system from New Wave Technologies coupled to an Agilent 7500ce ICPMS for the determination of trace elements in biological samples. The goal of our investigations was the development of calibration strategies for trace element determination in hair and leaf samples. Pressing powders of standard reference materials to tablets and mixing metal standards in synthetic resins were evaluated as calibrants. The results from these two calibration strategies were compared to NIST glass standards.

The optimized method was used to reconstruct a case of mercury poisoning with hair from the victim. In another application we determined the trace element distribution in fern samples grown on heavily contaminated soil.

TuPo44. PRE-CONCENTRATION AND DETERMINATION OF TRACE METALS TRAPPED ON CENTRIFUGAL MICROFLUIDIC DEVICES BY LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (LA-ICP-MS)

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It is often necessary in the analysis of environmental samples, such as drinking water and seawater, where analyte concentrations are very low to pre-concentrate the samples. Seawater also poses additional problems, as its saline composition can be a source of matrix and spectral interferences. Solid Phase Extraction (SPE) is commonly used for pre-concentration and matrix removal in trace metal determinations. Conventional methods of analysis by ICP-MS require elution of the metal complexes from the column, often with an organic solvent such as methanol, before being introduced in the plasma by solution nebulization. These methods are very susceptible to contamination by reagents, and the use of organic solvents can affect ICP performance. To eliminate the elution step, direct analysis of the analyte laden sorbent can be performed by LA-ICP-MS. Laser sampling of the material directly on the column rather then elution has several advantages. Higher pre-concentration factors can be

achieved since dilution with the eluent is avoided. Problems such as incomplete recovery, contamination by reagents and analyte losses due to incomplete extraction are reduced. Also, only the portions of the column containing the analytes of interest need to be sampled, thereby reducing analysis time.

The direct analysis of metal-8-hydroxyquinoline complexes adsorbed onto C_{18}-bonded silica gel by LA-ICP-MS will be presented. Miniature SPE columns were implemented on a centrifugal microfluidic device. This design is advantageous because centrifugal force is used to drive the liquid flow, eliminating the use of external pumps. The use of such a miniature centrifugal chromatograph in conjunction with LA-ICP-MS offers great potential for the rapid trace metal analysis of many environmental and biological samples in parallel. The results from trapping experiments will be presented for several heavy metals and calibration strategies will be discussed. The potential of this type of system for elemental speciation will also be discussed.

TuPo45. ELEMENTAL ANALYSIS OF SRMS BY FEMTOSECOND LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FS-LA-ICP-MS AT 785 nm 393 nm

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Many experimental investigations have indicated the advantages of femtosecond laser pulses over longer picosecond and nanosecond laser pulses for laser ablation ICP-MS . Some of these advantages include (1) fast deposition of laser energy into a very small volume of the target (no plasma shielding), (2) deposition of femtosecond laser energy to the target material at the solid density (no melting), (3) negligible thermal diffusion from the irradiated volume to the surrounding material. The non-linear mechanisms associated with femosecond laser-matter interaction (i.e. avalanche ionization and multiphoton ionization) leads to positive effects on the ablation characteristics, such as minimum thermal effects, less matrix-dependent ablation, reduced fractionation, and small particle size distribution.

In this work NIST and USGS SRMs are used to investigate the effect of wavelength on the precision and accuracy of Fs-LA-ICP-MS at 785 nm and 393 nm. Two approaches have been used for quantification: 1) internal standardization with Si, Ca and Fe as internal standards, 2) oxide scaled concentrations in which the elements are converted into their equivalent oxide concentrations, scaling the major oxides to 100%, and converting the scaled oxide concentrations back into element concentrations. Equivalent results are obtained using both approaches. The oxide-scaled concentration approach provides the advantage of quantitative analysis without prior knowledge of the concentration of an internal standard.

TuPo46. BIODIESEL TESTING USING A SIMULTANEOUS ICP SPECTROMETER

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Step-by-step within the last decade, biodiesel has established its share of the European fuel market. In Germany, almost 2000 filling stations throughout the country offer biodiesel at their pumps. Biodiesel is considered as an environmentally friendly and attractively priced alternative to conventional diesel fuel – both now and in the future. Biodiesel is one of the most important energy sources originating from renewable raw materials such as rapeseed.

Biodiesel is a mature fuel with a strictly specified qualitative minimum standard as described in the European standard DIN EN 14214. The major producers and distributors of biodiesel have joined forces in the "Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e. V."

(AGQM – Working Group for Quality Management of Biodiesel). AGQM has set up a controlled quality management system (QM) ensuring a high and long-term unvarying fuel quality. This describes not only the selection of raw material and production processes but also storage and transfer as well as transport of biodiesel.

Quality control according to DIN EN 14214 requires quantitative determination of the elements sodium, potassium, calcium, magnesium, phosphorus and sulfur in the concentration range of 5 up to 10 mg/kg. ICP spectrometers, presently considered as the most important tool in daily routine elemental analysis, are highly suited to carrying out of this task, especially when high sensitivity, a wide dynamic range and high sample throughput are called for.

Using the new simultaneous ICPE-9000 with CCD (Charge-Coupled Device) detector, Shimadzu introduces an ICP spectrometer equipped with a unique optical system setting new standards with respect to performance and speed. The system is highly flexible and is therefore easily adapted to all types of sample material. In the present case the sample is biodiesel diluted with kerosene, which has been measured using the radial view unit and the standard plasma torch.

TuPo47.REQUIREMENTS AND CHALLENGES IN THE ICP-OES ANALYSIS OF BIO-FUELS
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The sustainable and ecologically friendly use of earth's limited resources has been a high priority not least since the famous report to "Club of Rome", entitled "The Limits to Growth". Although today, more than 30 years later, (luckily) not all of the report's predictions have come true, an increasing use of replenishable energy sources in the form of bio-fuels or secondary fuels is reality, also dictated by economic requirements resulting from skyrocketing prices for primary energy sources like oil or natural gas.

As with other petrochemical products, to be useful e.g. as motor fuel, bio-fuels have to fulfil certain quality criteria, also with regards to the maximum contents of certain chemical elements. Thus, their determination has been standardized in several cases (for ICP-OES see e.g. EN 14107 for P or prEN 14538 or ASTM D7111-05 for Na, K, Ca, Mg and Cu in fatty acids methyl esters, FAME). Although many of those needs are not different from common fuels based on petrochemical feedstock, specific requirements e.g. for the alkaline metals (as possible remains from the trans-esterification of e.g. the rap seed oil feedstock) pose an additional difficulty in their ICP-OES determination.

To overcome those challenges, different approaches have been and can be employed. A very important step in the development of a suitable methodology is being capable of the direct analysis of the bio-fuel matrix, avoiding time-consuming and error-prone digestion steps. Especially for Bio-Ethanol, used e.g. as extender in motor fuel gasoline, direct ICP analysis without prior digestion represents a formidable challenge.

The presentation will discuss different approaches to the aforementioned requirements and challenges. The use of a mixed gas plasma is one possible solution to the sensitive ICP-OES determination of alkaline elements in a bio-fuel matrix. Alternatively, a background-subtraction method based on larger spectral areas can be employed. Figures of merit for both approaches in typical bio-fuel matrices will be presented and reviewed in the light of both the method's capabilities and routine usability.

