

INVESTIGATION OF THE SIMILARITY OF GROUND WATER SAMPLES
BASED ON MULTIVARIATE STATISTICAL EVALUATION OF TRACE
ELEMENT CHEMISTRY DATA OBTAINED BY ICP-TOFMS.

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In this work an attempt was made to determine the relationship between different subsurface waters – originating from two potable water production wells and surrounding monitoring wells – based on trace element chemistry data. The reason for this work was to provide background information for decision-makers concerning the similarities/differences and the possible natural communication of waters coming from different wells and a nearby river. Moreover this answer had to be given without the addition of any external contaminant/tracer to the aquifer of interest.

For this purpose 30 isotopes of 28 elements were simultaneously measured by an ICP-TOFMS in all the samples in order to generate a database of trace element data later used as the elemental fingerprint of the given water sample. Principal component analysis (PCA) was carried out on the samples where the variables were the monitoring wells. Since PCA was based on the statistical analysis of the correlation matrix of the data (working with normalised values) the quantitation of the samples were not necessary.

As a result, two subgroups of the samples could be identified where the first was containing the samples from production wells, and the other consists of waters sampled closest to the surface. Moreover, PCA results of the samples were in good agreement with their sampling depth.

ISOTOPE DILUTION ANALYSIS FOR TRACE ELEMENT SPECIATION

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Isotope dilution analysis (IDA) is a well known analytical technique based on the measurement of isotope ratios in samples where its isotopic composition has been altered by the addition of a known amount of an isotopically enriched element. Of course, isotope dilution analysis can be also applied to the determination of compounds instead of elements. The availability of different ^{13}C -labelled or deuterated compounds has caused a tremendous increase in the application of ID in organic and biochemical analysis. This is also due to the special requirements of this type of complex analysis in which the application of different off-line sample preparation techniques is usually needed prior to the final GC or HPLC separation. In the last few years we have seen the application of isotope dilution methodologies in some new analytical fields. One of those new fields is “elemental speciation” where the aim is the determination of the individual chemical species in which an element is distributed in a given sample. This new field has certain overlaps with both elemental and organic IDA. The enriched isotopes are those traditionally employed for “elemental” IDA (isotopes of Pb, Sn, Hg, Se, Cr, etc), although they are used here for the determination of elemental species or compounds as in conventional “organic” IDA. In most cases, the enriched isotopes are used to label an organometallic compound, such as methylmercury, but the label is on the metal and not on the carbon or hydrogen as it was traditional for organic IDA. This special type of labelling is particularly successful when ICP-MS detection is used for the measurement of the isotope ratios. However, that does not exclude the use of other ion sources, such as the electron impact source or the electrospray, with MS analysers.

During the application of IDA for elemental speciation new quantitation forms have been described. For example, post-column isotope dilution allows the accurate determination of elemental species even if the structure of the compounds is unknown while multiple isotopically enriched species can be applied for the evaluation and correction of species interconversion reactions. In this paper we will review different applications of isotope dilution analysis for elemental speciation. We will discuss also the particularities of the measurement of isotope ratios on transient signals by ICP-MS because an accurate and precise isotope ratio measurement is a pre-requisite for accurate concentrations to be determined, based on such measurements.

TRACE ELEMENT DETERMINATION IN THE EARTH SCIENCES: MEETING THE CHALLENGES

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The increasing pressure to generate extremely high quality data, for all available elements, in a timely and cost-effective way presents a great challenge to many ICP-MS facilities. Whereas 10-15 years ago geochemists would have been satisfied with data for perhaps a dozen elements, now there is an expectation that the complete suite of 40+ elements will be provided. Furthermore, in parallel with the development of laser ablation analysis, many studies now require the detailed trace element characterisation of extremely small samples.

Down-time related to daily or weekly maintenance (e.g., cone cleaning, replacement of tubing) can be dramatically reduced by employing the most sensitive instruments, as solutions are typically run after dilution by factors of 4 to >50 thousand times. Importantly, the ability to dilute samples to such an extent also makes single grain analysis possible (e.g., dissolution of single apatite crystals weighing less than a few tens of micrograms), without recourse to micro-sampling apparatus. Choosing an instrument with high sensitivity under normal operating conditions is therefore advantageous to any modern geochemical laboratory, irrespective of whether or not laser ablation analysis will be conducted.

One trade off in employing an instrument with high sensitivity has traditionally been the difficulty of analysing samples exhibiting large ranges in the concentrations of different trace elements. Rock samples with sub-ppm levels of some trace elements (e.g., Ta, Lu) may contain thousands of ppm of others (e.g., Ba, Sr). In addition, concentrations may vary considerably between rocks of a geologically related suite, and the ability to make comparisons between these is essential to the researcher. Clearly, the need for a reliable calibration of at least some elements across a large concentration range is critical.

We find the new Varian ICPMS routinely provides >300 million cps/ppm at In, in normal sensitivity mode, with oxide and doubly-charged levels less than 1% and 3% respectively. The novel 'dilution electrode' detector enables us to calibrate particular elements of interest that vary over many orders of magnitude in natural samples. We have monitored the abundances of >40 trace elements in a range of USGS standard reference materials (rock powders) over a period of several months and find that both reproducibility (<2%) and accuracy (routinely less than 5% for most elements) are outstanding. Importantly, these reference materials vary markedly in their trace element contents, yet memory effects are sufficiently low for us to place these sequentially within a run, without compromising data quality. In addition laser ablation analysis using a 193nm excimer laser ablation system has demonstrated that these features provide unparalleled opportunities for in situ analysis.

CORRELATION ANALYSIS IN ICP-OES: AN EFFICIENT TOOL FOR THE
DETERMINATION OF SUITABLE ANALYTE AND BACKGROUND EMISSION
REGIONS IN LINE-RICH MATRIX SPECTRA

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The introduction of solid state detectors in inductively coupled plasma optical emission spectroscopy (ICP-OES) about 10 years ago for the first time allowed the simultaneous registration of larger spectral regions or even total emission spectra of samples without the substantial reduction in throughput unavoidable with classical sequential systems. Combined with the computing power already available at that time, and even more so, available today, the use of chemometric methods for full spectrum evaluation, as applied extremely successfully e.g. in near-infrared spectroscopy, seemed a logical consequence.

Surprisingly, even with modern instruments, capable of simultaneous full-spectrum capture from the deep vacuum ultraviolet to the near infrared, most analytical applications of ICP-OES still use only negligible amounts of the available data, mainly in the form of peak positions (or peak areas) and background positions of only few, if not single, emission lines per element to be detected and quantified.

Reasons for this seemingly incomprehensible situation might be found in the already well developed ICP-OES methodology, which, frequently even standardized in prescribed methods, often contains both suitable analyte emission and background measuring positions, and even detailed methods for interference corrections. However, in difficult matrices and absence of such pre-developed methodologies, the analyst is often challenged in finding suitable measuring positions for the analytes of interest.

Using correlation analysis for complete sample emission spectra greatly assists in overcoming such problems. A suitable choice of standards and matrix blanks greatly simplifies method development in finding both suitable analyte and background emission regions in the spectrum, non-interfered by matrix contributions.

Based on a full-spectrum (ca. 45,000 individual pixel data) correlation analysis of the emission spectra of known standard and matrix samples, the algorithm allows the easy determination of suitable spectral emission regions for the determination of the analytes of interest. A figures-of-merit based approach selects, from user inputs, wavelength intervals, either resulting in the best signal-to-background ratio, best short-term stability, best background position, or a suitable compromise.

The presentation will discuss application examples of the described methodology for analytical method development and analysis of line-rich inorganic or organic samples. Specifically, analytical figures of merit shall be compared to more classical approaches, using only single or few emission lines per analyte element of interest.

IMEP - PLASMA SPECTROMETRY BASED MEASUREMENT CAPABILITIES
DEMONSTRATED ON ENVIRONMENTAL, CLINICAL AND FOOD SAMPLES
ACROSS THE INTERNATIONAL MEASUREMENT INFRASTRUCTURE

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The EC-JRC IRMM International Measurement Evaluation Programme (IMEP) is a tool to assess global equivalence and reliability of measurement results in areas where directives or regulations are applicable. Participating laboratories in IMEP receive the IMEP-certified test sample with undisclosed certified reference values with demonstrated traceability and uncertainty, as evaluated according to international guidelines. These certified reference values, as measured by reference laboratories, are completely independent from the IMEP participants' result. Participants in IMEP measure the analytes under investigation applying their routine measurement procedures and analytical techniques. In the last years due to the technical development in plasma spectrometry an increasing number of IMEP participants applied ICP-MS techniques. Also a representative number of participants used ICP-AES, ICP-OES techniques. IMEP participants are also invited to state uncertainty estimates for their reported results. In that sense IMEP serves also as a tool to monitor the implementation and efficiency of the European Accreditation multilateral agreement of equivalence, where accreditation bodies need to ensure compliance of their accredited laboratories with ISO/IEC 17025, reinforcing confidence of regulators in accreditation. Since 1989 IRMM enabled laboratories to demonstrate their measurement capabilities on Trace Elements and minor constituents analysis in various matrices like water, sediment, human serum, rice, tuna fish and others. Besides IMEP being a publicly accessible metrological tool, participants in IMEP are also nominated by international and European organisations from all levels of the measurement infrastructure. European Accreditation (EA), the International Federation of Clinical Chemistry (IFCC), the World Meteorological Organisation (WMO), the Community and National Reference Laboratories (NRLs), DG TAXUD and the International Organisation for Wine and Vineyards (OIV) nominated laboratories from their networks for participation in IMEP Interlaboratory Comparisons. IRMM assists the CIPM (International Committee for Weights & Measures) to support the CIPM-MRA (Mutual Recognition Arrangement) by making available the same samples as used in IMEP for Interlaboratory Comparisons in Chemistry among national metrology institutes and expert laboratories. These institutes are also free to measure the analytes under investigation applying their measurement procedures and analytical techniques of choice, but in order to support their measurement capability claims they need to report reliable results of highest metrological quality with demonstrated traceability and uncertainty. A majority of participants in CCQM comparisons apply ICP-MS. With this approach the competence of laboratories with different functions (e.g. reference, inspection, surveillance) applying plasma spectrometric and other analytical techniques can be compared throughout the European and International Measurement infrastructure.

APPLICATIONS OF FIELD-FLOW FRACTIONATION -
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Field- flow fractionation-inductively coupled plasma mass spectrometry (FFF-ICP-MS) has numerous applications for agricultural, biological, commercial, environmental, and industrial samples. Characterizing element-specific particle size distributions of natural and synthetic inorganic and organic materials is particularly useful in evaluating changes resulting from matrix variations. For example, polymerization and aggregation of bio- and environmental macromolecules can be characterized uniquely. Examples will be described.

The interaction between metal ions and humic matter was investigated using FFF-ICP-MS. Aggregation of a metal-spiked commercial Aldrich humic acid in the presence of calcium ion or in seawater was examined over suitable time intervals of 0 to 4320 min. The aggregation was demonstrated by shifts in peak maximum of humic size (2.9 nm) to larger size (5.1 or 5.8 nm in Ca²⁺ solution or in seawater, respectively), and also by the broadening of size distribution profiles. Size distributions of humic aggregates were characterized with FFF. Further, dominant particle size (2.9 nm), mean particle size (3.8 nm), and diffusion coefficient (1.51×10^{-6} cm²/s) of humic acid were determined. Associations of Cd, Cu, and Pb with humic aggregates were examined With FFF-ICP-MS. The mean diameters of Cd, Cu, and Pb in the original metal-spiked humic acid were 4.1, 4.5, and 5.8 nm, respectively. These diameters were shifted to 6.0, 6.0, and 6.9 nm, respectively, in the humic aggregate incubated with calcium solution; whereas, they were shifted to 6.5, 5.7, and 7.4 nm, respectively, in the humic aggregate incubated with seawater for 3 days.

RARE EARTH ELEMENT DETERMINATION OF ROCK SAMPLES BY
JY ULTIMA 2C-ICP-AES INSTRUMENT

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Geochemistry of the rare earth elements of rock samples is a very useful tool for the interpretation of genesis of geological samples. There are several instrumental techniques suitable for REEs determination like neutron activation analysis (NAA), X-ray fluorescent spectrometry (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES) and, more recently, inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS has advantageous detection limits for the REEs which are considerably better than the other methods mentioned above. In the laboratory of the Geological Institute of Hungary (GIH) ICP-MS technique is used for the REEs determination for about 10 years. Since the ICP-MS instrument of the GIH is rather old (VG PlasmaQuad II STE, 12 years old) and we had to face a lot of stability problems, an alternative method was developed for the REEs determination by the ICP-AES technique. A routine sample decomposition method was used (fusion with lithium metaborate in platinum crucible) which is the standard method for the major and trace element determination in the GIH laboratory. No separation or pre-concentration technique was used, the aim of this work was to see if this ICP-AES technique is good enough to analyse the REEs, and to get genetic information using the REEs' pattern.

Our JY ULTIMA 2C ICP-AES instrument was used for the analysis. This instrument has a 4320 gr/mm grating with very good constant resolution (5pm) in the wavelength range for the REEs of up to 430 nm. The sensitivity is not as good as the ICP-MS sensitivity, therefore the stock solution, (2 g/l in rock sample) was analysed compared to the ICP-MS determination, where a 10 times diluted solution (0.2 g/l rock sample) was used for the analysis. Results & some problems of the ICP-AES determination of the REEs are discussed in this lecture.

Even with high resolution, there are a lot of spectral overlaps for the REE lines. Some of them can be corrected using the inter-element correction (IEC) facility of the JY software. Some other overlaps occur where the interfering elements are also trace elements with normally less concentration than the analytes. For this reason their contribution to the signal is not huge, so this can be overcome using at least 2 sets of calibration standards. Their contribution is significant to the analyte only if they are together in a mixed calibration standard, but not in real rock samples. The overlapping pairs should not be in the same solution for example, La and Th; Ce and Dy; Nd and Tb and so on, these should not be present in the same calibration solution. The Pr 390.843nm line is overlapped by the Ce 390.854 nm line. The IEC correction is working, but not stable all the time. When IEC is used, the high resolution may cause instability because of the hyper-fine structure of the 390 nm Pr line. The effect of the resolution is studied for the IEC of this Pr line.

Very good results could be reached for the relatively higher "Clark" elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb, Hf, Th, Y, Zr). The relatively low "Clark" elements gave poor correlation with the certified values (Tb, Ho, Tm and Lu). The reason for

this is that the detection limits of these elements are very close to the low “Clark” values, this means much better results can not be expected for the low Clark elements. The REEs pattern had acceptable profiles, it means the method can be used for the genesis of rocks, except the very low REEs content rocks, like pure dolomite or Gabbro

QUANTITATIVE METALLOMICS AND TRACER STUDIES ON
METALLOPROTEINS IN HUMAN BRAIN SAMPLES BY LA-ICP-MS AND
MALDI-FTICR-MS AFTER 2D GEL ELECTROPHORESIS

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A new combination of atomic and molecular mass spectrometric methods was developed for the characterization and identification of several metalloproteins [1]. Human brain protein mixtures were separated by two dimensional (2D) gel electrophoresis and the protein 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 P, S, Cu, Zn and Fe. Selected protein spots in 2D gel containing these elements were identified after tryptic digestion by matrix assisted laser desorption ionization Fourier transform ion cyclotron resonance mass spectrometry (MALDI-FTICR-MS). Results of structure analysis of proteins by MALDI-FTICR-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, phosphorylation state and metal content as well.

In order to study the formation of proteins containing Cu, Zn and Fe in a human brain sample isotopic-enriched tracers (^{54}Fe , ^{65}Cu and ^{67}Zn) were doped to two-dimensional gels of separated Alzheimer-diseased brain proteins after 2D gel electrophoresis. The protein spots were screened systematically by LA-ICP-MS, Fe- $^{54}\text{Fe}/^{56}\text{Fe}$, Cu- $^{65}\text{Cu}/^{63}\text{Cu}$ and Zn- $^{67}\text{Zn}/^{64}\text{Zn}$ isotope ratios in metalloproteins were measured directly by LA-ICP-MS. The identification of singular protein spots from Alzheimer-diseased brain separated by two-dimensional (2D) gel electrophoresis [2] was attempted by high-resolution biopolymer mass spectrometry (MALDI-FTICR-MS) after excision from the 2D gel and tryptic digestion.

[1] J. S. Becker, M. Zoriy, U. Krause-Buchholz, J. S. Becker, C. Pickhardt, M. Przybylski, W. Pompe, G. Rödel, *J. Anal. At. Spectr.* 19 (2004) 1236.