TuPo48. TRACE ELEMENT ANALYSIS OF ALTERNATIVE FUELS USING ICP.
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The trace element analysis of fuels, their impurities and additives has historically been important for production control to limit the possible emission of toxins, plan maintenance and test integrity of new fuels. Lead-based additives were used to improve the fuel combustion characteristics in motor vehicles and other machines. With recent environmental concerns becoming more prevalent, the focus has changed somewhat, and most lead-based additives, for instance, are now being phased out.

Global warming and it's causes, are now intensely researched with a view to improving the carbon emissions and producing alternative, viable energy sources with a view to reducing man's effect on the world's climate. Alternative fuels and fuel sources such as electrically powered vehicles, wind power and fuel cells are becoming ever more prevalent but are unlikely to have significant impact on the world's energy supply and emissions for at least another decade. Alternative fuels for motor vehicles, unlike fuel cells, are already readily available and have become increasingly important in engine management as well as emission control.

Bioethanol and biodiesel, which can be produced via several processes from various sources like recycled grease and waste cooking oil as well as renewable crops like corn or wheat. Renewable crops are more environmentally friendly and are CO_2 –neutral since the original plant consumes as much CO_2 in its growth as the fuel produces in combustion. Fuels produced with the above methods contain fewer impurities and can reduce the total impurity level in a blended fuel, sometimes removing the need for further treatment.

The petrochemical industry, as well as most other industries, wants fast precise analysis of their feed and final product to ensure smooth, efficient and cost-effective operation. Provided that a capable instrument is used, advanced modern ICPs can provide simultaneous analysis of all the required elements in alternative fuels in diluted form or by direct aspiration. Traditionally, interferences from plasma loading, carbon buildup and excess vapor in the plasma from high sample volatility can make organic solvents difficult to analyse. Minimising these problems by reducing sample uptake, using a modified or cooled spray chamber and the addition of oxygen can reduce the solvent loading and attendant interferences.

The analysis process can be optimized by making use of recent developments in ICP spectrometry with software enhancements, powerful solid-state generators and tailored sample specific introduction kits. The use of the solid-state, higher efficiency generator improves stability while reducing the interference effects of high solvent loading in the plasma. The analysis of pure bio-fuel is used for the purpose of showing the ease with which analysis can be optimized for the petrochemical industry.

TuPo49. THE EFFECTS OF WEEE/ROHS LEGISLATION IN PLACE AND ITS ANALYTICAL CHALLENGES FOR SCREENING AND FULLY QUANTITATIVE ANALYSES.

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In June 2006, the European Union (EU) implemented the provisions of the "Restriction Of the use of certain Hazardous Substances in Electrical and Electronic Equipment Regulations 2005" (RoHS Regulations). These restrict the production and sale of new Electrical and Electronic Equipment (EEE) containing lead, cadmium, mercury, hexavalent chromium and both polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants from 1 July 2006. The maximum permitted levels are currently accepted to be 0.1% by weight for lead, mercury, hexavalent chrome, PBB and PBDE and 0.01% by weight for cadmium. Exemptions for Lead and Cadmium do exist where it is deemed vital to

maintain the integrity of the product, such as lead and cadmium in printing inks for ceramics on borosilicate glass or lead bound in crystal glass.

Scientific instrumentation does not currently fall within the scope of the Regulations but this situation is expected to change within the next 5 years. Therefore, in the near future, all original equipment manufacturers, with interests in the EU market for scientific equipment, will require component analysis to comply with regulations.

Apart from scientific equipment, all commercial and household electrical and electronic equipment components will require analysis for compliance with an attendant increase in general commercial laboratory workload.

Complete testing of materials is normally impractical, due to the numerous components used, and in often non homogenous material. Three sampling strategies are offered as guidance. Firstly, focus on sampling from "high concern" materials, such as PVC or red/orange/yellow plastics. Secondly, choose samples that can be easily separated from the product, and thirdly, if a sample is not homogenous and cannot be easily separated, then the entire sample must be analysed as one whole sample and digested appropriately. The following method is currently the industry standard guideline for this application, IEC 62321 - *Procedures for the determination of levels of six regulated substances in electrotechnical products*. Certified Reference Materials are currently being developed to suit this application, which will inevitably aid method development and ultimately, lead to the publication of a standardised digestion and testing protocol.

Technical data will be produced proving the efficacy of ICP for the elemental analyses involved in the WEEE/RoHS legislation. The influence and problems involved by applying the directives will be discussed as well as the relevance to the scientific community in general.

TuPo50. WHICH TRACE ELEMENT ANALYSIS TECHNIQUE FOR MULTI-ELEMENT MCERTS ACCREDITED ANALYSIS OF SOILS?

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The monitoring of contaminated land is more prevalent as the demand for housing and industrial builds increases. The contaminant levels in soils help to classify the sites as fit for use for further development, with around 300,000 hectares of contaminated industrial brown field sites in the UK currently identified for this use. Prior to any development taking place, a site must be classified in to one of three land uses – residential, allotments or commercial/industrial. This classification is based on the contaminant levels present in the soil, with the Soil Guideline Values (SGVs) being set by the UK Environment Agency (EA).

Under the Contaminated Land Exposure Assessment (CLEA) model, the analysis of soils falls under the EAs Monitoring Certification Scheme (MCERTS) performance standard for soils. Introduced in 2004, it aims to ensure laboratories deliver quality environmental measurements thought the certification of instruments, the competency of personal and the accreditation of laboratories. MCERTS instructs laboratories on acceptable levels for precision and accuracy and details a rigorous testing routine to gain accreditation. These guidelines demand a robust method for all aspects of soil monitoring, from sample collection and digestion, to analysis.

The industry standard for digesting soils is to use ISO 11466 -*Soil Quality – Extraction of Elements Soluble in Aqua Regia*, (or a variation of) which involves grinding and sieving soils, then using the portion <150um for further digestion by Aqua Regia (the method of acid digestion varies widely with hot plates, closed/open hot blocks or microwaves being used) and finally analysis by AAS, ICP or ICP-MS. AAS has been, for the most part, retired for

use with this application due to its inability to perform multi-element analysis, so this article focuses on analysis by ICP and ICP-MS and investigates the trade off between sensitivity and dilution for ICP-MS versus the all round robustness and ease of use of ICP.

This paper will include experimental data gained analysing soil based Certified Reference Materials using MCERTS guidelines, and produce precision and accuracy data for both ICP-MS (X Series II) and ICP (iCAP 6000 Series).

TuPo51. IMPROVED LA-ICP-MS ANALYSIS BY USING A SOLID-STATE 193 NM LASER, MPI-DING GLASSES AND GEOREM DATABASE

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Three important developments have recently improved the performance of our LA-ICP-MS facilities: the use of a new 193 nm Nd:YAG laser ablation system, the certification procedure of the MPI-DING reference glasses and the development of the database for geological and environmental reference materials GeoReM.

Our LA-ICP-MS analyses using a 193 nm Nd:YAG laser demonstrate that nearly all analytical features, such as precision, accuracy, sample consumption, and element fractionation, have been improved compared with a 213 nm laser. Pb isotope measurements on low Pb (1 – 10 ppm) samples show that the external precision is 0.05 – 0.2% using spot sizes of 50 – 100 μm. The mean reproducibility of trace element data obtained over a period of three months is about 2 %.

Highly accurate LA-ICP-MS analyses require suitable reference materials of similar matrices. The MPI-DING glasses having different major element compositions seem to be such samples for geoanalytical work. Recently, reference values for up to 74 elements and 9 isotope systems have been determined.

Because the amount of data for reference materials has significantly increased in recent years, we have developed the GeoReM database, which contains published analytical data with important metadata (e.g., uncertainty, analytical technique, laboratory). GeoReM has been used for interlaboratory comparisons of concentration and isotope data.

TuPo52. EMISSION FROM LASER INDUCED PLASMA OF PREHEATED COPPER SAMPLE

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Many industrial activities require adequate and time evaluation of material composition .Laser Induced Breakdown Spectroscopy (LIBS) technique can be used not only to identify elements in sample but also to quantitatively determine their concentration ratio. LIBS is based on rapid and real-time plasma spectrochemical analysis of atomic emission from laser induced plasma obtained by focusing a pulsed laser beam on the sample. In our case, the plasma was generated by means of nanosecond single pulse Q-Switched Nd-YAG Laser operating at fundamental wavelength in air at atmospheric pressure. The influence of sample temperature on signal to noise was investigated. The temperature of the sample ranged from 30˚C to 150˚C .As we investigated increasing sample temperature leads to increasing atomic emission from induced plasma that causes analysis of elements in sample to be enhanced. In different delay times reproducibility of results was assessed.

TuPo53. COMPARISON BETWEEN THE CADMIUM, ZINC, SELENIUM, IRON AND ARSENIC CONTENT IN FRESH AND PARAFFIN-EMBEDDED TISSUE SPECIMEN

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Prostate cancer is a major public health issue worldwide. There is evidence that prostate tissue Cd levels are markedly elevated in patients with prostate cancer and that Cd overload is present in the vast majority of patients. There is strong evidence that the loss of a unique capability to retain high levels of Zn is an important factor in the development and progression of malignant prostate cells. Research has found a distinct biological antagonistic effect between Zn and Cd in the human prostate gland and a decrease in Zn levels in prostate cancer. Increased Fe levels can enhance cancer cell invasion. On the other hand, studies have shown that men with higher levels of blood Se have decreased chance of developing prostate cancer.

The aim of this study is to compare levels of Cd, Zn, Se and As in both paraffin-embedded tissues and frozen tissue to provide validity for the use of archived paraffin-embedded materials for trace element research. For the study we used liver and kidney tissues for the initial method validation followed by prostate tissues. The prostate tissue samples were obtained from the Cooperative Prostate Cancer Tissue Resource prostate tissue bank. A non-cancerous section of the tissues was divided in two parts: (1) the first part was digested and analyzed for Cd, Zn, Se and As and (2) the second part was fixed and embedded in a paraffin block after which tissue was retrieved from the block, digested and analyzed for Cd, Zn, Se, Fe and As. The quantitative analysis was performed using a high resolution inductively coupled plasma mass spectrometer. We will discuss the reliability of Cd, Zn, Se, Fe and As in paraffin-embedded tissues for both liver and kidney specimens as well as for prostate tissues. Results show good correlation for Fe, Se, Zn and Cd in the various types of tissues under investigation. Therefore, this study validates the use of paraffin-embedded repository materials for research into the environmental etiology of prostate cancer and other diseases.

TuPo54. PATTERNS OF RARE EARTH ELEMENTS IN PUMPKIN SEED OILS BASED ON ICP-MS DETERMINATIONS

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The authenticity and origin of food products are important from the standpoint of both commercial value and health aspects. The distribution of rare earth element (REE) in pumpkin seed and pumpkin seed oils in relation to the geographical origin of soils of several agricultural farms in the Austria were investigated. It is fundamental to have knowledge of the REE concentrations in the source (soil) and their fractionation processes within the plant that occur during the transport of these non essential elements to the seeds. If the REE pattern in the soil is reflected in the pumpkin seed oil and if the regional variations are significant enough, it should be possible to use REE patterns as the basis for the identification of the geographic origin via fingerprinting.

Preliminary results applying an analytical procedure, using ICP-QMS, proved to be suitable for the determination of REEs not only for soils and seeds, but also for pumpkin seed oils.

One of the main challenges with the analysis are the ultra trace elements concentrations particularly of vegetable oil samples. ICP-MS excels by true multi-element capabilities together with extremely low detection limits.

TuPo55.   EVALUATION OF REFERENCE MATERIALS FOR THE APPLICATION IN LA-ICP-MS

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The quantitative analysis of a large variety of materials with laser ablation is still difficult due to the leak of available standard materials. Thus, the evaluation of new reference materials is an important point to make the method accessible to a number of applications. A series of pure copper standards was evaluated in terms of trace element analysis with LA-ICP-MS. A laser ablation system *Geolas Q Plus*® was connected to a Quadrupole ICP-MS from Varian. The ablation system is equipped with a 193 nm ArF Excimer laser (pulse width 20 ns) and allows ablation with an energy density between 1 and 35 J/cm^2 at 1 to 20 Hz. The spot size can be varied from 5 to 119 μm. The Varian Quadrupole ICP-MS provides a stable and powerful plasma that minimizes plasma based preferential vaporization. The 90 degree reflecting ion optics and the s-shaped prequadrupole reduce the background noise and focus the ion beam with the highest possible efficiency. Due to the use of a full digital DDEM detector, elements in a wide concentration range can be detected without a cross calibration.

The copper standards BAM M-381 to M-386 (BAM, Germany) were investigated with respect to homogeneity of the materials and recovery of the certified values. The analyses of the CRM were performed with variation of the energy density and repetition rate. Different quantification procedures were applied including the usage of an internal standard and the semi-quantitative analysis without an internal standard.

TuPo56.   ANTIMONY DETERMINATIONS IN TRAFFIC-RELATED AIRBORNE PARTICULATE BY AFS AND ICP-MS

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The importance of antimony in the environment is due to its toxicity and biological effects. Antimony has no known biological functions, and its toxicity depends on the oxidation state and the structure; inorganic Sb(III) is more toxic than Sb(V), and both more toxic than methylated species, such as trimethylstiboxide (TMSbO).

The presence of Sb in the atmosphere can be due to natural and anthropogenic sources. Natural sources (e.g. wind borne particles, volcanoes, sea salt spray) are important, up to a 41%. The main input corresponds to anthropogenic sources (fossil combustion, non-ferrous refining, waste incineration and incineration of sewage sludge). Traffic related emissions have also been considered in the last decades as an important local source of Sb, due to the brake ware of heavy duty vehicles.

In this study, Sb has been determined in traffic-related airborne particulate matter in filters collected in Argentina. The determinations of Sb by ICP-MS have been compared to those

obtained by Hydride Generation-Atomic Fluorescence Spectrometry (HG-AFS), an instrumental alternative which allows performing determinations in the $\mu g\ L^{-1}$ level.