[2] J. S. Becker, M. Zoriy, J. S. Becker, C. Pickhardt, M. Przybylski, *J. Anal. At. Spectr.* 19 (2004) 149.

PHOSPHO- AND METALLOPROTEOMICS BY COMBINATION OF MALDI-FTICR-MS
AND LA-ICP-MS AFTER 2D GEL ELECTROPHORESIS

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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-FTICR-MS (matrix assisted laser desorption ionization Fourier transform ion cyclotron resonance mass spectrometry) the quantitative determination of phosphorus and metal (e.g., Fe, Cu, Zn) concentration in brain tissues and fluids is required, because phosphorylation is one of the most important modifications of proteins, and metal ions as cofactors for enzymes are of crucial relevance for many physiological as well as pathophysiological processes such as in carcinogenesis and neurodegenerative diseases. A new combination of atomic and molecular mass spectrometric methods was developed for the characterization and identification of several phospho- and metalloproteins [1,2]. Several protein mixtures were separated by two dimensional (2D) gel electrophoresis and the protein spots were fast screened by microlocal analysis using LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) in respect to several elements. Selected protein spots in 2D gel containing P, S, Cu, Zn and Fe were identified after tryptic digestion by MALDI-FTICR-MS. Results of structure analysis of proteins by MALDI-FTICR-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, phosphorylation state and metal content as well.

- [1] J.S. Becker, M. Zoriy, U. Krause-Buchholz, J.Su. Becker, C. Pickhardt, M. Przybylski, W. Pompe, G. Rödel, *J. Anal. At. Spectrom.* 19 (2004) 1236.
- [2] J.Su. Becker, M. Zoriy, C. Pickhardt, M. Przybylski, J.S. Becker, *Int. J. Mass Spectrom.* (in press).

NEW HORIZON IN BRAIN RESEARCH USING LA-ICP-MS: PROTEOM ANALYSIS BY
COMBINATION WITH MALDI-FTICR-MS AND IMAGING OF BRAIN TISSUES

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For identification of metal-containing proteins and determination of Cu, Fe, Zn concentration in human brain proteins a combination of atomic and molecular mass spectrometric methods was developed. The protein mixtures were separated by two dimensional (2D) gel electrophoresis and the protein 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 P, S, Cu, Zn and Fe. Selected protein spots in 2D gel containing these elements were identified after tryptic digestion by matrix assisted laser desorption ionization Fourier transform ion cyclotron resonance mass spectrometry (MALDI-FTICR-MS). Results of structure analysis of proteins by MALDI-FTICR-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, phosphorylation state and metal content as well. In order to study the formation of proteins containing Cu, Zn and Fe in a human brain sample isotopic-enriched tracers (^{54}Fe , ^{65}Cu and ^{67}Zn) were doped to two-dimensional gels of separated Alzheimer-diseased brain proteins after 2D gel electrophoresis and analyzed by LA-ICP-MS and MALDI-FTICR-MS.

Furthermore, LA-ICP-MS was used to produce images of element distribution in 20 μm thin sections of brain tissues from the hippocampus. The quantitative determination of copper, zinc, uranium and thorium distribution in thin slices of human brain samples from the hippocampus was performed using matrix-matched laboratory standards. In addition, a new solution based calibration procedure using micronebulizer, which was inserted directly in the laser ablation chamber was applied for validation of analytical data. The mass spectrometric analysis yielded an inhomogeneous distribution (layered structure) for P, S, Cu and Zn in thin brain sections of hippocampus.

J. S. Becker, M. Zoriy, J. S. Becker, C. Pickhardt, M. Przybylsky, J. Anal. At. Spectrom. 19 (2004) 149.

DETERMINATION OF LITHIUM IN BRAIN SAMPLES

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Since the discovery of its antimaniac effect in bipolar disorder in 1949, lithium has been regarded as one of the most interesting metals in clinical science. Recent findings about its neuroprotective role against several kind of stress both in vitro and in vivo have underlined the importance of the element. Furthermore, its inhibitory effect on glycogene-synthase-kinase-3 -protein phosphorylation, which leads enzyme, the likely causative factor in -protein dephosphorylation, to neurodegeneration, together with its promotory effect on have even positioned lithium as a possible therapeutic agent in neurological disorders like Alzheimer's disease.

However, concentration data for this element in human brain tissue are scarce, although normal and pathological condition lithium levels could enhance the better interpretation of biochemical and clinical experience. This lack of information can mainly be attributed to the analytical difficulties associated to lithium quantification at naturally occurring levels in solid biological matrices.

Our present investigation focused on lithium determination in brain tissue samples from subjects having not suffered from central nervous system diseases. Four German (six brain areas studied) and one Hungarian (twelve brain region sampled) subjects were included in the investigations. After optimisation of sample dissolution, two methods were used in experiments: inductively coupled plasma - atomic emission spectrometry with ultrasonic nebulisation and inductively coupled plasma - mass spectrometry with quadrupole mass spectrometer. For concentration evaluation the 670,78 nm wavelenght and the ^7Li isotope were used, respectively.

Lithium concentrations were in the 3-21 ng/g (dry weight) range. Distribution pattern seems to be rather heterogeneous for this element, with apparently higher values in parietal and thalamus, regions responsible for knowledge and emotions, while lower levels occurred in substantia nigra and Ammon's horn, areas of extrapyramidal and autonom system. Left hemisphere values had a tendency to be lower in every brain part, though the difference between the two sides was not significant in statistical sense.

Results obtained by different methods showed a good correlation (significant at $p < 0,0001$ level). Finally, performance characteristics of the two techniques were compared, together with a discussion of their applicability.

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CATHODE AND ANODE MATERIAL INFLUENCE ON THE ELECTRICAL
AND OPTICAL PROPERTIES OF A RADIOFREQUENCY GLOW DISCHARGE
USED FOR OPTICAL EMISSION SPECTROSCOPY

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Glow discharge optical emission spectroscopy (GD-OES) is an analytical technique widely used in analytical chemistry for elemental analysis [1]. The technique is based on the analysis of the optical emission of atoms sputtered from the cathode and excited in the plasma.

The rf-GD-OES analyses were conducted using a RF source identical to the one of the JY 5000 RF instrument, manufactured by Jobin-Yvon Horiba (JY). The rf source was removed from the instrument to facilitate more fundamental studies of the source. The source used a 4 mm diameter anode. To monitor the current and voltage characteristics of the isolated source, two currents probes and a voltage probe were used as described in [2].

In this paper, we analyse the electrical properties (current, voltage, power) and the optical properties (750.4 nm argon line intensity) for different cathode and anode materials. We present results for conducting and non conducting samples. An electrical circuit is developed to take into account the capacitance of non conductive materials and we present how the capacitance influence the power coupling efficiency. Some possible improvements will be presented more particularly devoted to oil-bearing rocks analysis.

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FURTHER INVESTIGATIONS OF THE EFFECT OF MOLECULAR SPECIES ON
THE ANALYSIS OF ORGANICS WITH GD_OES

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In earlier work, it has been shown that molecular emission can give rise to elevated background signals in GD-OES [1,2]. This was first observed in near-surface analysis applications, but molecular emission has also been shown to be present throughout the sputtering of thicker organic layers. Several molecular bands have been identified in the emission spectrum; all of these originate from simple diatomic molecules, e.g. OH, NH and CH [3,4]. Since molecular emission bands are typically broad structures consisting of a very large number of poorly resolved lines, they give rise to line interference at several atomic emission lines used for elemental analysis.

In this work, the molecular background emission at wavelengths of several atomic analytical lines is investigated using a RF source to sputter a polyester paint coating. The results show that at constant power, the backgrounds increase with high voltage – low-pressure conditions. By contrast, at constant power the emission from atomic emission lines increase with high current – high-pressure conditions. This confirms earlier results using a DC source to sputter a conducting epoxy-based coating [4].

An additional observed problem in quantitative depth profiling of organic layers is that the emission yield from carbon is typically considerably lower than in metallic matrices. This means that with a calibration for carbon based on e.g. cast irons, the determined carbon content in an organic will be much too low. In this work, the correlation between the emission yield for carbon and the emission intensity of CH in a primer paint coat is studied. It is shown that there is an anti-correlation between the two. This is an indication, but not conclusive evidence, that the loss of carbon emission yield in organics can be due to substantial molecular formation in the plasma, reducing the fraction of atomised carbon.

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CONSTANT PRESSURE OR CONSTANT IMPEDANCE – A BRIEF HISTORY OF THE EMISSION YIELD CONTROVERSY IN GD-OES

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In 1985, the first “empirical intensity expression” for GD-OES was published by Bengtson [1]. It described the emission intensities as a function of voltage, current and sputtering rate, but explicitly did not include pressure as a parameter. This was motivated by “hand-waving arguments”, but not thoroughly investigated. In short, the first empirical expression showed that the atomic emission intensities increased as the square of the current and as the square root of the voltage. From this basic intensity expression, further refined in 1990 [2], a first expression for the emission yield (EY) was derived.

In 1993, Payling et.al. published a paper where it was argued that the EY in fact is a function of the pressure only, and the results of Bengtson were indirect manifestations of varying pressure.[3]. The result was that the EY simply increases linearly with the pressure. This claim was in fact at odds already with the results in [2], since consistent results for steels and an aluminium sample were then obtained, and these two materials run at substantially different pressures at constant voltage and current.

In the years to come, Payling, Bengtson et.al. and Marshall carried out several experimental investigations of the emission yield as a function of discharge parameters [4,5,6]. In all investigations, the technique was to vary all three discharge parameters by using sets of CRM’s of different alloy types with different electrical characteristics. At constant impedance, steels and copper base alloys operate at similar pressures, aluminium considerably lower, and Zn alloys somewhere in between. The results of all investigations were the same – the two most important parameters determining the EY are current and voltage, only a slightly decreasing trend with pressure could be found. This means that Payling’s 1993 paper was wrong both in magnitude and the sign of the pressure influence.

The implication of the investigation of the EY variations with the discharge parameters is that the best way to do a multi-matrix calibration is to lock down the electrical parameters of the source and allow the pressure to vary. Examples of calibrations using different operational modes will be shown and discussed.

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MULTI-ELEMENTAL SPECIATION IN ENVIRONMENTAL WATERS

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In environmental waters, elements can exist in a variety of forms, some of which occur naturally and some which result only from anthropogenic activities.

The various forms (or species) of elements may possess different characteristics which will cause them to have different health and environmental impacts. For example, Cr(III) is an essential nutrient to living organisms, but Cr(VI) is toxic. Therefore, the need exists to separate and measure the individual species of various elements.

Speciation analysis can be accomplished by coupling a separation technique to an elemental detector. In this work, an HPLC is coupled to a Dynamic Reaction Cell (DRC) ICP-MS. HPLC provides the powerful ability to separate many species, while ICP-MS allows low-levels to be measured. The use of a DRC is important because it eliminates the effects of spectral interferences resulting from the sample or mobile phase components, thereby allowing lower levels to be measured than by conventional ICP-MS.

Speciation analysis has traditionally focused on one element at a time, a necessity based on the chemistry required to separate species. However, by careful selection of the column, mobile phase, and chromatographic conditions, multiple elements can be separated in a single injection, taking advantage of the multi-elemental capability of ICP-MS.

This work will focus on simultaneous multi-elemental speciation in environmental water samples, specifically looking at As, Cr, and Se. By careful selection of chromatographic conditions, a total of seven species (AsIII, AsV, CrIII, CrVI, SeIV, SeVI, SeCN) can be separated in a single injection in under six minutes using ion-pairing chromatography. By selection of appropriate reaction cell conditions using oxygen as reaction gas, interferences on As, Cr, and Se can be greatly reduced, allowing major isotopes to be used for detection.

The ability to measure bromate and bromide will also be discussed. This separation is accomplished with ion-exchange chromatography. The method is applied to drinking water samples.

Future work will explore the possibility of developing a simultaneous drinking water speciation method, where Br and other elements (Cr, As, and/or Se) will be separated and measured in a single injection, simultaneously.

USE OF LANTHANUM HYDROXIDE AS A TRAPPING AGENT IN THE As
AND Sb DETERMINATION BY HG-ICPOES

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The use of lanthanum hydroxide as a trapping agent in a knotted reactor coupled to hydride generation-inductively coupled spectrometry (HG-ICPAES) was studied in this work to determine hydride-forming elements, specifically arsenic and antimony, in seawater samples.

After performing a pre-reduction of As(V) and Sb(V) with thiourea, sample pH was adjusted to 2.75 with NaOH and La added. In the next step, samples were introduced in a knotted reactor where As and Sb were retained in contact with a NH₃/NH₄ buffer. The optimisation of determination conditions was carried out using a continuous flow system where the analyte eluted with HCl was carried to the gas-liquid separator after forming the hydride and then to the ICP-torch using an Ar flow. A Plackett-Burman design 29*3/128 was proposed to select the main factors affecting pre-reduction, trapping and element determination. The factors for As analysis were the pH, [NaBH₄] and Ar flow, whereas factors for Sb determination were knotted reactor length, mg of La added to the sample, [NaBH₄] and [HCl].

Afterwards, a central composite design 25-1 + star design was proposed to select the maximum sensitivity (slope of the calibration graph) in the determination of As and Sb. The optimum conditions for As determination were: [HCl] = 2.05 M, [NaBH₄] = 1.28%, mg La added = 53.1 mg/100mL, tampon pH = 8.62 and Ar flow = 0.37 L/min. The optimum conditions for Sb were: [HCl] = 2.05 M, [NaBH₄] = 1.28 M, mg La added = 28.5 mg/100mL, tampon pH = 8.91 and Ar flow = 0.58 L/min.

Limits of detection (LOD) and limits of quantification (LOQ) were calculated in the conditions defined for Sb determination and introducing in the system 16,4 mL of sample. LOD and LOQ were 0.15 and 0.50 mg L⁻¹ respectively (As 188.979 nm) and 0.26 and 0.86 mg L⁻¹ (Sb 217.582 nm). Performing the trapping off-line (85 mL of sample), LOD and LOQ were 0.051 and 0.17 mg L⁻¹ (As 188.979 nm) and 0.091 and 0.30 mg L⁻¹ (Sb 217.582 nm).

THE ROLE OF PLASMA MASS SPECTROMETRY FOR THE
CHARACTERIZATION OF NUCLEAR SAMPLES AS WELL AS FOR THE
DETECTION AND SURVEILLANCE OF RADIOACTIVITY IN THE
ENVIRONMENT

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Radionuclides, particularly the long-lived ones along with trace elements, represent nowadays, an important category of inorganic pollutant that need to be determined not only in nuclear samples, like for instance nuclear fuels but also in environmental samples, as soils and sediments as well as waste materials.

In the field of nuclear research and technology, the chemical characterization of different type of fuels, cladding materials, nuclear wastes and smuggled nuclear samples, from the point of view of traces, major and minor elements as well as from their isotopic composition, is of high relevance. For instance, the acceptable levels of impurities in fresh nuclear fuels vary according to the characteristics of the reactor. In order to monitor contamination during the fabrication process, the determination of trace elements should be performed on the starting material as well as on the final pellets of fresh fuel. Moreover, among the several post-irradiation examinations carried out on spent nuclear fuel, chemical analyses are performed in order to assess the amount of fission products and minor actinides produced. These measurements are used to test experimentally the predictions of theoretical calculations.

In the environment, radionuclides containing samples can originate through different systems and processes. Human activities involving nuclear weapons and nuclear fuel cycle (including mining, milling, fuel enrichment, fabrication, reactor operation, spent fuel stores, reprocessing facilities, medical applications and waste storage) are important, and may lead to a significant creation of this kind of samples. Human technology also releases pre-existing natural radionuclides, which would otherwise remain trapped in the earth's crust. For instance, burning of fossil fuel (oil and coal) dominates direct atmospheric release at pre-existing natural radioactivity. The ability to develop adequate models for predicting the fate of inorganic contaminants, including radionuclides, in both surface and subsurface environments, is highly dependent on accurate knowledge of the partitioning of these constituents between the solid and solutions phases and ultimately on the capability to provide molecular-level information on chemical species distributions in both of these phases. Furthermore, the development of environmentally sound yet cost effective remediation strategies requires an understanding of the chemical speciation of the contaminants within the sediment, soil and waste material matrices in which they are contained.

To answer questions in both these two research fields, analytical methods with proven reliability, accuracy and precision are necessary. Among the currently available instrumental techniques, those based on plasma mass spectrometry provide excellent sensitivity, precision and good accuracy.