TuPo57.   ICP-MS TRACE ELEMENT DATA FROM ALLUVIAL AU AND ITS USE IN MINERAL EXPLORATION

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The ICP-MS trace element composition of alluvial native Au from 7 stream silt samples was compared with the composition of geographically-associated Au in 3 samples from a prospective ore-deposit in the Quenellia Terrane of central British Columbia. Based on present drainage directions, not all of the alluvial Au could have been derived from the ore deposit, but Pleistocene glacial ice-movement, and paleo-stream directions complicate inferring a source for the alluvial Au. The silt-sample Au, averaging 4 alluvial grains per sample and totaling 12 to 250 μg/sample, yielded measurable concentrations for V, Fe, Co, Cu, As, Pd, Ag, Sb, Pt and Bi. Deposit Au samples represent the three dominant rock types in the showing. Their Au trace-element compositions bracket those of the alluvial Au. Exploratory statistics (multidimensional scaling) suggest that trace elements in the native gold behave (vary) according to Goldschmidt's geochemical classification of the elements. This coherent element behavior indicates that all trace elements are dissolved in the Au crystal lattice (are not inclusions) and that a single geochemical system formed all the gold in one geologic environment. Literature information suggests that individual Au deposits show distinctly-different assemblages of detectable elements. Given the previous two observations and that the suite of detectable elements in the deposit Au match those of the alluvial Au, with concentrations that bracket those of the latter, it is concluded that the deposit-source of the alluvial Au has probably been identified. Apparently ICP-MS data on the trace element composition of Au can be used in exploration programs to help determine whether the bedrock deposit-source of alluvial Au has been identified. Further, this study shows that silt-sample exploration in glaciated terranes must recognize that paleo-ice movement and paleo-stream directions can yield geographic distributions of alluvial Au grains that are not consistent with present-day drainage patterns.

TuPo58.   THE DISTRIBUTION OF DISSOLVED AND PARTICULATE IRON IN A COASTAL ENVIRONMENT USING ICP-MS

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Here we show that productivity in the coastal region offshore of Oregon and Washington (USA) is not iron limited by comparing the concentration of dissolved and particulate iron, generated using inductively coupled plasma-mass spectrometry (ICP-MS) with a Finnigan Element, to data on biology productivity and macronutrient concentrations. Dissolved (<0.4 μm) and soluble (< 0.03 μm) samples were acidified to1.8 pH aboard ship. Prior to ICP-MS analysis these samples were adjusted to pH 2.0 and oxidized with hydrogen peroxide to ensure all the iron existed as Fe(III). A μsampler was used to load the sample on a column of NTA-resin, followed by a MilliQ rinse, and elution with 1.5 N nitric acid to a PFA-ST nebulizer. Particulate samples (> 0.4 μm) were collected on filters aboard ship. The filters were exposed first to a chemical leach (25% acetic acid, 0.02 M hydroxymaline

hydrochloride, and a short heating step). The remaining particles on the filter were bomb digested (concentrated hydrochloric acid, nitric acid, hydrofluoric acid, and heat). Leachable and refractory particulate samples were taken to dryness and reconstituted in a 1 N TMG nitric acid matrix prior to analysis using a PFA-ST nebulizer.

TuPo59.   DETERMINATION OF SELECTED ELEMENTS IN SNOW SAMPLES

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Artificial snow is used and produced in periods and areas with little snow or no snow at all, in order to prolong the skiing season. Various impacts on the environment induced by artificial snow production are addressed. The snow samples were collected on Medvednica Mountain, near Zagreb, Croatia, from ski race track where FIS World Cup race, "Snow Queen" is held. Samples were collected in February 2005, and February 2006, after the sport event was held, and in April 2005, at the beginning of snowmelt season. The collected samples were analyzed in laboratory after melting into water. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for metal content determination. Sample preparation procedures were based on preconcentrations from large volume of melted snow. Higher concentrations of alkaline and alkaline earth metals compared to natural snow were obtained for artificial snow samples. Chemical modifications of snow piste conditions were established. The results obtained for essential and toxic metals content show different elemental composition of artificial snow compared to natural snow and water.

TuPo60.   MERCURY POLLUTION DETERMINATION IN RIGA BY ZEEMAN ATOMIC ABSORPTION SPECTROSCOPY

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Chemical element mercury has an important role in different technologies used today, and it is widely distributed, but monitoring and control of its pollution is a relatively new activity. Therefore, relevant investigations are of particular importance.

Practical mercury pollution measurement sessions were performed in several districts of Riga (Latvia), using Zeeman atomic absorption spectrometer RA 915+. The measurements have been performed mainly from the driving car. GPS was used to create a solution to enable measurement results assignment to particular measurement places. The solution gives a possibility to establish a digitalized pollution database for different geographic coordinates in different times.

As an example for such survey, the measurements at Spilves street (Riga) will be shown. According to the press news item on 17th of June, 2005 about mercury wastage on Spilves street, liquid mercury was scattered in the area of around 30 square meters. It was stated that area clean-up was performed. Our measurements carried out few days later showed that high mercury concentration was still present there, and somewhat lower mercury concentration was registered in spring of this year (2006). More detailed investigation of surroundings showed pollution did not disappear at all – in the pit mercury concentration reached much higher level.

TuPo61. DETERMINATION OF PLATINUM GROUP ELEMENTS IN LAGOON SEDIMENTS BY ICP-MS WITH A SENSITIVITY ENHANCING SPRAY CHAMBER

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Increasingly restrictive regulations governing air pollution from cars means that catalytic converters have to be used to drastically reduce the emissions of noxious gases. Unfortunately, despite the ever increasing importance of these devices, their employment under extreme conditions causes a gradual release of their main active components, platinum, palladium and rhodium, into the environment.

An evaluation of the dispersion of these elements, often referred to as Platinum Group Elements (PGEs), into the environment can be done by analysing environmental archives, such as sediments.

Due to the very low concentrations of PGEs in the environment, ever more sensitive analytical methodologies need to be developed for their analysis.

This work reports the development of an analytical methodology based on ICP-MS for the determination of PGEs. The method is based on the employment of an *ad hoc* made heated spray chamber in addition to the standard quartz double pass spray chamber in order to increase the sensitivity of an Agilent 7500i ICP-QMS for these elements. This method was validated by the analysis of the certified reference material BCR-723 urban road dust. Detection limits of 0.047 ppt for Rh, 0.30 ppt for Pd and 0.12 ppt for Pt on digested solutions, were obtained.

This analytical technique was then applied to the analysis of dated sediment cores taken from the Venetian Lagoon at different distances from the bridge that connects Venice to the mainland.

TuPo62. APPLICATION OF ICP-MS AS A TOOL FOR ENVIRONMENTAL MONITORING.

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A key requirement in the field of environmental monitoring is the measurement of elements at trace and ultratrace concentrations in a variety of materials, including waters, soils, and biota.

This presentation outlines some key application areas, including the analysis of drinking water, river water and other natural waters, along with the analysis of more challenging materials, such as seawater and digests of soils. Major sample preparation and analysis details are presented in each case. For more challenging samples, major benefits are provided by the use of collision cell technology for the removal of polyatomic interferences formed from the major matrix constituents of the sample. These benefits are highlighted.

In addition, a developing area of interest for environmental scientists is the determination of the concentrations of specific species of particular elements present in a sample, rather than just the total concentration of an element. This is particularly important when assessing the environmental impact of a contaminated sample. Most speciation determinations are performed by combining a separation technique, such as liquid or gas chromatography with the sensitive, element specific detection of ICP-MS. Technological solutions for performing such analyses are presented along with topical example applications.