In this lecture plasma mass spectrometric techniques such as GDMS and ICP-MS (both quadrupole and magnetic sector based) are discussed as for the characterization of nuclear samples as well as for the measurement and surveillance of radioactivity in the environment. Moreover, the importance of hyphenation methods is highlighted as applied to samples of different origin. The necessity to have complementary techniques in order to have independent results (in terms of Quality assurance/quality control) as well as to attain a complete inventory of the radioisotopes is shown. The figures of merit of the different techniques are discussed on the basis of more than ten years of their applications in our laboratories to real samples.

THE ON-LINE COUPLING OF GEL ELECTROPHORESIS (GE) AND
INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS)

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Today gel electrophoresis (GE) provides the most powerful separation technique in bioanalytical research and is the method of choice for the separation of proteins, DNA fragments and other high-molecular biological compounds. On the other hand, elemental mass spectrometry, e.g. ICP-MS, offers isotope-selective detection, which has been and still is of great interest in genomics, proteomics and metalloproteomics.

Several approaches have been undertaken to combine the separation power of electrophoresis and the detection power and high elemental selectivity of ICP-MS, e.g. on-line coupling of capillary electrophoresis (CE) with ICP-MS and 2-D GE with laser ablation-ICP-MS. None of these developments has yet entered the basis of routine analysis, mainly due to complex handling, low reproducibility and difficulties in quantification.

In this paper we present the development of the on-line coupling of GE and ICP-MS. The principle bases on the preparative GE in which the analytes are first electrophoretically separated and afterwards eluted from the gel. The separated compounds are introduced on-line into the ICP-MS by a continuous-flow system (100 $\mu\text{L}\cdot\text{min}^{-1}$) coupled to a μ -flow nebulizer for sample introduction. Separation of metalloproteins and DNA fragments are examples for the applicability of this method.

CHARACTERIZATION OF A NEW ORTHOGONAL ICP-TOFMS SYSTEM

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In the field of multielemental analysis inductively coupled plasma mass spectrometry (ICP-MS) has demonstrated excellent analytical utility and found use in a wide range of applications. But most of the commercially available mass spectrometers have predominantly been constructed around scan-based, quadrupole or double-sector mass filters, which show some disadvantages compared to time-of-flight (TOF) mass analyzers. In such systems the measurements are performed sequentially, only one mass at a time, which results in a loss of precision and/or sensitivity with an increasing number of isotopes monitored.

Since time-of-flight mass spectrometers (TOFMS) are operated in a truly simultaneous fashion, they provide several important advantages over conventional ICP-MS detection systems. TOFMS not only permits the measurement of almost all elements and isotopes in a transient sample pulse but also enables a great number of complete atomic mass spectra to be recorded each second. Typical instruments can collect tens of thousands of such spectra each second and the software enables hundreds of summed spectra to be displayed within the same time frame. This high spectral-generation rate makes TOFMS ideally suited for the measurement of very short transient signals and even chromatographic peaks that exhibit tailing can be recorded with high fidelity. Furthermore, because each complete mass spectrum is derived from the same brief (nano-second level) pulse of ions, high precision can be achieved by using either isotope-ratioing or internal standardization techniques. As a result the compromise between mass coverage and sensitivity and precision inherent to scanned systems does not apply to the TOFMS.

In this presentation, the analytical performance of a novel orthogonal ICP-TOFMS system will be presented and the corresponding figures of merit, such as detection limits, mass resolution and precision will be compared to other TOF- and quadrupole-based systems. Advantages and disadvantages of the new system will be explored, and future developments in ICP-TOFMS will be outlined.

DEPTH PROFILING OF ION IMPLANTS USING LASER ABLATION AS ION SOURCE AND CHARACTERIZATION MICROPROBE

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Ion implantation is important in many materials science applications [1] whenever optical, electrical, or thermal properties must be tailored. Ions for implantation are generated either by means of complex ion-gun beamlines or within plasmas. Laser-induced plasmas as sources for ion implantation are a recent advance, showing several benefits over traditional approaches, not least the possibility to combine processing and characterization on the same system. The working principle is based on the fact that a laser beam ablates a reservoir material to produce a compositionally-controlled plasma. By means of a pulsed voltage, ions are extracted from the laser-induced plasma source and accelerated toward a workpiece for implantation. Then, the laser beam might be directed toward the workpiece and perform locally depth profiling analysis in combination with inductively coupled plasma mass spectrometry (LA-ICPMS).

As reservoir materials Ge, Al, or Cu targets were ablated and these elements were implanted in Si single crystals (111) or (100) at 40 kV. Then LA-ICPMS was used for depth-resolved characterization of the samples. LA-ICPMS showed high detection power matching with the low implanted dose, combined with competitive lateral resolution, determined by the focusing optics chosen to obtain a compromise among spot size, working distance and depth of focus. Depth resolution was originally degraded to a micron by sample introduction delay (transient signal waning time) and also limited by ICP-MS detection speed and data point sampling frequency. Single shot analysis, aerosol gating, and mathematical signal processing were deployed to improve depth resolution down to few tens of nm, still providing reasonable SNR's. Multiple quantitation strategies were implemented to obtain spatially resolved element content information. External calibration using silicon powder (NIST 57a), ferrosilicon powder (NIST 58a) as pressed pellets or glass (NIST 610, 612) certified reference materials (CRM) was evaluated first. Matrix-dependent as well as crystal-orientation-dependent ablation yields were observed, which suggested use of internal standardization over matrix element. Calibration using powder turned out to be less reliable for these samples than use of matrix-unmatched bulky CRMS's. Alternative quantitation algorithms were developed and tested using signal structure characteristics.

In order to validate the measurements, both theoretical and experimental work was done. Monte Carlo simulations were performed to figure out theoretical depth profiles of Ge, Al and Cu in the Si host. Results showed that the expected implanted doses were laterally and depthwise variable. Maximum implantation depths for a 40 kV extraction voltage were of few hundreds of nm, namely 160 nm for Ge, 330 nm for Al, and 200 nm for Cu, which were a factor of 2 smaller than first results using LA-ICPMS depth profiling. Other analytical techniques [2], like Rutherford backscattering spectroscopy (RBS), electron recoil diffraction analysis (ERDA), scanning electron microscopy (SEM-EDX), auger emission spectroscopy (AES),

secondary ion mass spectrometry (SIMS), and glow discharge optical emission spectroscopy (GD-OES) were implemented.

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EXPERIMENTAL INVESTIGATIONS ON ICP-INDUCED VAPORIZATION OF
SOLID PARTICULATE
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Direct solid sample analysis (DSSA) using plasma-source spectrometry (ICP-OES or ICP-MS) offers the advantage of minimizing time-consuming sample preparation steps, reducing mineral acid related contamination risk as well as opening the possibility of spatially-resolved analysis. Any sample introduction technique for DSSA, e.g. laser ablation, slurry technique etc. is based on the introduction of a solid particulate into the atomization source, with impact on atomic excitation and ionization equilibria.

The mechanism and efficiency of solid particulate vaporization was theoretically and experimentally investigated. A frame model was applied to the results. Controlled introduction of several particulate ensembles into the ICP permitted to determine signal characteristics from plastic, metallic, and glass particles spanning from 30 nm up to a few microns. Certified reference material as well as particle size standards were used and introduced into the ICP as dispersion in aqueous solution.

Particle introduction velocity, as determined by the carrier flow rate, was found to be the most effective parameter. Variation of radiofrequency power, influencing the energy budget in the ICP, did not show relevant impact on transient signal response. Element-dependent response was observed which was attributed to mass load into the plasma-source and excitation/ionization equilibria. Kinetic factors of the vaporization process seemed to be more decisive than thermodynamic aspects.

MULTIELEMENTAL CHARACTERIZATION OF COMPOST LEACHATES BY
SEC AND FIFFF COUPLED TO ICP-MS

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The increasing use of compost for different purposes, such as soil amendment to improve soil structure or as fertiliser to provide macro- and micronutrients to plant growth, has led to several regulations (i.e. European Commission 2001/688/EC) to control contaminants and ensure environmental and human health and safety.

Since a long time it is recognized that humic substances (HS) play a key role in many environmental processes, such as surface adsorption on soil and aquatic colloids, or complex formation with ionic compounds. These complexing properties are considered to be an important factor controlling the solubilization, speciation, and transport of natural species as well as of anthropogenic pollutants. Since HS represent a complex mixture of heterogeneous organic materials with different structures and a broad size distribution, a variety of separation methods are widely used to isolate or fractionate the HSs before further investigation. Among these separation methods, chromatographic techniques based on a size-exclusion effect and Flow field-flow fractionation (FI-FFF), which separates components strictly by their hydrodynamic size, have been commonly applied to HSs characterization 1. The combination of these techniques with on-line elemental detectors such as ICP-MS offers extremely powerful particle size fractionation and multi-element determination of major, minor and trace elements with low detection limits.

In this study a method for the characterization of a compost leachate derived from urban solid waste has been developed by high-performance size-exclusion chromatography (HPSEC) and FI-FFF coupled to ICP-MS. By these two methods it can be recognized that trace elements are either bound to humic matter like polyelectrolytes, where at least two colloid types of different size could be resolved, or exist as dissolved ionic species. Results have been also compared with those obtained by ultrafiltration studies.

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LA-ICP-IDMS USING HIGH PULSE ENERGY LASER RADIATION: CROSSING
THE BORDERS IN DIRECT TRACE ELEMENT ANALYSIS IN SOLID
SAMPLES

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During the last decade, the application of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has constantly increased and a great number of publications demonstrate the merits of this method for the direct analysis of trace elements in solid samples for almost all fields of science and technology. Nevertheless "...much more work is needed to improve its use even further" as Gary M. Hieftje noted at the 2004 Winter Conference on Plasma spectrochemistry [1].

In the present work high energy laser with pulse energy of up to 210mJ is coupled with a sector-field ICP-MS for direct determination of usually "difficult-to analyse" elements in solid samples. The much higher ablation rate results in a higher by about two orders of magnitude sensitivity compared with the common LA systems and improves precisions which makes this system suitable for precise analyses of less homogeneous samples. Isotope dilution (ID) technique is applied for quantification which compensates inter-element fractionation effects and matrix effects in LA-ICP-MS.

Application of high pulse energy laser radiation in this work allows extending the number of elements and the concentration range usually analysed by LA-ICP-MS. The full use of high sensitivity is demonstrated on an example of direct analysis of long lived actinides in environmental samples. Furthermore, LA-ICP-IDMS is applied for a direct and simultaneous determination of chlorine, bromine, and iodine in rocks, sediments and similar samples. Inter-halogen and analyte/spike fractionations have been investigated for LA-ICP-MS measurements to evaluate possible errors in halogen determinations. LA-ICP-IDMS is also used for analysis of silicon concentrations in environmental and industrial samples whereas direct solid sampling without dissolution and dilution of samples minimizes possible losses of analyte and improves detection limits.

Finally, a possible employment of gas-phase reactions in laser induced plasma for reducing particular interferences in LA-ICP-MS will be discussed in the talk.

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ICP-MS DETERMINATION OF EXTREME URANIUM ISOTOPE RATIOS
USING A NEW MICROFLOW NEBULIZER SYSTEM
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A double-focusing ICP-MS was coupled with the new microflow nebulizer system APEX for uranium isotope analysis, in particular for the determination of extreme $^{236}\text{U}/^{238}\text{U}$ isotope ratios. The new sample introduction system allows an improvement of the sensitivity by a factor of six and a reduction of the oxide and hydride molecular ions by up to two orders of magnitude. Thus, a sensitivity of more than 5000 counts/fg can be achieved for uranium, which is significantly higher than the sensitivity provided by other nebulizers. The abundance ratio sensitivity for $^{236}\text{U}/^{238}\text{U}$ is as low as 0.3ppm at mass resolution of 4000. ICP-MS coupled with an APEX system therefore allows to expand the measured concentration range of ^{236}U by about one order of magnitude.

^{236}U was used to monitor spent uranium (i.e. the main nuclear fuel component having been burned in a nuclear reactor) in soil samples collected in the vicinity of the Chernobyl Nuclear Power Plant (NPP) from nuclear fallout using inductively coupled plasma mass spectrometry (ICP-MS). A comparison of $^{235}\text{U}/^{238}\text{U}$ isotope ratio measurements with the $^{236}\text{U}/^{238}\text{U}$ ratio provides more sensitive and accurate determinations of the portion of spent uranium in soil samples down to 0.01% by using the last mentioned isotope ratio. Concentrations of ^{236}U in the upper soil layers (0 cm – 10 cm) of samples from Belarus were found to be 0.1 pg/g to 810 pg/g depending on the distance to the Chernobyl NPP.

ICP-MS coupled with APEX can also be used as a very powerful method for ultratrace isotopic analysis of long-lived plutonium nuclides (after chemical separation of Pu from U with a decontamination factor of about 10^6 or more) in environmental monitoring, forensic studies etc.

DIRECT SOLIDS ANALYSIS OF REFRACTORY POWDERS BY PLASMA ATOMIC SPECTROMETRIC METHODS

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Refractory powders, as they are the base for many new technologically important materials still constitute a challenge with respect to their trace elements characterization, which is of great importance for challenging fields of application in which they are used. This applies to ceramic powders such as Al₂O₃ a.o. with respect to their trace elements contents and to powders of potential use as precursors for the production of high-temperature superconductors, where the knowledge of the stoichiometry is very important. For both fields inductively coupled plasma atomic emission spectrometry (ICP-OES) and mass spectrometry (ICP-MS) will be shown to be powerful methods, when combined with suitable techniques of sample introduction.

With electrothermal evaporation from a graphite furnace coupled to ICP-OES, a number of trace elements can be determined down to the µg/g-level in industrially important Al₂O₃ powders, without the particle size of the powders being too critical. By using standard addition with multielement solutions trace concentrations of Ca, Fe, Ga, Mg, Mn, Na, V and Zn can be reliably determined in powders with good accuracy and precision, as also shown by the analysis of a standard reference material. The use of evaporation aids such as AgCl could be shown to be favorable both for optimizing the evaporation efficiency and the peak form of the transient signals [1]. With ICP-MS using electrothermal evaporation of dry suspension residues from a graphite furnace, reliable determinations down to the µg/g level also for elements like Fe and V, are possible. Especially the use of thermochemical aids like PdCl₂ was found useful for elements like Mn, V and Ni. [2]. Both approaches will be shown to enable reliable determinations in Al₂O₃ by comparing the analysis results with those of sample dissolution in combination with ICP-OES and MS as well as with totally independent methods such as total reflection X-ray fluorescence spectrometry [3].

For the study of the stoichiometry of new materials and especially in the optimization of their synthesis high-precision determinations of metals and non-metals at the major elements concentration level are a particular challenge. Here at the example of Y-Ba-Cu-O, (Pb)Bi-Sr-Ca-Cu-O [4] and other materials microwave-assisted sample dissolution with subsequent analyses by CCD-based ICP-OES will be shown to obtain an absolute precision of 0.1 % , which is hoped to be still surpassed by applying internal standardization.

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DIRECT DETERMINATION OF TRACE ELEMENTS IN ALUMINA CERAMIC
POWDERS BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY
USING ELECTROTHERMAL VAPORIZATION

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The determination of elemental impurities in refractory materials, such as ceramic powders, still is an analytical challenge. For this type of samples, direct analysis procedures are preferable to procedures involving sample dissolution, since the digestion of such materials is time consuming and involves the risk of contamination. There are several possibilities for the introduction of powder samples into an ICP for plasma spectrometry, a most prominent of these is electrothermal vaporization (ETV). Its advantages are the applicability for both the analysis of solutions and of powder samples entered in the furnace as slurries as well as the possibility of solvent removal and analyte-matrix separation through the use of suitable temperature programs.

A special feature of this sample introduction technique, however, are the transient signals in electrothermal vaporization. In the case of a need for multielement determinations by ETV-ICP-MS, both quadrupole and scanning sector-field mass spectrometers may be limited by their sequential mode of measuring. Indeed, with a mass spectrometer capable of recording the signals of many analytes simultaneously and continuously, a substantial gain in sensitivity might be possible.

In the work presented ETV-ICP-MS with different types of mass spectrometers, including quadrupole instruments but also simultaneous spectrometers, such as time-of-flight mass spectrometry and array mass spectrometry, will be compared. The figures of merit for the determination of several elements in slurries of alumina powders will be presented.

As an independent analysis method, being required for validation of the results of the analyses of Al₂O₃ powders, total reflection x-ray fluorescence analysis (TXRF) has been used. Herewith both direct analyses of slurries of alumina powders and the analysis of the solutions obtained by microwave-assisted digestion of the samples were performed. The limits of detection for the determination of a number of relevant trace elements in technologically important Al₂O₃ powders by TXRF are presented and shown to be considerably higher than those of ETV-ICP-MS. However, calibration is much easier.