TuPo63.   ANALYSIS OF SEAWATER USING DIFFERENT ICP-MS TECHNOLOGIES

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Seawater represents one of the most challenging matrices to be analyzed by ICP-MS. The high salinity and the low concentrations of trace elements which can be below ppt level require careful sample preparation and advanced ICP-MS instrumentation. Before analysis seawater has to be diluted and acidified which bears the potential risk of contamination and degradation of detection limits. Typically a dilution factor of 10 is applied before analysis which will require an analysis down to single digit ppt concentrations for some elements. Consequently the ICP-MS with the highest signal to noise ratio will guarantee results of uppermost accuracy. High resolution ICP-MS has the advantage of high signal to noise ratios, and can therefore maintain excellent detection limits in the diluted sample. Detection limits of HR ICP-MS and Q-ICP-MS which are obtained under the same conditions will be compared.

Due to the matrix composition seawater creates numerous spectral interferences in the ICP-MS, consequently the ICP-MS to be used has to have an very effective strategy to overcome the interference problem. High resolution ICP-MS with its inherent high selectivity has the advantage to clearly separate interferences such as $^{40}Ar^{35}Cl$ and $^{40}Ar^{35}Cl$ from ^{75}As, $^{38}Ar^{40}Ar$ and $^{38}Ar^{40}Ca$ from ^{78}Se, $^{40}Ar^{16}O$ and $^{40}Ca^{16}O$ from ^{56}Fe, $^{35}Cl^{16}O$ and $^{37}Cl^{14}N$ from ^{51}V; collision cell technology has to rely on complete elimination of the interference by adding different gases and/or apply kinetic energy discrimination. The presentation will examine if the use of cell gases in combination with a Q-ICP-MS is sufficient to enable accurate determination of trace elements in seawater, or if high resolution ICP-MS is the choice when data of highest quality are required.

Furthermore non-spectral matrix effects require special attention when calibrating the instrument. The present work has studied if standard addition calibration is mandatory or if external calibration comprising internal standardization can be sufficient, and if there is an different performance in this regard when comparing high resolution and Q-ICP-MS.

Drift effects caused by deposition of salt on the cones can impair the accuracy of the measurement as well.

In principle Quadrupole ICP-MS as well as high resolution ICP-MS can be used for the analysis described above.

The presentation will evaluate the differences in performance and ease of operation between high resolution and Q-ICP-MS for the direct analysis of seawater.

TuPo64.   NEW LIGHT THROUGH OLD WINDOWS: AN INVESTIGATION OF POLYATOMIC INTERFERENCES AND MATRIX INDUCED SUPPRESSION IN MARINE SEDIMENT ANALYSIS BY HR-ICP-MS

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Since its inception in the late 1970s, it was appreciated that the accuracy and precision of ICP-MS would be degraded by matrix induced polyatomic interferences and suppression, particularly in complex matrices. Attempts have been made to mitigate these problems by recourse to the use of high resolution mass spectrometers, collision cell technology, sample dilution or simple recourse to an alternative lower abundance isotope free from such interferences.

Marine sediments represent a complex, heterogeneous matrix which requires a high pressure, mixed acid dissolution procedure to ensure quantitative digestion prior to analysis by ICP-MS. It is inevitable, therefore that the reagents employed will generate additional polyatomic interferences.

X-ray fluorescence is a non-destructive analytical technique well suited to the analysis of solid samples. It can be used to characterise marine sediments by the provision of compositional data. This information can be used to predict the likelihood of the presence of a given polyatomic interference.

This paper will present the results of a systematic study using marine sediment reference materials, synthetic sediment mimics, dilution and recourse to higher resolution settings to elucidate and identify the sources of bias for selected analytes in marine sediment samples. In addition to the comparison of the observed results against their stated property values, isotopic information will be used to evaluate freedom from interferences. The hypothesis that reagents used in sample digestion may result in a different pattern of polyatomic interferences in the presence of a matrix compared to a reagent blank will be tested.

TuPo65. DIRECT ANALYSIS OF DILUTED AND UNDILUTED SEAWATER BY HR-ICP-MS M.

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Recent advances in sample introduction have improved the capabilities of HR-ICP-MS for direct seawater analysis. SC-Fast sample injection is combined with methane addition using a conventional spray chamber and APEX desolvation for the analyses of 10 fold diluted and undiluted seawater, respectively.

The rapid high throughput method for analyses of 10-fold diluted seawater samples is used for the determination of potential tracer elements (P, V, Mn, As, Mo, Ba and U) in seawater collected from ballast tanks of cargo ships. SC-Fast injection and methane addition minimize cone deposition providing >700 continuous determinations. The method has a long term precision < $\pm$ 7% (2-SD) and accuracy within the certified (2-SD) values for NASS-5 (n=103).

Accurate determination of trace and ultra-trace metals in 10 fold diluted seawater is often compromised by blanks and associated detection limits. Through elimination of the dilution step, both procedural and sample introduction blanks are greatly reduced. SC-Fast injection at 10 µL min^{-1} combined with APEX desolvation and methane addition result in high sample transport efficiency (> 90%) and low oxide formation, minimizing both cone deposition and MoO^+ interferences. The method is capable of 120 continuous determinations of undiluted seawater samples in 6 hrs.

TuPo66. INTERCOMPARISON EXERCISES FOR TRACE METALS ETERMINATION IN WATER SAMPLES BY ICP-MS

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In Inductively coupled plasma mass spectrometry (ICP-MS) analysis, mass discrimination effect occurs due to different transmission efficiencies through the mass analyzer depending on the mass of the isotope measured. Therefore, mass discrimination leads to a non-uniform sensitivity across the mass range and inaccurate isotope ratio measurements. Different alternatives have been adopted to correct mass discrimination effect and to minimise its associated uncertainty.

It is well know that very precise isotope ratio measurements can be obtained by multicollector ICP-MS instruments but the correction is still limited by the uncertainty in the isotope composition of the element used as isotopic reference standard. In the present work, the performance of three mathematical algorithms (linear, exponential and potential) for mass bias correction have been studied for the precise and accurate measurement of cadmium isotope ratios. Different models for mass bias correction were evaluated including single isotope ratio and multiple isotope ratios with and without weighing of the certified uncertainties. These algorithms have been evaluated for quadrupole, double focusing and multicollector ICP-MS instruments.

Based on these results, a new correction model will be proposed by means of a weighed least squares adjustment in the determination of the mass bias factor, in which the associated uncertainty of each certified isotope ratio is taken into account. This new model provides the lowest mass bias uncertainty in each instrument tested.

TuPo67. METAL CONTENT TO ASSESS THE SEDIMENT QUALITY STATUS OF A PROTECTED MARINE AREA

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Chemical investigation of the coastal area of the Castelporziano Marine Protected Zone (Tenuta Presidenziale di Castelporziano, Central Tyrrhenian Sea) were carried out during three sampling cruises (2003-2004); total content of selected metals (Cu, Fe, Mn, Ba, Zn, Pb, As, Cr and Ni), were determined in the surface deposits to characterize the area.

The experimental activities were carried out through a dedicated sampling scheme.

Total metal content was extracted by microwave digestion and the acid solution analyzed by Sequential ICP-OES. In order to guarantee QA/QC, quality parameter such as accuracy, quantification limit, detection limit and repeatability were estimated (ISO 17025). The accuracy was evaluated using Certified Reference Materials: PACS-2 and GBW 07314.

Almost all of metals analysed, showed a gradual concentration's increase from coast line to offshore, in agreement with increase of fine sediment grain size. Just As showed a distinctive behaviour in all three sampling cruises: this metal, in fact, presented the highest concentration in a station near the coast (CPc15). Moreover arsenic concentration couldn't follow the fine fraction of sediment.

The results obtained by the analysis were compared with the Italian Environmental Quality Standard (EQS) for marine sediments showing a good quality status of area.

TuPo68. IMPLEMENTATION AND VALIDATION OF A METHOD FOR DETERMINATION OF METALS IN DRINKING WATER BY ICP-MS

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The *EPAL S.A.* is a water supplier company responsible for distribution of drinking water for Lisbon city and others 25 Town Halls near Lisbon.

The methodology followed by the *Laboratório Central da EPAL* for the implementation and validation of a method for determination of metals by ICP-MS in drinking waters, is described in this work.

The method developed by the Laboratory involves simultaneous analysis of Li, Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Pb and U.

The validation process consisted in several steps: optimization of the instrumental parameters, study of interferences, estimation of correction equations for poliatomic interferences, estimation of detection and quantification limits, definition of the working range, evaluation of repeatability and accuracy and estimation of analytical uncertainty.

The results obtained demonstrated that the performances of this method are in agreement with the requirements of the European Directive 98/83/EC concerning metals monitoring in drinking waters. The analytical method is validated and is in use in routine analysis in the *Laboratório Central da EPAL*.

TuPo69. EXTENSION OF EN13656* STANDARD MICROWAVE DIGESTION METHOD TO TRACE ELEMENTS MEASUREMENTS IN SEDIMENTS BY ICP-MS: VALIDATION AND UNCERTAINTY CALCULATION

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Standards for environmental monitoring have been traditionally developed matrix by matrix. In this way a number of standards describing the measurement of the same parameters have been developed in parallel, resulting in lack of consistency in methods and in relatively high efforts for field laboratories. For that reasons CEN has started a process on development of standards covering more matrices. The first application of an "Horizontal" approach was in the fields of sludge, soil and treated biowaste.

Sediments represent the principal sink for trace elements in aquatic ecosystems and if contaminated can represent a secondary source of these contaminants for the aquatic ecosystems. The evaluation of the environmental risk assessment requires generally a full characterization of sediments. The lack of standards for the digestion of sediments using microwave assisted procedure before instrumental trace element measurements, induced APAT, following the horizontal approach, to extend to sediments the European Standard EN 13656 already validated for different kind of wastes. After matrix digestion, an ICP-MS equipped with collision cell was used for measurements of As, Cd, Co, Cu, Ni, Pb, and Zn contents in sediments.

In this paper the results of the validation in APAT laboratory of EN 13656 application to sediments for subsequent ICP-MS measurements, will be presented. The following performance characteristics were tested: selectivity, digestion conditions, robustness, precision, trueness, recovery, limit of detection, limit of quantification. For trace elements generally near to the detection limits in sediments, different methods to assess detection limits were applied and discussed. The uncertainty budget was calculated following the procedure

reported in the GUM: a) identifying the different uncertainty sources, b) quantifying the different A and B contribution types, c) converting them to standard uncertainties and d) calculating the combined standard uncertainties. As expected, the dominant contributions to the uncertainty budget were method precision and method recovery.

* European Standard CEN EN13656:2002: Characterization of waste - Microwave assisted digestion with hydrofluoric (HF), nitric (HNO_3) and hydrochloric (HCl) acid mixture for subsequent determination of elements

TuPo70. DETERMINATION OF CHROMIUM, IRON AND SELENIUM IN FOODSTUFFS OF ANIMAL ORIGIN BY COLLISION CELL TECHNOLOGY, INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY, AFTER CLOSED VESSEL MICROWAVE DIGESTION

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A number of elements suffer from major spectral interferences in ICP-MS analysis. The argon-based polyatomic ions ($^{40}Ar^{12}C$, $^{40}Ar^{16}O$ and $^{40}Ar^{40}Ar$) interfered with the determination of the major isotopes of several elements of interest in foodstuffs such as ^{52}Cr, ^{56}Fe and ^{80}Se, respectively. Different techniques have been described to diminish the impact of these interferences (correction equations, use of alternative less abundant isotopes (^{53}Cr, ^{54}Fe and ^{82}Se), high resolution, "cool" plasma approach) but they have limited applications and were unsatisfactory for a multi-elementary routine analysis.

The aim of this study was to develop a method for the determination of chromium (^{52}Cr), iron (^{56}Fe) and selenium (^{80}Se) in foodstuffs of animal origin by ICP-MS using collision cell technology (CCT) mode after closed vessel microwave digestion. Optimization of the method for the 3 elements considered will be discussed. Finally, we will present results of nine different certified reference materials (CRMs) on foodstuffs of animal origin and on an external proficiency testing scheme which were used to estimate some analytical figures of merit (limits of quantification, trueness, precision under repeatability and intermediate precision reproducibility).

TuPo71. MICROWAVE DIGESTION FOR THE DETERMINATION OF AVAILABLE ALUMINA AND REACTIVE SILICA IN BAUXITE

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Bauxite is the main commercial mineral source for aluminium oxide, which in turn is smelted to form aluminium metal. The viability of a bauxite deposit is assessed by determination of "Available Alumina" and "Reactive Silica".

Available Alumina defines the net amount of Al_2O_3 that can be extracted from the bauxite using conditions simulating the extraction of alumina in the Bayer process. Reactive Silica is a measure of the amount of silicious materials that will react with the caustic soda in the Bayer process. It is an important parameter of a bauxite deposit since the dissolved silica is subsequently precipitated as a form of sodium aluminium silicate, resulting in significant cost due to consumption of caustic soda.

Traditionally, stainless steel high pressure vessels have been used to carry out these digests in laboratory scale, commonly at 145 °C but up to 250 °C to simulate conditions in some processing plants. Difficulties have always been experienced in controlled pre-heating of

those vessels to working temperature and then maintenance of the digestion temperature for the holding time of (typically) 30 minutes.

Proper control of these parameters in microwave heated vessels offers an elegant and more efficient way of performing this process.
The purpose of this evaluation was:

1.   To determine analytical precision under a specific set of digestion conditions.
2.   To monitor possibility of vessel leakage during digestion.
3.   In the case of the 48 position rotor, to determine if there was any systematic variability between the three circles of vessels.