DETECTOR TECHNOLOGIES FOR ATOMIC EMISSION: A BRIEF REVIEW
WITH A FOCUS ON THE CURRENT STATE-OF-THE-ART

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Since the introduction of ICP atomic emission in the early 1970's there have been two principal technologies used to detect the light dispersed by the optical spectrometers employed in these instruments. This presentation will provide a very brief review of PMT and solid-state detector technologies and will provide an unbiased overview of the analytical pros and cons of each. We will also present a snapshot of today's state-of-the-art detector technology and the new analytical capabilities which it affords the user.

THE ONLINE COUPLING OF GEL ELECTROPHORESIS WITH ICP-MS -
METHOD DEVELOPMENT AND FIRST APPLICATIONS

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Since decades gel electrophoresis (GE) has been the standard method to separate proteins and DNA-fragments. Due to its enormous choice of variability – e.g. Disk-GE and 2D-PAGE – GE offers the possibility of focussing the separation parameters explicitly on the analytes' characteristics.

The detection methods are just as manifold. The palette of available methods goes from molecules' colouring with specific colorimeters to marking with radioactive reagents and to many different blotting methods. Nevertheless, all these methods cannot give any information about the element or their structure. Thus, new developments are directed to the combination of the high performance separation power of GE and the high sensitivity of the element-selective detector ICP-MS via laser ablation (LA), which should offer a powerful offline coupling.

In order to overcome the general disadvantages of the offline coupling we developed an innovative online system based on the coupling of GE and ICP-MS.

Our method exploits the principle of preparative GE, which is based on a continuous elution of the separated compounds from the gel during the electrophoresis. The specific design of the electrophoresis unit will be described in detail and allows us to analyse the eluted molecules by ICP-MS. The optimisation of separation and detection parameters leads to first applications on high-molecular species determination which emphasises its potential for future applications.

THE DETERMINATION OF SELENIUM IN ICE SAMPLES FROM
ANTARCTICA BY HG-ICP-QMS AND ICP-SFMS

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The ocean is the primary source for atmospheric selenium [1], with biomethylation being an important process in its flux from the ocean to the atmosphere, so concentrations of selenium are linked with oceanic primary production. Over the last decade, the study of heavy metals in ice and snow from polar and high altitude regions has revealed important information on both anthropogenic influences on the atmospheric burden of metals [2] and to a lesser extent, the natural variability of these elements over previous glacial-interglacial fluctuations [3].

The study of polar snow and ice from Vostok station in central Antarctica allows us to study variability over long time scales, and allows us to access lake Vostok a large sub-glacial water body that has been preserved from atmospheric exchanges for millions of years. This pristine environment is of particular interest because it may give clues about the understanding of life development in extreme environment, climate evolution, and the tectonic structure of the Antarctic [4]. The study of Se in the accreted ice from the Vostok Lake can lead to a better understanding of the geochemical processes occurring in the lake.

Analyses of selenium in these rare samples were carried out by hydride generation-inductively coupled plasma mass spectrometry (HG-ICP-QMS) and by direct analysis with high-resolution sector field ICP-MS (ICP-SFMS). For HG-ICP-QMS the detection limit based on 3 x the standard deviation of the blank was 0.5 ng L⁻¹, with quality control carried out by analysis of diluted aliquots of the NASS-5 CRM, results (18 ± 2 ng/L⁻¹) were in good agreement with the indicative value for Se IV (18 ng/L⁻¹).

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STUDY OF MERCURY-SELENIUM INTERACTION IN ANIMAL TISSUE BY
ION EXCHANGE AND SIZE EXCLUSION CHROMATOGRAPHY
INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

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Mercury (Hg) is a widely distributed and persistent pollutant in the environment and is among the most highly bioconcentrated trace metals in the human food chain. Mercury toxicity, bioavailability and environmental mobility are well known to be highly dependent on its chemical form, being methylmercury (MeHg) one of the most toxic species. Therefore, risk assessment and risk prevention of human exposure to mercury is a milestone in Food Safety.

On the other hand, several authors addressed that selenium (Se) can act as a potential antagonist of mercury toxicity, but the way in which it interferes with mercury is still questionable and several mechanisms have been proposed to explain this interaction, however, none of them is conclusive.

In order to clarify the mechanism of interaction between Se and Hg (both inorganic mercury and MeHg), toxicological assays in vivo were carried out. For this purpose 64 chickens were feed under two different controlled conditions. In the first one, chickens were exposed to Hg and MeHg added to feed. The second set was exposed to dietary Se supplementation plus Hg(II) or MeHg. This experiment let the study firstly, of the mercury distribution and possible modifications in Se natural occurring levels and secondly, of the effect of selenium on mercury distribution and bioaccumulation.

The identification and determination of total mercury and selenium and their species were achieved without and with previous chromatographic separation steps respectively. CV-AFS, HG-AFS, GC-AFS and HPLC-ICP-MS were the techniques employed.

Selenium and mercury species present in soluble fractions of proteins of chicken liver samples were analysed by size exclusion chromatography coupled to both inductively coupled plasma-mass spectrometry (SEC-ICP-MS) and UV spectrophotometers.

The results showed that addition of sodium selenite induced a surprising decrease up to 60-100 % in the inorganic mercury bioabsorption.

Mercury speciation in chicken liver and kidney suggested that the addition of Se to the MeHg-containing diet meant promotion of MeHg conversion into a less toxic form (inorganic Hg), because an increase up to 145-280% of MeHg demethylation in these organs was observed.

Fractionation of mercury and selenium compounds by SEC-ICP-MS has been investigated in order to clarify the mechanisms involved in the interaction between Se and Hg(II)/MeHg.

DISTRIBUTION OF SELENO SPECIES IN VEGETAL TISSUES BY SIZE
EXCLUSION MOLECULAR AND CATION EXCHANGE CHROMATOGRAPHY
HYPHENATED INDUCTIVE COUPLED PLASMA MASS SPECTROMETRY

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Selenium is recognised as an essential element for living organisms. The potential health benefits of some selenocompounds have increased the interest to study the biochemistry of this element. Many studies have demonstrated the anticarcinogenic activities of some Se organic compounds against certain types of cancer. Then, the capability of some plants to accumulate and transform selenium is not only important for the environment, but also for human nutrition and health.

In this work selenium accumulation in lentils (*Lens esculenta*) plants was studied. The plants were grown in hydroponic culture containing inorganic selenium, Na₂SeO₃ and Na₂SeO₄. The solution was renewed each three days during 16 days. After that, the plants were divided in two parts, shoots and stem, which were then analysed to determine the Se species and Se binding proteins.

Seleno species were identified and quantified in the enzymatic digest of water soluble fraction by HPLC-ICP-MS (HP-4500 Instrument) by monitoring ⁸²Se using a cation exchange column (Hammilton PRP-X100) with 10 mM ammonium citrate at pH 5 as mobile phase.

Plants grown in Se (VI) have shown a big capability of accumulating high quantities of selenium, but this inorganic species did not suffer any transformation during the accumulation process. However, plants grown in Se (IV) were less tolerant but showed transformation in seleno aminoacids, such as selenocystine (35%), selenomethionine (5%) and Se-methylselenocysteine (15%).

Soluble proteins in Tris-HCl were analysed by size exclusion chromatography using a Biosep-SEC-2000 column with 25 mM Tris-HCl, at pH 6.8 as mobile phase at a flow rate of 1.0 mL/min coupled to ICP-MS and UV spectrometers.

In this work the proteic profile within the range 300-1kDa was evaluated. The coupling of SEC to ICP-MS was used for the analysis of selenium-binding proteins fraction. The results obtained could contribute to understanding the mechanism of selenium accumulation in plants, the remediation of soils and the production of enriched food as complement of the diet.

ADVANCES IN ENZYMATIC SAMPLE TREATMENT FOR SPECIATION
USING ULTRASONIC PROBE
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Solid sample treatment has been the Achille's hell of the speciation, mainly due to time consumption, yield of the process and risk of species interconversion. In this respect, sonochemistry (chemistry enhanced by ultrasound) has emerged as an interesting alternative to traditional sample pre-treatment methods for total metal and species determination in different matrices (1-2).

Arsenic and selenium have been two of the most investigated elements for speciation analysis due to their toxic and essential/anticarcinogenic properties respectively.

The most common species extraction methods are based on organic solvents extraction and enzymatic hydrolysis. These methods are in general time-consuming (above 12 hours) with tedious sample handling. This increases the risk of contamination, analyte losses and species interconversion.

In this communication a critical evaluation on the use of conventional treatments and enzymatic ultrasonic probe for both elements speciation in several food matrices such as rice, meat, fish, animal feed, yeast, etc is presented. After optimization of the most relevant parameters affecting the process, the speciation was carried out by the LC-ICP-MS coupling. Quantitative results of arsenic and selenium species have been attained by applying ultrasonic probe enzymatic treatment with protease in a few minutes. The mechanism of the process involved will be discussed.

As a result, the technique described here is expected to be widely used for analytical purposes in the future, owing to the simplicity, speed, safety and performance attributes of this sample preparation technique.

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PLASMA MASS SPECTROMETRY VERSUS THE WORLD

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In 2002, the IAEA organised a proficiency test for the determination of (up to) ten trace elements in a lichen reference material. It attracted participation from 165 laboratories from 65 countries. Participants were required to provide a minimum of three independent results and also to analyse an external quality control lichen, a trace element solution and their own choice of QC material. Participants were encouraged to provide full details of methodologies used. The performance was judged against IAEA ascribed values using the z-score approach with the target standard deviations set on the basis of results from a long term temporal and thermal stability study on the material. Individual reports were dispatched to laboratories in autumn 2003. This paper presents the overall conclusions for the exercise and compares the performance of laboratories using ICP-MS against their peers using ICP-OES, Atomic Absorption, Neutron Activation Analysis, or X-ray based techniques.

VALIDATION OF SPECTROMETRIC METHODS IN THE FOOD SECTOR
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As defined by the International Standard ISO/IEC 17025 General Requirements for the Competence of Testing and Calibration Laboratories, validation of analytical methods is *the confirmation by examination and the provision of effective evidence that the requirements for a specific intended use are fulfilled*. Validation can be accomplished basically either by an intercomparison exercise among expert laboratories or just by one laboratory developing a given method (the so-called in-house validation). From a general viewpoint, the process of validation aims at ascertaining a wide range of parameters, namely, applicability, selectivity, calibration, linearity, trueness, accuracy, precision, recovery, range, limit of detection, limit of quantification, sensitivity, ruggedness, robustness, fitness for purpose, matrix variation and measurement uncertainty. In practice, while some of these quantities are necessary in all cases, others can be skipped, depending on the specific needs, provided that the reason for doing so is well documented. Recently, a tiered approach to validation has become mandatory for all Community and National Reference Laboratories for residues, as prescribed by the Commission Decision 2002/657/EC of 12 August 2002 implementing Council Directive 96/23/EC of 29 April 1996 concerning the performance of analytical methods and the interpretation of results.

Spectrochemical methods play a key role in the quantification of residues and contaminants in foodstuff. This holds true all the more as regards the importance of plasma-based techniques in the determination of trace and ultratrace elements. This presentation describes the general context of validation of analytical methods and illustrates how it is actually carried out in the case of plasma spectrochemical techniques through two representative examples, *e.g.*, the determination of As, Cd, Cu, Hg and Pb in milk by Sector Field Inductively Coupled Plasma Mass Spectrometry and the determination of As, Cd, Cu, Hg and Pb in fish by Dynamic Reaction Cell Quadrupole Inductively Coupled Plasma Mass Spectrometry.

ACCURATE MEASUREMENT OF ISOTOPE RATIOS FROM MOLECULAR
CLUSTERS IN BUTYLTIN MASS SPECTRA

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Since the 1960's various organotin compounds have been extensively used as broad spectrum biocides and lately the need to measure butyltin species in environment on a routine basis has increased due to the global ban on the application of tributyltin. To meet the legislative criteria, isotope dilution GC/MS is regarded as an attractive choice for routine testing laboratories, however, unlike GC/ICP-MS, electron impact ionization GC/MS produces molecular ions in contrast to atomic spectrometric methods and this complicates the use of ID methods as elemental isotope ratios need to be measured from molecular clusters.

The isotope dilution equation used for elemental analysis can only be applied if a pure molecular cluster can be selected that avoids isobaric interferences. In this study we apply the isotope pattern reconstruction algorithm to study the butyltin electron impact mass spectral fragmentation pathways using both standards of natural Sn isotope abundance and mono-, di-, and tributyltin labeled with enriched ^{119}Sn . Isotope composition of the enriched species and data verification was obtained using GC/ICP-MS. The results obtained showed that pure interference-free molecular clusters were obtained only for certain R_3Sn^+ ions where no isobaric overlap with R_2SnH^+ ions occurred (e.g. BuEt_2Sn^+ overlapped with Bu_2SnH^+). These ions are ideal candidates for accurate Sn isotope ratio measurements while isotope pattern perturbing interferences are observed for other molecular fragments down to Sn^+ . So far ID analysis of butyltin species with GC/MS has been performed using various fragment ions from their electron impact mass spectra. For example, ID analysis of ethylated tributyltin has been performed using clusters $\text{C}_8\text{H}_{19}\text{Sn}$ ($m/z = 235$), $\text{C}_{10}\text{H}_{23}\text{Sn}$ ($m/z = 263$) and $\text{C}_{12}\text{H}_{27}\text{Sn}$ ($m/z = 291$) and ethylated dibutyltin has been determined using clusters $\text{C}_8\text{H}_{19}\text{Sn}$ ($m/z = 235$) and $\text{C}_{10}\text{H}_{23}\text{Sn}$ ($m/z = 263$). However, the only justification of such selections seems to be the abundance of the ion fragment and indirect measure of validity of such selection remains the accuracy of the obtained results. We have seen the $\text{C}_8\text{H}_{19}\text{Sn}$ cluster should not be used for TBT nor for DBT as it is a dialkyltin ion (Bu_2SnH^+) possessing minor interferences. Selection of other higher TBT ions is valid according to our results, which will be discussed in this presentation.

ANALYSIS OF ORGANOPHOSPHORUS CHEMICAL WARFARE
DEGRADATION PRODUCTS BY HPLC-ICP-MS

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Recent increases in terrorist activity and the threat of chemical weapon attacks has lead to the demand of a rapid and reliable method for analysis of chemical warfare agents (CWA) and their degradation products. The nerve agents Sarin and VX as well as many others pose a deadly threat to the human population if released. These phosphorus containing nerve agents along with their degradation products present difficulties for ultra-trace analysis due to their low volatility and lack of a good chromophore. Previous studies have successfully utilized methods such as gas chromatography/mass spectrometry (GC-MS), ion mobility/mass spectrometry (IMMS), and liquid chromatography/mass spectrometry (LC-MS) for the analysis of organophosphorus containing degradation products with detection limits in the ng/mL range(1-3). However, these studies did not report detection limits at the more desirable lower levels.

Phosphorus analysis by inductively coupled plasma mass spectrometry (ICP-MS) coupled with ion-pairing reversed phase high performance liquid chromatography (IP-RP-HPLC) has recently been proven as a rapid and reliable speciation technique with detection limits in the ng/L range(4). Monitoring ^{31}P with ICP-MS is a difficult task due to its high ionization potential (10.5 eV) as well as the presence of polyatomic interferences, primarily $^{14}\text{N}^{16}\text{O}^{1}\text{H}^{+}$ and $^{15}\text{N}^{16}\text{O}^{+}$ which overlap the only phosphorus isotope, ^{31}P . In order to minimize these interferences an octopole reaction cell with He gas is utilized to obtain the maximum signal-to-noise ratio for the samples of interest.

In this work a novel method for the rapid analysis of phosphorus containing Sarin (GB) and VX hydrolysis products by IP-RP-HPLC-ICP-MS is described. Analytical figures of merit consisted of detection limits less than 0.263 ng/mL with precision values of less than 6% (RSD) for peak area and less than 1% (RSD) for retention times.