TuPo72.   MICROWAVE ASSISTED PRECONCENTRATION AND SEPARATION OF Pt AND Pd FROM LIQUID SAMPLES FOR ICP-MS DETERMINATION

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The low concentration of Pt and Pd in industrial and environmental samples, together with the presence of interferents, are the main causes of problems in their quantification. Thus, a preconcentration and separation procedure with microwave assisted elution for the determination of Pt and Pd by ICP-MS from liquid samples is proposed. A glass microcolumn, packed with adsorbent 3-(1-Thioureido)propyl, functionalized silica gel and placed inside a domestic microwave oven, was used to quantitatively collect Pt and Pd from the sample solutions. 0.5% aqueous solution of thiourea was used to elute the analytes under microwave radiation. Optimisation studies were carried out in order to obtain the best values for the sample acidity, sample and eluate velocities, adsorbent quantity, eluate concentration, reducing agents, etc. The factor of preconcentration was found to be up to 100, RSD (for 5 ng/L Pt and Pd) was lower than 5%, limits of detection in the ng/L level were achieved. Common interfering ions for the ICP-MS determination of Pt and Pd were effectively separated and did not influence the procedure proposed. As a real sample, tab water was analysed - directly and spiked with 2 ng/L of Pt and Pd, with results in agreement with the values obtained for model solutions.

TuPo73.   OPEN DIGESTION UNDER REFLUX FOR THE DETERMINATION OF TOTAL ARSENIC IN SEAFOOD BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY WITH HYDRIDE GENERATION

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A method for the determination of arsenic in seafood by inductively coupled plasma atomic emission spectrometry with continuous hydride generation is described. Several analytical parameters have been investigated and optimised. The analytical features of the method (recovery, precision, accuracy and limit of detection) were calculated. Practical detection limit of 3.6 µg/kg fresh weight for As have been reached. The precision of the method expressed as relative standard deviation (RSD) was in the range of 2.7 – 3.7 % and the recovery percentage ranged from 98.4 to 101.8 %. The reliability of the developed method was checked by analysing several certified reference materials. A complete mineralisation was obtained for arsenobetaine containing reference material with a mixture of nitric and sulphuric acids followed by adding hydrogen peroxide in an open digestion system. This method can be applied to routine analysis without any risks of interferences.

TuPo74.   CLEAN LABORATORY TECHNIQUES FOR TRACE METAL ANALYSIS

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Analytical laboratories are routinely asked to report metals at ppb and ppt levels. However analysis at these levels is not possible unless trace metal contamination is minimized, identified, and if possible reduced to low ppt levels. Contamination can originate in sampling, reagents, reference materials, sample handling and introduction, or in the laboratory environment.

We all try to keep our labs free from contamination. But unless you work in a "clean lab", which has little or no exposed metal and is fed with HEPA filtered air, you will have contamination; but at what levels? The first step is to identify the level of contamination, usually by running blanks or QC samples that have been prepared and processed the same as the samples to be analyzed. This is not always as easy as one would think since there are so many ways for contamination to gain entry to your results. While there is no way to eliminate trace metal contamination, you can identify the sources, monitor the levels and constantly make improvements in techniques to reduce those levels.

References:

1. "Guidance in establishing Trace Metal Clean Rooms in Existing Facilities" :USEPA 821-B-95-001
2. Accuracy in Trace Analysis : NBS Special Edition 422
3. Guide to Environment Analytical Methods :Roy-Keith Smith
4. Clean Manufacturing :A2C2; April 2003
5. Water Environment Laboratory Solutions :April/May 2003

TuPo75.   DEVELOPMENT AND PERFORMANCE OF LOW-COST CLEANROOM DEVICES.

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The role of particles in many complex environments is poorly understood and quantified.

For example, there is a considerable gap between the complexity of particles characterised in the atmosphere and those studied in controlled laboratory measurements. Human beings are the main reason for any contamination because bacteria and particles do using the skin and working dress as shuttle.

Cleanroom technology is one of the most increasing developments also in analytical chemistry nowadays. The only way to detect lower and lower concentrations is to work out the total procedure under cleanroom conditions. So, complete analytical laboratories were built in special cases as walk-in-cleanrooms and equipped in addition with workbenches, which become flowed by purified air. Beside all the technical problems like to maintain the filters or to check the velocity of the pure air flow permanently and , last not least, to avoid each source of turbulence, the operators remain as important risk factors. They can introduce in addition to other sources particles and germs in an amount of millions per day. After a short definition of cleanroom technology and its goals the international standards and regulations have to be discussed. A comparison between U.S. Federal Standard 209 E and ISO 14644-1 shows the general confusion the standardization can arrange. The emerging demands given by all the regulations can be fulfilled only in small units of volume in an economical and meaningful way. For this reason the Spetec company has developed a vari--able „Laminar Flow Box" family. The different types are working all with an equal filter module including a stable running ventilator. Inside the boxes a cleanroom is created by a displacement flow poor in turbulence The isolation factor of such a clean area totals more

than 105. When positioning such a box in walk-in-cleanrooms of the classes 100 000 to 1000 a working area free of particles is achieved.

From the fundamental module also a type was developed meanwhile with an exhauster system to remove the warmth or the vapour. The sucking off performance totals maximum 1 m3/min. Additionally, the hanging up of the filter module and the surrounding with a plas-
tic lamellate curtain has proven good, generally, and allows to work without producing a whirl-up effect or any kind of turbulence. The shower of purified air prevents the ascent of the particles of the floor and the lateral intrusion of particles. This has led ultimately to the construction of larger cleanrooms by using two or three filter-modules. Such a low-cost walk-in-cleanroom can cover a complete analytical procedure including an automated pre-paration of thesample as well as its input and measurement.
The measurement of particle numbers was carried out by laser diffraction.. It can be shown that for a surrounding air, which was burdened with 1 million of particles (being thoroughly a normal case of a room persons do work in) only individual particles were measurable in-side our box. Both the box as well as the shower version offer thus a considerable protection
of any kind of pollutions. They are not only flexibly usable but also a low-cost possibility to prevent your analytical work for contaminations.

TuPo76.   APPLICATIONS OF HIGH-SPATIAL RESOLUTION TRACE METAL ANALYSIS OF *PERNA* SHELLS BY LASER ABLATION ICP-MS IN MARINE POLLUTION MONITORING.

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TuPo77.   DIRECT SPECTROMETRIC DETERMINATION OF TOTAL FLUORINE IN GEOLOGICAL MATERIALS BY CONTINUOUS POWDER INTRODUCTION INTO HELIUM MICROWAVE INDUCED PLASMA

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A sensitive direct spectrometric method for the determination of total fluorine content in a wide variety of geological materials has been developed. Solid samples were grained in a centrifugal mill and sieved prior to the continuous powder introduction microwave induced plasma optical emission spectrometry (CPI-MIP-OES) determination with helium plasma. Materials were introduced as a solid/gas aerosol. The effects of operating conditions and sample particle size on the analytical signal were evaluated. The amount of fluorine was measured using calibration standards prepared by dropping of standard fluoride solution on a suitable powdered support e.i. silica or activated carbon with a wide range of particle sizes of 0-63 μm.. A matrix matching was applied for external calibration in both soil and coal analysis. Calibration functions for fluorine are linear in the wide concentration range 20-5000 μg g^{-1}. Experimental detection limit for fluorine at line 685.6 nm obtained with the CPI-He-MIP-OES method was of the order 3-7 μg g^{-1} (depending on support composition); uncertainty was about 7-10%. These values are similar to DL of 4 μg g^{-1} obtained for aqueous fluoride using ultrasonic nebulization with aerosol desolvation and helium MIP sustained in a Beennakker-type cavity by Gehlhausen and Carnahan. Comparing direct techniques for

geological materials, the CPI-MIP-OES offers similar DL for fluorine that obtained by proton induced γ-ray emission (PIGE). The developed method was validated by carrying out the analysis of different certified reference materials including soils, fly ash and coals.