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SPECIATION OF SELENIUM-CONTAINING PROTEINS IN SELENIUM-
ENRICHED AGARICUS BISPORUS AND LENTINULA EDODES
MUSHROOMS BY VARIOUS CHROMATOGRAPHIC TECHNIQUES COUPLED
TO ICPMS

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Selenium is an essential trace element for humans and animals. Since the work of Clark et al[1] involving the role of selenium in cancer chemoprevention, potential "Se-delivery systems" have been explored. Mushrooms were examined as possible a "Se-delivery system" because it has been shown that they can accumulate large amounts of selenium. Organic forms of selenium such as methylselenocysteine (MSC), selenomethionine (SeMet) and selenocysteine (SeCys) have received much attention due to their possible chemopreventive characteristics.[2] The latter two can be bound to proteins. However, this is a relatively unexplored area and the investigation of the presence of a SeCys-containing protein in plants is of high interest.[3] Since mushrooms contain relatively high protein levels, and they can accumulate large amounts of selenium, it is reasonable to expect that selenium could be incorporated into the proteins. Agaricus bisporus and Lentinula edodes were the mushrooms of interest in this study. Water soluble proteins were extracted from the samples using a Tris-HCl buffer to dissolve the proteins followed by acetone for precipitation. In this study, size-exclusion chromatography coupled to ICPMS (SEC-ICPMS) followed enzymatic digestions (using Trypsin, Proteinase K and Protease XIV). A combination of trypsin/protease XIV gave the best digestion and the selenoamino acids were analyzed using reversed-phased ion-pairing high performance liquid chromatography (RP-IP-HPLC) and cationic exchange liquid chromatography (CEX-HPLC). Selenomethionine, selenocysteine and methylselenocysteine were identified along with several unknown peaks now being further studied by peak collection and subsequent ESI-qTOFMS for identification. The progress of these studies will be reported.

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IDENTIFICATION OF WATER SOLUBLE PROTEINS IN AGARICUS
BISPORUS AND LENTINULA EDODES MUSHROOMS BY VARIOUS
CHROMATOGRAPHIC AND MASS SPECTROMETRIC METHODS

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Because of its benefits to human health, selenium biochemistry is an expanding area of study. Since the work of Clark et al[1] involving the role of selenium in cancer chemoprevention, sources of selenium have been investigated. The focus of this project is to characterize and identify various types of selenoproteins in plants. Many selenoproteins have been found in mammalian samples, however, little is known about seleno-proteins in plants. Mushrooms were chosen as a possible selenoprotein source, due to the fact that they have a relatively high protein content (roughly 20% by mass) and have been shown to accumulate high concentrations of selenium. The amino acids have been studied and their presence has been confirmed in many different plant samples including mushrooms, soybeans, Indian mustard, and onions. It has been shown that mushrooms do accumulate Se at high molecular weight fractions, but the identification of these proteins has not been made. This study has begun with the water soluble proteins in mushroom samples from *Agaricus bisporus* and *Lentinula edodes*. One important objective of this research is to separate the water soluble proteins and then determine if they contain selenium. Water soluble proteins were extracted from the samples using a Tris-HCl buffer to dissolve the proteins followed by acetone to precipitate the proteins. These protein mixtures were then studied with MALDI-MS. To simplify the protein mixture, various processes were carried out including the use of centrifugal filters and various chromatographic techniques such as SEC-ICPMS, FPLC-ICPMS and RP-LC-ICPMS. An earlier enzymatic digestion study showed Se-methionine, Se-cysteine, and methyselenocystein, suggesting both specific and nonspecific selenium containing proteins might be present. To further study and identify these, trypsin digests were ultimately taken to ESI-qTOFMS and then peptide fragments submitted to the MASCOT data base for further identification.

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ELEMENTAL SPECIATION: FROM SMALL ATOMS TO BIG MOLECULES

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For two decades elemental speciation research has been steadily growing to the point that now the element selective detector of first choice is ICP-MS with a wide variety of liquid chromatographic (LC) methods to provide the species separation. As these techniques have become established, gas chromatography (GC) and capillary electrophoresis (CE) have gained popularity as separation methods.

Contemporaneous with these methods have been advances in ICP-MS instrumentation that have produced lower detection limits, greater spectral resolution and markedly enhanced capabilities to probe elements whose performance a decade ago with ICP-MS detection, were sufficiently poor to make the experiment not worth doing. However, as reliable and robust high resolution and collision/reaction cell ICP-MS instruments have emerged, the power of ICP-MS has been enhanced for numerous metals/metalloids and extended to very important non-metals.

Small molecules involving phosphorous, sulfur and certain halogens can be detected and quantified in ways often superior to conventional trace organic molecular methods. These include pesticides, fire retardants, various bromo- and iodo-compounds in a number of different sample types such as seaweed, land plants, pharmaceuticals and plastics. Further with multidimensional chromatographies as well as electrophoretic separations, the extensions to peptides, proteins and other macromolecules make ICP-MS an important screening technique for these large molecules, enhancing the ability to identify and quantify in conjunction with other MS methods. Further, advances in metalloid detection have led to both enhanced plant phytoremediating capabilities, while simultaneously forming chemotherapeutic entities, such as methylselenocysteine. This talk will focus on the development and importance of the chromatographic and multiple MS methods to speciate from small to big molecules.

HPLC-ICP-MS AND MALDI-TOF / ESI-Q-TOF FOR CHARACTERIZATION OF THE DIFFERENT HUMAN SERUM TRANSFERRIN GLYCOFORMS

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Human serum transferrin (hTf) is the main iron-transporting glycoprotein in plasma and contains two iron-binding sites. It is synthesized in the liver and it consists of a single polypeptide chain of 679 amino acids [1] with two glycosylation sites at Asn413 and Asn611 (asparagine at positions 413 and 611, respectively) in the C-terminal domain. Each of these two N-glycan chains of Tf differ in their degree of branching showing bi, tri and tetra-antennary structures, each antenna terminated in a negatively charged sialic acid (N-acetylneuraminic acid) molecule. Carbohydrate-deficient Tf (CDT) comprises transferrin isoforms lacking one or both of their carbohydrate chains and can be used as biochemical markers for congenital disorders of glycosylation (CDG) and chronic alcohol consumption. The most abundant form of hTf is this showing 4 sialic acid residues (70-80% of total Tf) also called tetra-sialo Tf but a group of isoforms with zero to eight sialic acid residues per molecule can be also detected in control individuals. The molecular masses of these isoforms vary from 75.37 to 79.61 kDa [2].

The aim of the present work is to evaluate the potential use of HPLC-ICP-MS as complementary tool for “element-tagged” proteomics, since Fe saturation of the protein is required in order to perform an adequate separation of the isoforms. For this purpose, Apo-Transferrin is saturated with iron by incubation with 10 mM FeCl₃. After iron saturation, Tf is incubated with neuraminidase enzyme and aliquots are removed at specific intervals in order to split off sialic acid residues and to obtain the different sialo-forms with lower sialic acid content. The separation of transferrin glycoforms is achieved on a MonoQ (HR5/5) anion-exchange column using an ammonium acetate gradient (0-0.25 mol.L⁻¹) in the mobile phase and the Fe associated to each isoform detected by octapole ICP-MS collision/reaction cell (ICP-ORS-MS) system. Additionally, MALDI-TOF and ESI-Q-TOF are used to characterize the different glycosylated forms and/or Fe-protein complexes of Tf after neuraminidase treatment.

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CHEMICAL VAPOUR GENERATION USING HALIDES OF Sb(III)/Sb(V),
AND Ti (IV)

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The generation of volatile halides as a mean to enhance the yield of sample introduction in atomic spectrometry has been applied (1) for elements such as Si(IV), As(III and V), Se(IV and VI), Ge(IV) and Sb(III and V). The halide vaporization is commonly obtained by reaction of elements with halides (bromide, chloride and fluoride) in sulphuric acid media. The aqueous sulfuric dilution heat is enough to increase the reaction temperature, in an homogenous procedure, up to 100°C, which allows a significant volatilization of compounds with boiling points, in the order, up to 200°C.

Considering the entire 'halide group', it can be seen as less sensitive than other volatile compounds but offers interesting possibilities for speciation and inclusion of other less common volatile elements. In this field of chemical halide volatilization, Sb(III) and Sb(V) have been gasified by means of bromide. Their introduction into an Inductively Coupled Plasma-AES has been published (2). The volatilization of both species offers great similarity but also present certain differences. Initial works (3) demonstrated that the presence of As(III) allows a differentiation between the two inorganic species of Sb. Here, we present a more detailed study on the differentiation between Sb(III) and S(V) and the reliability of speciation method has been evaluated by analysis of synthetic mixtures. The vaporization of Sb(III-V) have been characterized by a 'volatilization coefficient', individually, and also in presence of the 'As effect'. Their values has correspondence with their analytical characteristics which confirms the results.

At the first time, titanium(IV) has been studied by this methodology and its volatilization with chloride has been obtained. The titanium tetrachloride halide is known, with a 136°C boiling point, in the chemical bibliography but it is the first time that it has been volatilized in a way to be applied in analytical atomic emission spectrometry. The method allows the titanium determination by ICP-AES and the developed works included an optimization procedure based in the use of experimental designs. The results showed a dependence on four principal factors: acid media, concentration and volume of halide (sodium chloride) and flow of carrier gas.

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GEL ELECTROPHORESIS AND
FEMTOSECOND LASER ABLATION – ICP/MS
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A major application for LA-ICP-MS is as a micro-analytical tool for determining the spatial distribution of elements in a sample. In general, shorter laser pulses (picosecond or femtosecond) can provide improved accuracy versus nanosecond laser pulses. Femtosecond laser pulses might be favourable for providing reduced fractionation because of minimal thermal effects. Femtosecond laser ablation offers the possibility of no fractionation and no matrix dependence, because the surface (irradiated volume) explodes before the photon energy is dissipated as heat in the lattice; melting is reduced and the ablation process can produce a stoichiometric aerosol. Ultrafast laser ablation provides no laser plasma interaction and smaller aerosol particles.

LA-ICP/MS has been used to determine trace elements in only a few organic materials, mainly, polymers, vegetable materials, and some kinds of soft tissue. Laser Ablation would be a novel sampling interface between gel electrophoresis and ICP-MS. This hyphenated technique can be complementary to laser desorption mass spectrometry for characterization of proteins separated by gel electrophoresis. The type of laser used is very important in providing reliable data, but until now only lasers with nanosecond pulses at 193nm ArF, 266 nm Nd:YAG and some times infrared wavelength at 1064nm have been used to ablate metalloproteins separated by gel electrophoresis.

In this presentation we will discuss laser ablation with femtosecond pulses coupled to an ICP/MS to measure the composition of samples (proteins) separated on gel (polyacrilamide) electrophoresis plates. The experimental system included a femtosecond laser consisting of a Spectra Physics Mai Ta, Ti:sapphire seed laser and Spitfire regenerative amplifier. The 100 fs pulses at 800 nm were frequency tripled to obtain the 266 nm used for ablation. An ICP/MS (VG PQ3 from VG Elemental) was used for analysis. These data will be compared to those obtained with nanosecond Laser Ablation of the same gel electrophoresis plates using a Nd:YAG 213 nm laser from New Wave Research, coupled to a Sciex Elan 6000 ICP/MS .

This work was supported by Project BQU 2003-01993 of the Spanish Science Ministry, and the US Department of Energy at the Lawrence Berkeley National Laboratory.

SAMPLE PREPARATION AND CALIBRATION STRATEGY ON MULTI-
ELEMENTAL ANALYSIS OF ORGANIC SAMPLES BY
LASER ABLATION-ICP-MS
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Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a rapid and sensitive tool for trace elemental analysis. This technique provides both bulk and spatially-resolved information and offers many advantages for the analysis of solids samples; among these, pg mL⁻¹ detection limits for many elements, wide elemental coverage, a linear dynamic range of up to 10 orders of magnitude, and direct elemental isotopic analysis of solids. Successful utilization of LA-ICP-MS involves consideration of a number of parameters. For example, the laser (wavelength, energy, pulse width, laser spot size, beam profile, etc); the samples and standards (chemical and physical properties, surface condition, availability, etc); environment surrounding the sample and transport of the material (carrier gas, flow rate, pressure inside de chamber, chamber size, gas dynamic, etc); and detection system (sensitivity, stability, etc) all must be optimized to achieve accurate and precise analysis.

In many of the widely adopted applications of LA-ICP-MS (forensic chemistry, geological, environmental, material sciences, polymer chemistry, etc) quantification remains a challenge. The most common calibration method is external calibration using matrix- matched solid standards. Unfortunately, such standards are often not available for a particular sample of interest. Creation of fused beads or pelletized solids are two approaches to the generation of solid standards. Alternatively, calibration using solution standards either added to the solid sample or introduced separately from a nebulizer has been also described in various forms.

Although there is a extensive bibliography about inorganic samples such as geological, metallurgical, glass, ceramics, etc, there are less studies about organic materials .Some of them have been of biological origin. In most cases compact tablets are the most popular approach for sample preparation.

In this work we have studied the application of LA-ICP-MS in samples with inorganic content such as a titanium screw for dental use, and both, organic and inorganic content, such as compost. This material shows an inhomogeneous structure. For compost compact pellets have been used as sample preparation method. Different parameters affecting to laser, ICP-MS and sample preparation have been studied. With respect to laser, spot size, repetition rate, pulse energy, the use of preablation and scan speed have been optimized. The parameters of ICP-MS optimized have been: nebulizer gas flow, dwell time, number of readings per sweep and number of sweeps. Sample preparation in laser ablation is one of the most important variables related to precision of the technique. In our case, as we said previously, the sample is very heterogeneous. For this reason different parameters with relation to sample preparation such as sample amount, the effect of sample grinding (time and particle size) and time and required pressure of hidraulic press, have been also optimized.

For ICP-MS measurements of compost, results from semiquantitative and quantitative analysis methods have been compared, using for calibration certified reference materials: Agromat-Compost CP-1, sewage sludge CRM029-050 (RTC) and sewage sludge CRM 144 R (BCR). The effect of the previously mentioned parameters on accuracy and precision have been studied.

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DETERMINATION OF METHYLMERCURY IN FISH SAMPLES USING
ISOTOPE DILUTION GAS CHROMATOGRAPHY WITH MASS
SPECTROMETRIC DETECTION: COMPARISON OF EI GC-MS AND ICP-MS
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Methylmercury is a highly toxic substance with a number of adverse health effects associated with its exposure in humans and animals. Epidemics of mercury poisoning following high-dose exposures to methylmercury in Japan and Iraq demonstrated that neurotoxicity is the health effect of greatest concern. These epidemics led to observation of methylmercury effects on the fetal nervous system. High-dose human exposure results in mental retardation, cerebral palsy, deafness, blindness, and dysarthria in utero and in sensory and motor impairment in adults. The major pathway for human exposure to methylmercury is consumption of contaminated fish. Dietary methylmercury is almost completely absorbed into the blood and is distributed to all tissues including the brain; it also readily passes through the placenta to the fetus and fetal brain. Therefore, valid measurements of methylmercury in fish are required. Sensitive, specific and precise analytical methods are needed to perform studies at ambient levels.

Already the first step in the analysis, the isolation of methylmercury from the sample matrix can be troublesome. Since recovery of the analyte from some matrices is not always quantitative, recovery factors during isolation must be determined. This is usually done by standard addition techniques or recently using isotope dilution mass spectrometry (IDMS). Isotope dilution (ID) methodologies provide superior accuracy and precision compared to more common calibration strategies. Since quantitation is done by ratio measurements, quantitative separation procedures are not required and non-quantitative analyte recoveries do not affect the final results. ID application to species-specific determinations has been limited by the commercial non-availability of species-specific enriched spikes [1].

ID for trace element speciation has been widely applied using inductively coupled plasma mass spectrometry (ICP-MS) as detector for HPLC or GC separation, but few papers can be found in the literature dealing with the application of ID with GC-MS. The use of ICP-MS as detector for GC separation offers certain advantages over traditional electron impact GC-MS: simple mass spectra, superior sensitivity and freedom from spectral interferences. Also, the measurements of isotope ratios by GC-ICP-MS is simpler than by GC-MS, because there is no need to take into account the ^2H and ^{13}C isotope composition of the molecular ion. However, there are some practical disadvantages in the use of ID-GC-ICP-MS as routine technique in testing laboratories: the ICP-MS is an expensive and not generally available instrument and the GC-ICP-MS interface is commercially available only from one ICP-MS manufacturer. Under those circumstances, the development of a GC-MS isotope dilution procedure which could be immediately applied in testing laboratories, where GC-MS instrumentation is widespread, was considered to be of interest.

Hence, the objective of this work was to take the advantage of the high accuracy and precision offered by isotope dilution in combination with gas chromatography with mass selective detection (GC-MS). The technique was evaluated for the accurate determination of methylmercury in fish samples and compared with GC-ICP-MS. The advantages and limitations of both MS ion sources (ICP and EI) are discussed for the accurate determination of methylmercury in fish.

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INVESTIGATION OF INTERFERENCES CAUSED BY MATRIX ELEMENTS
WITH LOW SECOND IONIZATION POTENTIAL IN INDUCTIVELY COUPLED
PLASMA-ATOMIC EMISSION SPECTROMETRY

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Matrix effects in inductively coupled plasma—atomic emission spectrometry (ICP-AES) have been widely reported in the literature. However, the mechanism that leads to these interferences is not fully understood. A recent study[1] revealed that matrix effects caused by elements with a low second ionization potential are more severe than those from matrix elements having a low first ionization potential (the so-called easily ionizable elements, EIE). Although it was reported that the matrix effect is correlated unambiguously with the second ionization potential of a matrix, there now appear to be other factor(s) that are operative; for example, barium has the lowest second ionization potential (IP) in the periodic table (2nd IP = 10.0 eV), yet the matrix effects from rare earth elements (2nd IP ranges from 10.5 to 12.1 eV) are more severe than those produced by Ba1. The objective of the present study is to investigate the fundamental mechanism that leads to interference effect by these low 2nd IP matrix elements in the plasma.

The investigation involves study of matrix effects induced by a comprehensive list of low 2nd IP elements (virtually all low 2nd IP matrices). Through study of a large pool of matrix elements, it becomes possible to identify another critical parameter that defines the magnitude of the matrix effect; namely the presence of low-lying energy levels in the doubly charged matrix ion. In this presentation, the correlation between the matrix effect and energy levels of the doubly charged matrix ion will be examined and plausible mechanisms for the matrix effect will be offered.

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APPLICATIONS OF RF-GD-OES TO THERMAL SENSITIVE MATERIALS_e
WITH A PULSE RF SOURCE AND COUPLING A RF-GD-OES TO A DC ARC
FOR THE ANALYSIS OF POWDERED MATERIALS

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The RF Glow Discharge Optical Emission Spectrometry is a recognised tool for the bulk, surface and depth profile analysis of conductive and non-conductive materials.

In depth profile the technique induces thermal effects on the materials to be analyzed that could bias or jeopardize the analysis of fragile and heat sensitive coatings. The use of a RF source that could operate in pulse mode extends the range of applications. Results will be presented on glass coatings and polymers.

It is also difficult in GD to get good bulk results on powders even after preparing pellets. The inevitable presence of air in the pellets greatly affects the plasma conditions and the obtained results. The sensitivity for traces is also questionable as the operating conditions could not be optimized.

The coupling of a DC arc source known to provide high signals for traces to a GD is a solution to the problem of direct measurement of powders. A stable DC arc system permits to generate reproducible results and the GD acquisition mode fits with the time resolved nature of the DC source. Results coming from a Round Robin will be presented showing the interest of the combination.

Finally, as the technique is now used for ultra thin layers (down to 1 nm – even results on 1 atomic layer coating will be shown), the limitations of the traditional quantification method have been pointed out and new modes of quantification have been proposed and will be illustrated on practical examples.

CHARACTERIZATION OF SURFACES AND THIN FILMS DOWN TO THE
NANOMETER SCALE OF CONDUCTIVE AND NON-CONDUCTIVE
MATERIALS BY RF-GD-OES
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RF Glow Discharge Optical Emission Spectrometry has been applied to the analysis of thin films from 1 micron to several tens of microns for several years.

Ultra thin layers (less than 1 micron down to less than 1 nanometer) have also been successfully characterized on various samples such as glasses, anodized aluminum, hard disks, surface oxides on steels, etc. Some practical results obtained on various samples will be presented.

However various aspects are crucial to consider in order to obtain relevant information with RF-GD-OES at the very surface. This paper will describe the necessary criteria for GD to be applied to ultra thin film measurements.

Operating parameters will be investigated, as well as surface preparation and treatment.

Quantification issues will be extensively discussed and improvements to the classical methods in use for thick layers will be presented.

AN ORIGINAL NUCLEARISATION of a GD/OES
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The analysis of uranium and plutonium samples requires the "nuclearisation" of specific apparatus like ICP/AES-MS or GD/AES. In the aim to characterise C,H,O,N elements in metallic pieces, the nuclearisation of the technique has been conducted in a glove box. In fact, to optimize time and accuracy, this GD lamp has been chosen to replace classical techniques. This paper describe the adaptation and the upgrading of the spectrometer and the results obtained on uranium and plutonium samples are discussed.

THE ANALYSIS OF PHARMACEUTICALS BY ICP-MS: A STIFF CHALLENGE

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Counterfeit pharmaceuticals have recently caused a number of deaths in Africa and elsewhere. Furthermore, counterfeit drugs may also be less effective than the genuine article and leave patients untreated, causing further economic loss to already impoverished nations. In the light of this, quick and easy methods to distinguish between genuine and counterfeit pharmaceutical products are required. Currently, this is achieved by the identification and quantification of other compounds e.g. Sorbic acid¹ by LC-MS, added during manufacture and the characteristic impurity fingerprint of the drug². An ICP-MS method has also recently been developed for the detection of low molecular weight carboxylic acids, used as preservatives in pharmaceuticals, after phosphorus derivatisation³.

This paper presents a further tool in the identification of counterfeit pharmaceutical products. Many drugs, such as Sildenafil citrate, contain sulphur, which exhibits a range of isotopic compositions, mainly due to bacterial activity but also because of fractionation during chemical syntheses. Variations in the ³⁴S:³²S isotope amount ratio can be used to distinguish between genuine and counterfeit product. A precise, accurate and reliable method for the determination of sulfur isotopic ratios by multi-collector ICP-MS is presented. Using silicon to correct for instrumental mass discrimination and high resolution measurements to overcome oxygen based interferences, internal precision of <0.01 % RSD is possible. The method was developed using a suite of mineral ³⁴S variations of 1 ‰, taking into account the full water samples⁴, where measurement uncertainty, could be resolved. Subsequently, laser ablation was used to introduce genuine and counterfeit samples of Sildenafil citrate into the ICP-MS, where significant differences between the samples of at least 8‰ were observed.

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INVESTIGATION OF THE STABILITY OF AN ARSENOSUGAR IN MOUSE
CECUM SAMPLES USING IC-ICP-MS AND LC-ESI-MS/MS DETECTION
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Arsenosugar exposures occur mainly through seafood and seaweed ingestion, and the major metabolite present in urine is DMA. Understanding the pathway of this conversion is the goal of this ongoing study. Preliminary studies indicated that very little of the arsenosugar degraded to DMA in a synthetic stomach or in pH adjusted control samples. The data presented will examine the stability of an arsenosugar, As(392), in anaerobic cultures of the microflora isolated from the ceca of laboratory mice. These data are relevant in assessing the role of the gastrointestinal microflora in degradation of ingested arsenosugars.

Specifically, data will be presented which indicate that the arsenosugar is converted primarily to its sulfur analog in the small intestine. This conversion appears to take place quickly at 37°C. IC-ICP-MS data indicate a good mass balance between the spiked arsenosugar and the resulting by-products. In addition, LC-ESI-MS/MS spectra of the sulfur containing arsenosugar in the cecal samples compare well with those of a synthetic standard. Details regarding the chromatographic conditions used in the characterization of the standard will also be reported.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

RF-GD-OES FOR NON CONDUCTIVE MATERIALS: SOME FEATURES
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Some recent developments on radio frequency-Glow Discharge-Optical Emission Spectroscopy (rf-GD-OES) sources allow fast and accurate analysis on non conductive samples. The scope of this paper is to present the last results obtained on different kinds of materials. We compare the results acquired by non pulsed rf source and pulsed one. Several samples have been tested: phosphate matrix for radionuclide waste storage, concrete material altered, archaeological samples with thin film trapping heavy metals, and geological samples who present a chemical gradient. All this samples has been previously analyzed using spectrometry for the chemistry, imaged by SEM/X-EDS, TEM/X-EDS and or AFM (Fig.1). The crater generated by the rf-GD-OES has been also characterized to visualize depth, potential artefacts (by or co products generated by the interaction between the argon beam and the materials, texture and when available the structure of the crater, amorphisation or on the contrary re crystallization of second generation products...). All these data are required to estimate the ablation speed. The results show that multilayer, alteration layers, chemical gradient can be revealed quickly without or minimizing artefacts especially using pulsed-RF modes. The erosion speed has been estimated and can vary strongly from a sample to another one. This matrix effect and the crater texture and structure need more study to assess their effect on the chemical profile obtained. Discussion put into evidence that ablation is speed is heterogeneous both in time but also in depth. So for quantitative aspects, some corrections must be taken into account. In conclusion the rf-GD-OES is a surface analysis technique of first attempt to check thickness and chemical composition of the samples. Its future must oriented toward high sensibility analysis (concentration of less than 1ppm); able to analyze hydrated or liquid material and of course non conductive ones as done in this work

Fig.1: SEM and AFM images of the bottom of the crater obtained on a multi layer glass. They reveal the textural and structural modifications generated by the beam in a classic mode.

DETERMINATION OF IR AND PT AT SUB-PPQ LEVEL IN POLAR ICE BY
ICP-SFMS WITH PRE-CONCENTRATION AND DESOLVATION SYSTEM

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A new analytical methodology, based on inductively coupled plasma sector field mass spectrometry (ICP-SFMS) coupled with a micro-flow nebulizer and desolvation system, has been set up for the quantification of Ir and Pt down to the sub ppq level (1 ppq = 1 fg g⁻¹ = 10⁻¹⁵ g g⁻¹) in polar ice samples. Ultra-clean procedures were adopted during the pre-treatment phases in our laboratories in order to avoid possible contamination problems. To determinate Ir and Pt down to the sub ppq level, a pre-concentration step by evaporation at sub-boiling temperature was necessary. We have obtained a procedural detection limit of 0.02 ppq and 0.08 ppq for Ir and Pt respectively. The repeatability of the analytical procedure at the ppq level was about 50% for Ir and 30% for Pt and the recovery was 75% for Ir and 93% for Pt. Procedural blanks were always found negligible and thus any subtraction to the samples concentrations was performed. Spectral interferences, affecting the determination of Ir and Pt, were strongly reduced by using a desolvation system for sample introduction. The contribution of interfering species was determined and subtracted. This new method allowed to analyse Ir and Pt in remote uncontaminated ice samples from Antarctica and Greenland down to the sub ppq level. The concentration ranges from 0.1 up to 8 ppq for Ir and from 0.2 up to 12 ppq for Pt. These measurements represent the first data of Ir concentration in unfiltered melted ice samples and the lowest ever recorded for Pt.

INVESTIGATIONS ON THE SPATIAL DISTRIBUTION OF GAS AND ELECTRON TEMPERATURES TOGETHER WITH ATOMIC AND MOLECULAR EMISSION IN THE ELECTROLYTE CATHODE ATMOSPHERIC GLOW DISCHARGE (ELCAD)

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In an electrolyte cathode atmospheric glow discharge (ELCAD) operating in a capillary cell with a discharge current of 65 mA, and a discharge voltage of 950 V, the distribution of gas (T_{gas}) and electron (T_{el}) temperatures were investigated along the discharge axis. The intensity distribution of selected metal and background emitted lines were also measured to optimize the signal-background ratio in use as an atomic emission analytical source.

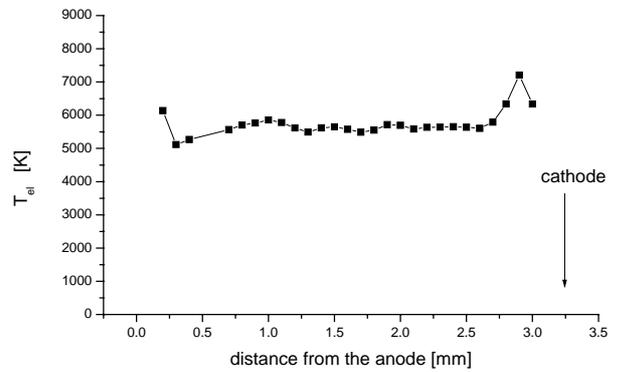
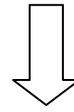
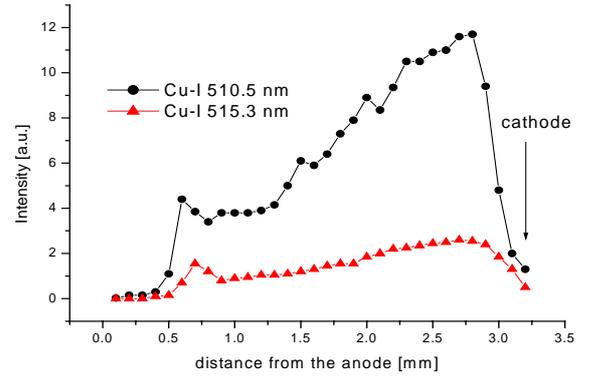
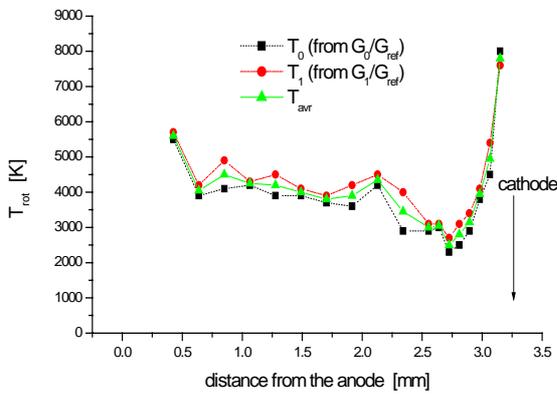
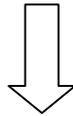
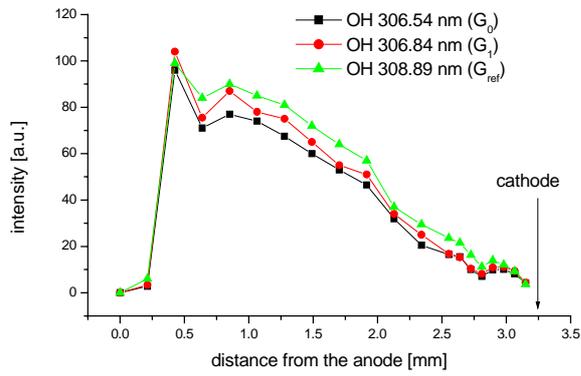
In earlier experiments performed on ELCAD-like plasmas the T_{gas} was determined by means of the rotational temperature (T_{rot}) of N_2 molecule [1,2,3,4]. These data are confuse and generally too low comparing to the alumina probe melting. The possible main reason of this, that the N_2 molecule is not an inner component of the ELCAD plasma. Since the ELCAD runs in a saturated water vapor the observation of the OH band intensities is the only correct tool, we selected OH rotational bands for determination of gas temperature in the ELCAD discharge. The T_{rot} derived from intensity ratios of G_0 / G_{ref} , G_1 / G_{ref} : $G_0 = 306.5$ nm, $G_1 = 306.8$ nm and $G_{\text{ref}} = 308.9$ nm unresolved band heads of OH radical is close to the gas temperature [5,6,7]. The T_{rot} distribution in ELCAD shows a maximum of ~ 8000 K near the cathode and its values were found to be ~ 6000 K near the anode and ~ 4000 K in the positive column. The distribution of electron temperature was calculated from the measured intensity ratio of the Cu-I 510.5 nm and Cu-II 515.3 nm lines [8]. In the near cathode and near anode region the ratio of $T_{\text{el}} / T_{\text{gas}}$ was received to be close to 1, while at the other places of discharge was observed to be 0.6-0.8 depending on the distance from the anode. This result is in accordance with our earlier data [9,10] and with the literature, by which T_{gas} and T_{el} approximate each other at the atmospheric pressure because of high number of collisions [11, 12].

The intensity distribution of measured OH band heads show much higher value in the bulk of plasma than that obtained in the near cathode region. Considering the data of Dolan related to the collision of H_2O molecules with electrons [12], this distribution refers to that the excited OH radicals are generated in the discharge plasma and not sputtered from the electrolyte cathode.