The CPI system proved to be an attractive tool as coupled with helium MIP-OES. The proposed method is adequate for the analysis of soils and fly ashes containing more than 30% of silica. The matrix influence of the different materials is relatively low, and thus it is possible to calibrate the analyses with just one material. The detection of fluorine in materials containing high concentrations of silica was improved using this method. Fluorine was determined in soil CRMs in the 300 to 2000 µg g^{-1} range. For all silica-based CRMs under study the values found agreed well with those certified, however, all found values were higher than respective certified values. It should be noted that these certified values were determined using an indirect procedure with ion selective electrode or spectrophotometry, hence, losses of the analyte were possible.

The proposed method is recommended for the analysis of coals as a rapid, precise and accurate technique that requires simple and minimal sample preparation at low cost. Low fluorine concentration of 25 µg g^{-1} was successfully determined in the NIST 1635 coal material.

TuPo78. DEVELOPMENT AND APPLICATION OF MICROANALYTICAL METHOD FOR INVESTIGATION OF BRAIN TISSUE BY LA-ICP-MS

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was used to determine the distribution of Zn, Cu and Pb in three brain areas, namely an insular region, a central cortex, and the hippocampus.

For investigation of brain samples a commercial laser ablation system (Ablascop, Bioptic, Berlin) was coupled to a double-focusing sector field ICP-MS (Element, ThermoElectron Corporation, Bremen, Germany).

From human control brain tissue surface (thickness 20 m) interest regions were cut out. The sample surface was scanned (raster area ~80 mm^2) with a focused laser beam (wavelength 213 nm, diameter of laser crater 200 µm, and laser power density 3×10^9 W cm^{-2}). Ion intensities of ^{208}Pb$^+$, ^{63}Cu$^+$, ^{64}Zn$^+$, were measured within the area of interest of brain tissue by LA-ICP-MS. The quantitative procedure was performed using matrix matched laboratory standards. The element distribution images as well as the concentration of selected elements are disscused.

TuPo79. NEW STAINING TECHNIQUE IN MEDICINE USING HEAVY METALS: IMAGING OF URANIUM AND NEODYMIUM IN RAT BRAIN SECTIONS BY LA-ICP-MS

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Specific toxicity of any compound or agent depends largely on its bioavailability in different organs or compartments of the organism considered. Traditionally, in toxicological research a compound of interest is fed to some test-organisms. Subsequently, these are dissected into different organs or compartments. Of these, homogenates are submitted to dedicated instrumental analysis.

This general procedure has some shortcomings. The way to the identification of the most harmful combinations of agent, formulation und critical structure is laborious and presupposes that the right formulation of the agent of interest is tested at the right dose and the right structure dissected.

New micro-local and imaging analytical techniques (e.g., by LA-ICP-MS [1-3]) enable an alternative rational test design for toxicological screening: Incubation of slices of post mortem tissue with the compound of interest followed by imaging mass spectrometric analysis allow to identify structures of interest and to estimate the relevant dose range.

We exemplify the first step of this procedure by a binding study of neodymium and uranium to rat brain sections. Rat brain tissue sections mounted on glass slides were incubated for 3h in 100 µg g^{-1} solutions of Nd and U, respectively, obtained by dilution of calibration standard stock solutions followed by 3 x 2 min washing in Milli-Q water and air drying. Imaging of U and Nd was carried out on adjacent sections by LA-ICP-MS. As the results of imaging mass spectrometry was found for U and Nd a high affinity to white matter contrasting with very low binding to gray matter. In addition U bound to the striatum somewhat more than in the cortex and Nd could not be detected in the cornu ammonis of the hippocampus. The developed technique can be applied as new staining technique in medicine. Imaging LA-ICP-MS of tissues incubated with compounds of interest provides an informative, versatile and rapid tool for toxicological research allowing the differentiation of critical substructures within organs.

[1]   J. S. Becker, M. V. Zoriy, C. Pickhardt, N. Palomero-Gallagher, and K. Zilles, *Anal. Chem.*, 2005, **77**, 3208.

[2]   M. V. Zoriy, M. Dehnhardt, G. Reifenberger, K. Zilles, and J. S. Becker, *Int. J. Mass Spectrom.*, 2006, **257**, 27.

[3]   J. S. Becker, M. V. Zoriy, C. Pickhardt and K. Zilles, *J. Anal. At. Spectrom.*, 2005, **20**, 912.

TuPo80.   IMAGING OF SELENIUM, COPPER AND ZINC IN THIN SECTIONS OF BIOLOGICAL TISSUES (SLUGS – GENUS ARION) MEASURED BY LA-ICP-MS

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Quantitative imaging analysis of essential and toxical elements within biological tissues is required for understanding of bioavailability, transport processes, to study possible contaminations and to monitor environmental risks by analyzing indicator organisms. An imaging mass spectrometric technique using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS [1, 2]) was developed to analyze selenium and metals distributions in thin sections of biological tissues (thickness: 100 µm), especially of slugs (genus arion). Slugs were fed with either placebo or solutions containing 1000 µg ml^{-1} Se as Na$_2$SeO$_3$ either alone or in combination with 160 mM NaNO$_3$ over 60 h. Thin sections of biological tissue together with synthetic laboratory standards were scanned (raster area: 25 mm x 45 mm) with a focused beam of a Nd:YAG laser (wavelength, 266 nm; diameter of

laser crater, 50 µm and laser power density, 3 x 10^9 W cm^{-2}) in a large laser ablation chamber. The laser ablated material was transported with argon as carrier gas to the ICP ion source at a double focusing sector field ICP-MS. Ion intensities of selenium (^{78}Se$^+$, ^{82}Se$^+$) were measured together with ^{13}C$^+$, ^{63}Cu$^+$ and ^{64}Zn$^+$ within the entire tissue section. Selenium was quantified using home-made homogeneous matrix-matched laboratory standards with added selenium at concentrations from 1 to 1000 µg g^{-1}. The regression coefficient of the calibration curve measured by LA-ICP-MS on these standards was 0.998. By imaging mass spectrometric analysis inhomogeneous distributions for Se but also for C, Cu and Zn in thin section of biological tissues were found. Selenium was enriched in the kidney (175 µg g^{-1} in Se-treated animals versus 15 µg g^{-1} in the placebo-treated animal, respectively) and in the digestive gland (125 µg g^{-1} versus 25 µg g^{-1}). Highest Se concentrations were detected in the gut of Se-treated slugs (250 µg g^{-1}) and additional Se occurred in the skin of these animals. Cu was enriched in the heart and the mucous ventral skin. Interestingly, in addition to the localization in the digestive gland, Zn was detected only in the dorsal skin but not the ventral skin. The developed analytical technique allows the quantitative imaging of selenium together with the imaging analysis of selected metals or non-metals in thin cross sections of biological tissue with limits of detection at sub µg g^{-1} range.

[1]   J. S. Becker, M. V. Zoriy, C. Pickhardt, N. Palomero-Gallagher, and K. Zilles, Anal. Chem., 2005, **77**, 3208.

[2]   M. V. Zoriy, M. Dehnhardt, G. Reifenberger, K. Zilles, and J. S. Becker, Int. J. Mass Spectrom., 2006, **257**, 27.