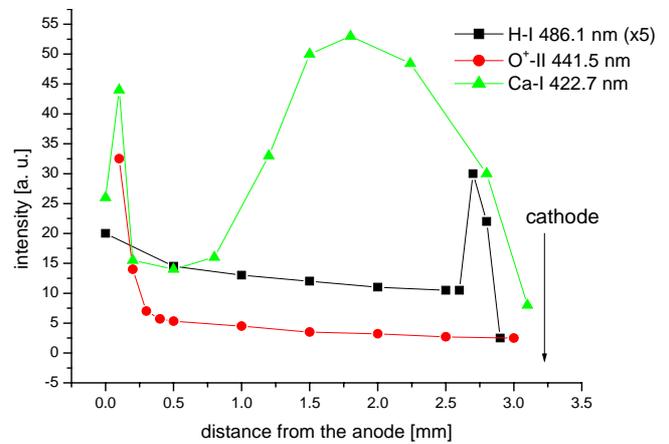
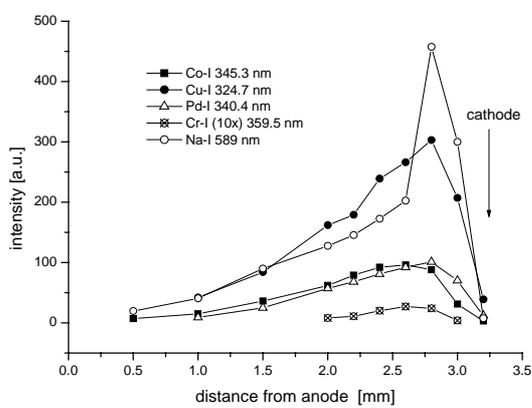
The N_2 337 nm band showed an intense peak in the near anode region and at the other places low intensity was observed. This clearly indicates that the N_2 originates from the outer gas atmosphere. The intensity of the other band of N_2 could not be detected.

The intensity maximum of metal lines (i.e. Na 589, Cu 510.5, Cu 324.7 nm, Co 345.3, Pd 340.4, Cr 359.5 nm) and $\text{H}_\beta = 486.1$ nm line occur in the negative glow due to the place of the highest electron impact excitation. In the case of Ca-I 422.7 nm line, the highest intensity could be measured rather in the positive column. The O^+ 441.5-7 nm ionic lines ($E_{\text{exc}} \approx 25-28$ eV) show observable intensity only in the near-anode range.

Temperature measurement data:



Line intensity distributions:



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MULTIMETAL DETECTOR BASED ON ELCAD OPTICAL EMISSION SPECTROMETRY PRINCIPLE FOR CAPILLARY ANALYTICAL SYSTEMS

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The Electrolyte Cathode Discharge (ELCAD) is a new optical emission source invented for direct analysis of aqueous electrolyte solutions¹. The ELCAD- OES provides wide element selection practically covering metals from the alkalis to Al, Cu, Co, Pd, Pb. A single capillary cathode construction showed sub-nanogram absolute detecting power for heavy metals but it was running with 3.5 mL/min sample flow which is too high for capillary analytical systems (CE, Ion-chromatography, etc.)². As a further disadvantage the sample solution in that case is required to have composition with good electric conductivity (i.e. pH 1.5).

In this work we show the performance of an advanced ELCAD detector construction which operates with two solution streams within the cathode compartment. The concentric double capillary arrangement separates the supporting electrolyte flow from the sample solution flow, hence the operation of the glow plasma itself becomes independent from the sample ionic conductivity.

The detector dead volume is about 2 μ L, the sample flow can be accepted between 0.1-0.6 mL/ min with water miscible composition (i.e. alcohols). The plasma supporting electrolyte is pH 1.5 HCl of 120 mL/h flow. The detector was tested by applying flow injection of 0.2-1 μ L of a multiple metal stock solution with 500 ng/ μ L concentration for each metals.

Preliminary sensitivity figures (absolute LOD): Cd 10 ng, Zn 30 ng, Cu and Pb 50 ng per elution peak. Response time is less than 1 s.

The details of the detector construction and typical peak records with evaluation will be shown.

¹ T.Csefalvi, P.Mezei, Direct Solution Analysis by Glow Discharge : Electrolyte-Cathode Discharge Spectrometry, J.Anal.At.Spectrometry 9 (1994) 345-349

² T.Csefalvi, P.Mezei, Subnanogram sensitive multimetal detector with atmospheric electrolyte cathode glow discharge, J.Anal.At.Spectrometry 18 (2003) 596-602

INVESTIGATIONS ON THE ELEMENT DEPENDENCY OF SPUTTERING PROCESS IN THE ELECTROLYTE CATHODE ATMOSPHERIC GLOW DISCHARGE (ELCAD)

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In this work we investigate the element dependency of the electrolyte sputtering process and suggest a chemical model for the mass transport and atomization in the cathode glow region.

ICP plasma source with pneumatic sample nebulizator may provide element-independent reference measurements to investigate the element-dependency of other sample introduction techniques. The glow discharge sputtering process can be investigated by replacing the nebulizer unit with an ELCAD discharge cell while applying the same sample solution for the analysis. Then the ICP signal ratio of every investigated element observed for the different aerosol generation methods provides a characterization of the overall element-dependency of the ELCAD sputtering process.

Experimental: the ELCAD cell was applied as sputtering source instead of the standard pneumatic nebulizator unit for the ICP. All generated products coming out from the ELCAD plasma were carried by the inner argon stream (total sample gas) to the torch. The sample solution then was applied either to the nebulizator unit of the ICP or to the ELCAD cell. Averaged results of three experiments show strong element dependency of ELCAD sputtering:

	line intensity ratio (± 14% error) $I_{\text{elcad}} / I_{\text{pneum}}$
Ba	0.08
Ca	0.06
Mg	0.13
Al	0.40
Cr	0.25
Pb	0.27
Zn	0.18
Cd	0.30
Cu	0.13
B	0.03
Hg	17

Explanations of the observed effect can be derived from: 1. Ion sputtering through direct ion-ion collision, 2. Neutral or quasi-neutral particle sputtering. When mapped against the energy transfer factor of the elastic direct ion-ion collision, the ICP signal ratio data show no correlation. The neutral atom sputtering (which assumes solvated electron capturing before the ejection) has some effect. However, the metal electronegativity values provide a well defined function versus the ICP signal ratio data which are peaking at the electronegativity value of OH radical.

The situation can be clearly discussed through the polarizability of the M--OH bond. This neutral compound is considered to be the final decomposition step of the desolvation process taking place in the cathode dark space, where the positively charged particles are forced back to the solution cathode by the strong electric field (10 MV/m). Only neutral particles of strong covalent M-OH bond can travel to the atomizing and exciting regions of the plasma. An M-OH stability factor was constructed on the base of the Pauling bond covalency concept, and ICP signal ratio data of Table II show good linear correlation with it.

A mass- transport scheme with four consecutive zones is proposed for the cathode dark space of the ELCAD (Fig.9). The element dependency can be associated with the zone **B** where the electric field produces cleavage of polarizable bonds.

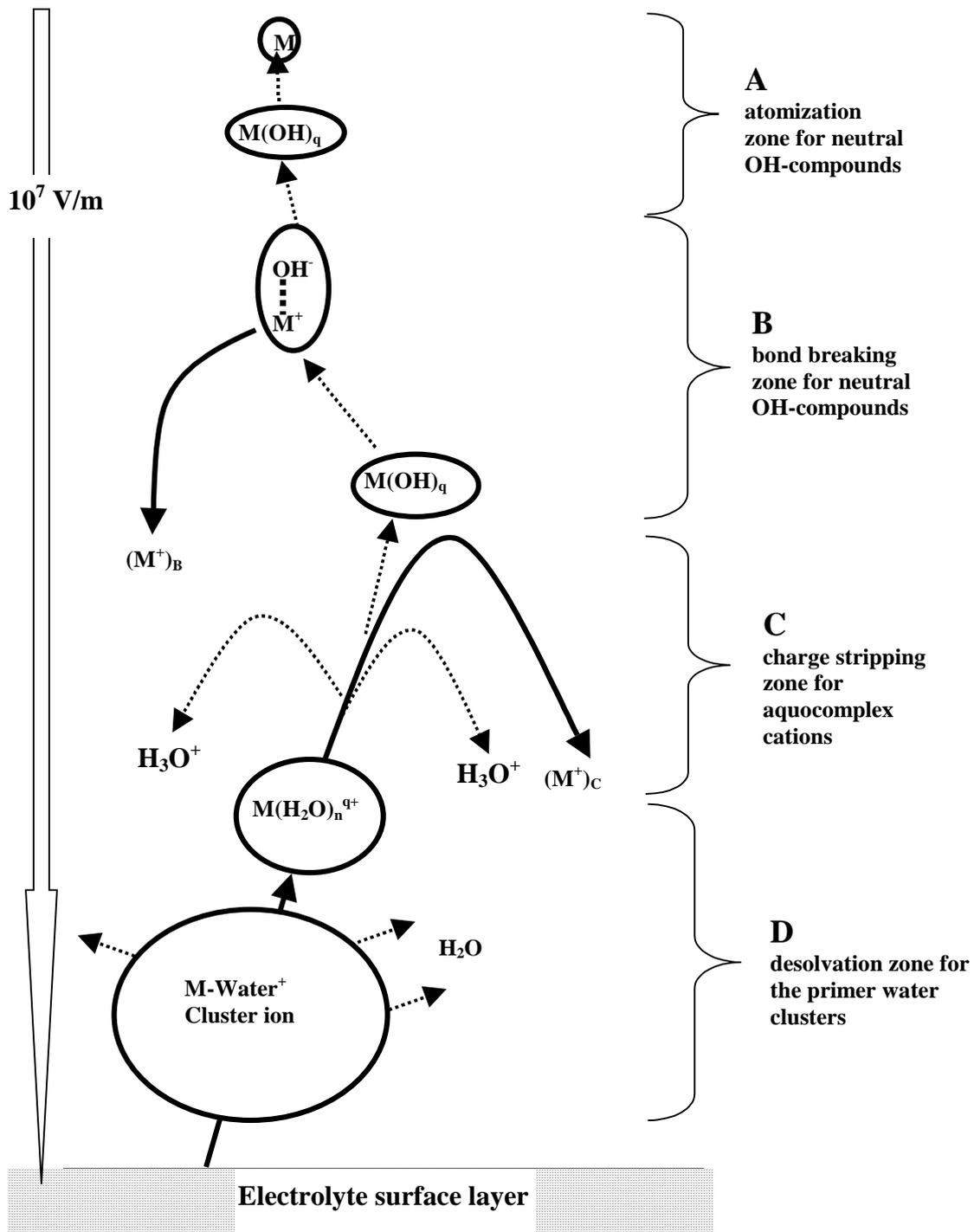


Fig. 9
Cserfalvi, Mezei

SPECIATION OF SELENIUM AT THE NG(SE) L-1 LEVEL WITH ICPMS
EQUIPPED WITH COLLISION/REACTION CELL SYSTEM: ADVANTAGES,
DRAWBACKS AND HOW TO OVERCOME THEM....

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In the last few years, the use of ICPMS equipped with Collision/Reaction Cell (C/RC) technology has greatly risen due to the possibility of monitoring elements suffering from polyatomic interferences. In the case of selenium, the most abundant isotope ^{80}Se is interfered by argide ions such as ArAr dimmer. Thus, without C/RC equipment, a less interfered, but also less abundant isotope, usually ^{82}Se , is monitored. Detection limits are consequently too high for the analysis of selenium in the aquatic environment as reported total selenium contents can vary between 0.05 and 1 μg (Se) l⁻¹ in non polluted waters. The determination of dissolved selenium speciation in such samples requires sensitive methods allowing quantification per species in the ng (Se) l⁻¹ level. Selenium speciation including inorganic, i.e selenite (SeIV) and selenate (SeVI), and organic species, i.e selenomethionine (SeMet) and selenocystine (SeCys), is conveniently achieved with HPLC - ICPMS coupling.

The ICPMS instrument used was the Agilent 7500c equipped with an octopole reaction cell. In order to efficiently remove interferences without important loss in sensitivity, careful optimisation of the C/RC (including nature and flow rates of added gases) was performed using experimental design methodology. Influence of ionic lenses voltage setting was also investigated to improve focalisation of the ion beam. A mixture of 3.8 ml min⁻¹ of H₂ and 0.5 ml min⁻¹ of He was selected as the best compromise. Detection limits were lowered by a factor of 3 for total analysis, reaching 30 ng (Se) l⁻¹. When coupled with HPLC, detection limits vary between 70 and 180 ng (Se) l⁻¹ depending on the species l.

Nevertheless, these detection limits remain too high to determine selenium speciation in the aquatic environment. In addition, hydridation of Br was observed when using C/RC, which creates new interferences such as ^{79}BrH and ^{81}BrH . Selenium quantification based on ^{80}Se and ^{82}Se is therefore unusable without the help of equations of interferences. The use of isotope ^{78}Se remains valid but with half abundance compared to ^{80}Se .

Changing the sample introduction from classical nebulisation to hydride generation (HG) represents an interesting alternative to avoid these new interferences. As only selenite can be directly hydridated, an on-line UV conversion step was inserted at the end of the HPLC column. In addition to quantitative sample introduction, numerous elements present in the sample or in the mobile phase are eliminated and background is lowered. Detection limits achieved without C/RC system are close to 10 ng (Se) l⁻¹ for inorganic selenium species monitoring ^{82}Se . If C/RC mode is used, ^{80}Se is monitored without BrH interferences as no bromine is introduced in the ICPMS. Detection limits found are thus in the ng(Se) l⁻¹ level, required for the analysis of aquatic environment. Some applications to real samples are also presented.

1: J. Darrouzès, M. Bueno, G. Lespes, M. Potin-Gautier, JAAS, 2004, submitted

THE DETERMINATION OF METAL CONTENT IN HERPES SIMPLEX VIRUS
WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Metals and metal-containing compounds are known to play important roles in many biological processes, including metabolic and detoxification pathways as well as the formation and function of proteins. Like all organisms, viruses contain a number of different metals. These metals, either by themselves or in the form of metalloproteins, are believed to be involved in the virus' ability to infect as well as replicate within healthy cells. The identification and speciation of these metals can be helpful in elucidating these mechanisms, which can, in turn, be vital to the development of more effective treatments.

However, to date, there have been no extensive investigations into the metal or metalloprotein content of viruses.

Inductively coupled plasma mass spectrometry (ICP-MS) is an obvious tool with which to perform such studies. Not only has it been established as a means by which to obtain total metal information, but is also effective in determining metal species when coupled with various liquid chromatographic techniques and has recently emerged as a viable technique in the analysis of metal-containing proteins.

This study aims to investigate the metal content of Herpes Simplex Virus (HSV) with ICP-MS detection. It focuses on the development of a flow-injection method for the determination of total metal concentrations in this particular virus. The concentrations of several metals are determined through the comparison of uninfected cells and HSV-infected cells, with the effect of different viral inactivation procedures also being explored. This work represents the first step in the characterization of metals, metal-containing compounds and metalloproteins in viral particles and is expected to provide useful information for future studies centering on the identification of metalloproteins in these same viral particles.

COMPARATIVE DETERMINATION OF PROTEIN BOUND METAL(OID)S IN
HUMAN SERUM AND BLOOD SAMPLES BY NATIVE VS. SDS GEL
ELECTROPHORESIS COUPLED WITH LA-ICP-MS
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The monitoring of metals and in particular their binding to the proteins in biological samples has become a vital issue in biochemical investigation. Gel electrophoresis laser ablation inductively coupled plasma mass spectrometry (GE-LA-ICP-MS) is a promising multielement method for analysis of metalloproteins.

As metalloprotein complexes have limited stability which depends on the three dimensional structure of the proteins the preservation of the protein conformation during the electrophoresis is essential.

We studied and compared the ablation from proteins separated by GE with sodium dodecyl sulphate (SDS) after heat-denaturation, without heat-treatment, and without SDS under native conditions. These methods were used for the speciation of metal(loid)s in human blood and serum from persons who ingested bismuth citrate and from workers from a facility recycling Hg-contaminated sludge from chlorine alkaline electrolysis as well as from unexposed controls.

After GE with SDS after heat-denaturation almost no species were detectable; in contrast GE without heat-treatment showed better results. A significant increase of detectable species for example of Mg, Mn, Fe, Ni, Cu and Zn were found under native conditions in human blood. In blood of persons exposed to metals additional species were detected. Similar pattern of metal species were found in blood and serum sample. The results of native GE agreed well with SEC-ICP-MS.

In this study we showed successfully that GE-LA-ICP-MS is a promising multielement method for analysis of metalloproteins in human blood.

A NEW METHOD FOR THE DETECTION OF PROTEINS BY LA-ICP-MS
USING GOLDCLUSTER LABELED ANTIBODIES

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Laser ablation ICP-MS (LA-ICP-MS) has recently been applied to the determination of protein-bound metals using gel and gel blots. A novel application of LA-ICP-MS for the detection of proteins on gel blots will be presented using commercially available metal labelled antibodies. After separation by gel electrophoresis and Western blotting, proteins were marked using the sandwich technique. In this standard method first a protein-specific primary antibody and then a labelled secondary antibody, which is specific for the primary antibody, is applied. By using goldclusters as labels the secondary antibodies can be determined by LA-ICP-MS. In comparison to single atoms, metal clusters increase the sensitivity in correlation to the number of metal atoms in the cluster. Quantification was carried out by comparing the signal of the antibody with the signal of the complete ablation of known amounts of a standard. In comparison to other antibody detection techniques LA-ICP-MS shows detection limits in the zmol (10⁻²¹ mol) range as well as excellent linearity over a broad dynamic range.

MULTI-ELEMENT SPECIATION OF PROTEIN-BOUND METAL(LOID)S IN
HUMAN BLOOD BY SEC-ICP-MS

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We studied the speciation of protein-bound metal(loid)s in human blood by coupling size-exclusion liquid chromatography (SEC) simultaneously to both ultra violet diode array detection (UV-DAD) and inductively coupled plasma mass spectrometry (ICP-MS). Citrate buffer and a Superdex 200 column with a separation range between 10 kDa and 600 kDa were used. Blood from uncontaminated persons, from persons who ingested bismuth citrate and from workers from a facility recycling Hg-contaminated sludge from chlorine alkaline electrolysis were analysed. Blood was divided into serum and blood cells by centrifugation and investigated separately. A number of different metals species were detected. For several metals (e. g. ^{24}Mg , ^{56}Fe , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{118}Sn , ^{209}Bi) the ICP-MS signal correlated well with signal from the UV-DAD. A comparison of uncontaminated and contaminated human plasma and cell extracts is presented here. The results obtained SEC-ICP-MS are compared with gel electrophoresis laser ablation ICP-MS analyses of the same sample.

COMPARATIVE ANALYSIS OF PROTEIN BOUND METAL(LOID)S USING
NATIVE AND SDS GE-LA-ICP-MS AND SEC- ICP-MS

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The metabolism of trace elements, in particular their binding to proteins in living systems is of great importance in toxicological and biochemical studies. The main problem of the analysis of non-covalent bound metal-protein complexes is the preservation of the three dimensional structure of the protein during preparation and separation.

In this study two different analytical approaches were compared: size-exclusion chromatography inductively coupled plasma mass spectrometry (SEC- ICP-MS) and gel electrophoresis laser ablation ICP-MS (GE-LA-ICP-MS). These methods were used for the speciation of metal(loid)s in human blood and serum of humans who ingested bismuth citrate and of workers from a facility recycling Hg-contaminated sludge from chlorine alkaline electrolysis as well as from unexposed controls.

GE was carried out with SDS heat-denaturation, without heat-treatment, and under native conditions. After SDS with heat-denaturation almost no metal species were detectable. SDS without heat-treatment revealed more signals. Significantly more species of for example Mg, Ni, Zn, Cu, and Bi were detected under native conditions. The results of native GE agreed well with SEC-ICP-MS.

Proteins were detected by an ultraviolet diode array detector in the case of SEC. For GE usually staining or labelling methods are used for the detection of proteins. We present a new method for detection of specific proteins on gel blots by LA-ICP-MS. Proteins were marked by the standard sandwich technique, using goldclusters as labels for the secondary antibody. This method provides excellent detection limits for secondary antibodies in the zeptomol (10^{-21} mol) range. In comparison to other methods for detection of labelled antibodies, LA-ICP-MS provides a broad dynamic range. Quantification is performed by comparing the signal of the antibody with the signal of the complete ablation of known amounts of a standard.

The advantages and disadvantages of GE and SEC for the speciation of protein bound metal(loid) are discussed.

COMPARISON OF QUANTITATIVE SELENIUM SPECIATION IN
COMMERCIAL AND SELENISED AGARICUS MUSHROOMS

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Se is an essential element for animals and humans, playing important biological roles as antioxidant, as regulator of thyroid hormone metabolism or as anti-carcinogenic agent (1). The element enters the body mainly through food and, among vegetables, mushrooms are one of the most important Se sources.

Some mushrooms, including those of the Agaricus family, are able to accumulate Se when grown in soils with high contents of the element. Moreover, the consumption of Se-enriched Agaricus bisporus has shown to retard the growth of chemically induced tumours (2).

As very limited information exists so far on the levels of different Se species in foodstuffs, accurate and precise analytical methodologies for the quantitative speciation analysis of Se in this kind of samples are mandatory. In this sense, Se speciation studies in biological materials are mainly carried out by HPLC coupled to an ICP-MS.

However, the accurate quantification of the separated Se species is not always possible by the more “traditional” techniques (e. g. external or standard addition calibration methods) if the species are unknown, of course, in such cases no commercially available standards for calibration can be used. As an alternative, the application of isotope dilution analysis (IDA) using the species-unspecific spiking mode (3) on-line with the HPLC separation allows accurate quantification of the heteroatom measured in the compound, even in such unknown species.

The aim of this work was the comparison of nature and content of Se species naturally occurring in Agaricus mushrooms with those present in selenised specimens of the same mushroom. For that purpose, three different extractions of each sample were performed and the corresponding extracts were analysed by HPLC-ICP-ORS-MS using post-column IDA. Results showed marked differences not only in the total Se contents but also in the Se species nature found in the two types of Agaricus mushrooms investigated. Selenomethionine was detected and determined in both of them together with a number of unknown selenocompounds.

(1) M.P. Rayman, Lancet, 2000, 356, 233.

(2) M.R. Spolar, E.M. Schaffer, R.B. Beelman and J.A. Milner, Cancer Lett., 1999, 138, 145.

(3) K.G. Heumann, L. Rottmann and J. Vogl, J. Anal. At. Spectrom., 1994, 9, 1351.

LAYER-BY-LAYER ANALYSIS OF SEVERAL NEW MATERIALS IN HOLLOW CATHODE DISCHARGE

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The possibility of the hollow cathode discharge as depth profiling technique is demonstrated by analysis of several new materials:

AlN thin films deposited on glass substrate;

Ag-covered BSCCO high temperature superconductors: clarifying the catalytic role of Te additive for diffusion of the rest elements into the Ag sheath;

Planar optical waveguides fabricated by $\text{Ag}^+\text{-Na}^+$ and $\text{K}^+\text{-Na}^+$ ion exchange processes in glasses: optimization of both ion-exchange process and waveguide characteristics;

$\text{SnO}_2/\text{SiO}_2/\text{Si}$ structure modified with hexamethyldisilazane and processed with rapid thermal annealing in the temperature range of 800-1200°C, developed as a basis of gas sensing solid state devices;

CVD- WO_3 thin films deposited on soda lime glass substrate: optimization of the technological conditions for WO_3 film fabrication;

CVD-W and WC layers deposited on Co metalloceramics, designed for cutting tools.

The results obtained by depth profile analysis in the hollow cathode discharge were compared with the results from different complimentary standard methods.

HYDROGEN NEGATIVE ION FORMATION IN HOLLOW CATHODE GLOW DISCHARGE

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Negative ion plasmas are of great interest for various regions of both science and practice but recently their importance has increased especially for the purposes of the modern plasma technologies.

We have performed experimental and theoretical investigations of Hydrogen negative ions in the hollow cathode glow discharge and the glow discharge with a positive column. The concentration of Hydrogen negative ions has been measured by laser photo-detachment method in both discharges at pure Hydrogen and (Ne+H₂) mixture. In the hollow cathode glow discharge and the glow discharge with a positive column the contribution of various elementary processes to the formation of the negative Hydrogen ions has been revealed by appropriate theoretical model including more than 30 processes and the vibrational kinetics as well. Our results show that the Hydrogen negative ions have two orders of magnitude higher concentration in the hollow cathode glow plasma than in the glow discharge with positive column. Besides, in the hollow cathode glow discharge higher concentration was measured at (Ne+H₂) mixture than at pure Hydrogen.

Based on all results obtained the optimum conditions have been found for maximum Hydrogen negative ion concentration in hollow cathode glow discharge.

SPECIATION ANALYSIS: ERRORS, SUCCESS, EVOLUTIONS, MATURITY AND TRENDS OR “DO WE STILL NEED A PLASMA?”

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The number of publications dealing with trace metal species determination has been steadily growing over the last 20 years. If it is now well understood that metals occur in the environment in a wide variety of chemical formulations regulating their toxicity or beneficial aspects, their fate, uptake and translocation between the different compartments of the ecosystem, one can wonder why it has taken so long to properly address these issues. Indeed, it is now more than 40 years after the outbreak of methylmercury poisoning in Minamata (Japan) and yet routine, robust and reliable hyphenated methods are just arriving in every one laboratory.

So what has changed over these last 15 years? Considerable amount of changes have occurred during the last decades. First, the concept is better understood and if issues dealing with environmental issues are becoming mandatory for some species, cost-effectiveness of speciation analysis in industry, food safety and the now well accepted objective of sustainable development clearly highlight the fact that we cannot waste the information related to the occurrence of metal in the matrix of interest. Hyphenation of instrumentation is also now commercially available, starting from rapid and reliable methods of sample preparation to robust detection techniques. The use of plasma techniques (using either optical or mass detection) is now fully necessary and is now the standard for hyphenated methods for both liquid and gas separation techniques. Only they can provide robust, selective and sensitive detection limits. When using ICP/MS based techniques, we can also now have full access to the reactivity and the chemical process taking place in the question of interest, correcting for bias results when using speciated isotopic dilution methods. These analytical facilities allow to better assess the reactivity of the ionic, organometallic or metal-organic species in their context. Aside from success stories, we also have made a series of mistakes during the last decades and have learned from them, understanding better the crucial role of reference material as stepping stones of metrology in speciation analysis.

Further to the tremendous rationalization and simplification efforts made in instrumentation made to promote the approach of speciation analysis, other initiatives will help to simplify and diffuse the knowledge associated with speciation analysis. The European Virtual Institute for Speciation Analysis is a coordinated effort from different academic groups and industrials willing to bridge the gap between legislators, analytical chemists, environmental scientists and industry.

New roads still continue to open. Plasma spectrochemistry coupled to ICP/MS is the pathfinder for proteomic and metallomic research before refining the information with MSⁿ instrumentation. However, new techniques move into the field to allow a direct access of the speciation of the element imbedded in its matrix. Beam spectroscopies such as XPS or XANES bring a whole array of new information helping defining the structural aspects of the molecules of interest where the metals are located.

So, will we still need plasma spectrometry in the future? More than ever since this technique is reaching its mature stage, allowing the implementation of routine applications to the laboratory for speciation analysis, strengthening our knowledge and opening new doors. This definitely needed to improve the quality of our daily life and establish sound concepts for sustainable growth.

GDOES ANALYSIS FROM THICK TO THIN LAYERS
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A survey will be given on the needs for routine analysis in the different fields of application of GD OES. This covers sample preparation for bulk or depth profiling, the cleanness and the choice of discharge conditions. All parameters influencing the instrument stability will limit the quality of the analytical result. While these limits might be accepted in the standard range of applications, improvements are still possible and will be demonstrated. These improvements are a prerequisite on those demanding applications that are getting more importance nowadays, the analysis of thin layers approaching the nm range. The second part is focused on depth profiling of thin layers. Even on conductive material the rf excitation can be preferable to dc due to the soft startup conditions. A better accuracy of the quantification of rf measurements is achieved by new measurement techniques to determine the electrical parameters of the rf discharge. The use of pulsed discharges will be discussed as well.

A HIGH RESOLUTION CCD DETECTOR SYSTEM FOR GDOES

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With CCD detectors or a monochromator it is possible to register complete spectra of the emission lines typical for the analytical glow discharge. This is not only adding flexibility to the analysis, it is very helpful for basic studies. Recent developments using new CCD devices allow a continuous, highly resolved spectra detection even for layer structures. In this contribution examples will be given on standard materials showing the influence of impurities, possible molecular background signals and other effects. Other examples will be devoted to the identification of element emission lines. Even the relative emission line intensity in glow discharge is very often different to arc or spark sources that are listed in standard data bases. High resolution CCD detectors can be very helpful to create an emission line data typical for GDOES.

LASER ABLATION ICP-MS IN FORENSIC GLASS ANALYSIS:
WAVELENGTH DEPENDENT CHANGES OF REFRACTIVE INDEX OF GLASS
FRAGMENTS AFTER LASER ABLATION

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Float glass is one of the major types of evidence encountered in crimes such as burglary, traffic accidents and vandalism. In forensic laboratories refractive index measurements are carried out on small fragments of glass to compare the refractive index from glass from the scene of crime with glass collected from suspect clothes. In case of indistinguishable refractive index measurements elemental analysis can be carried out in order to increase the evidential value of glass examinations. Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) has been proven to be a sound technique for the quantitative analysis of float glass. Due to the fact, that for the refractive index measurements the small fragments have to be crushed, resulting in even smaller fragments, a possible alternative of the procedure would be to carry out LA before the refractive index measurements.

In this study the possible change of refractive index caused by the laser ablation process was examined. The refractive index of small glass fragments of a very homogeneous optical crown glass (K5) and a float glass were investigated after laser ablation at three different laser wavelengths (193 nm, 213 nm, 266 nm).

The size, mass and geometry of small glass fragments (size length < 3mm) were documented and different sizes were selected for laser penetration. The resulting change of RI was determined.

Critical parameters for laser ablation on small fragments using LA-ICP-MS of different laser wavelength will be presented.

MULTI-ELEMENTAL ANALYSES OF WINE BY INDUCTIVELY COUPLED
PLASMA MASS SPECTROMETRY AND THEIR POSSIBLE USES

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Inductively coupled plasma mass spectrometry (ICP-MS) has become an established technique for the rapid trace elemental analysis of diverse geological, metallurgical and biological matrices. Solution nebulisation (SN) is the commonest form of sample introduction to ICP-MS and many protocols have been developed to suit the samples being analysed. Direct semi-quantitative analysis of wine was reported more than a decade ago, and more recently, flow injection has been employed to determine elements such as Li, Al, Cr, Mn, Fe, Cu, Zn, As, Cd and Pb in Spanish and English wines to ascertain their origin. Microwave digestion followed by sector field high resolution ICP-mass spectrometry has been used to determine rare earth elements in German wines, revealing their concentrations to be dependent on the wine-producing process. Therefore, such analyses are not generally suitable as fingerprints to indicate the provenance of wines. Owing to the global economic importance of wine production, however, studies such as these are potentially of high impact if they can help source wines, identify adulterated specimens, determine the presence of potentially harmful elements or confirm good quality. In this study, high resolution SN-ICP-MS was employed for the multi-elemental analysis of wines from Brazil, Argentina and Uruguay. Wine samples (5.0 ml) were diluted 1:1 with 2% HNO₃ containing In at 20 ng ml⁻¹. Allowances were made for the different alcohol contents of the wines, which may produce variations in the responses obtained from a fixed analyte concentration. Inorganic ion concentration of wine is related to quality and the concentration data obtained in this study are discussed in relation to this and the possibility of wine sourcing.

MEASUREMENTS OF GUNSHOT RESIDUES BY SECTOR FIELD
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY -
FURTHER STUDIES WITH PISTOLS

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The investigation of gunshot residue (GSR) is essential in the forensic examination of suspected cases of firearm use. In São Paulo State, Brazil, about 1500 firearms are seized each month with the following distribution: 70 % single round barrel revolvers, 20% pistols e 10% other types, i.e. sub-machine guns, shotguns, rifles, etc. Although the total number of weapons seized appears to be extremely large, it represents only a small fraction of the number of firearms possessed by criminals, citizens and employees of private security firms. For this reason, firearms are a major concern in public safety. Antimony, lead and barium are the major elements present in GSR. The amount of these elements on the hands of shooters depends on several factors, such as the type of weapon and ammunition used, the age and condition of the weapon, the suspect's personal hygiene and occupational habits, biometrics, the time elapsed since the firing and the quality of the sampling procedure. Several techniques have been used for GSR analysis, each exhibiting advantages and drawbacks. More recently, a sector field inductively coupled plasma mass spectrometer (SF-ICP-MS) was used to successfully identify GSR from .38 caliber handguns (single round barrel revolvers) supplied with .38 SPL LRN (lead round nose cartridges). The sampling regions were the back of the thumb and forefinger or palm areas of volunteers chosen at random who did not handle fire arms. Samples were obtained by scrubbing one of these regions with swabs moistened with 2% EDTA solution. This type of weapon is associated with a relatively great emission of particles and the concentrations of the elements of interest recovered ranged from one to several hundred mg/L. In this work, the same methodology was used to identify GSR from 9 mm and .40 in caliber pistols on the hands of 20 volunteers. Two types of ammunition were tested: 9 mm Taurus and clean range. For the first, the quantities of the elements of interest recovered were one order of magnitude less than those obtained for caliber .38. Clean range ammunition, generally considered free from metals, also clearly exhibits the presence of the elements examined. The use of a technique with high sensibility, such as SF-ICP-MS, permits the identification of low concentrations of metals (less than 1 mg/L) in firearm residue and constitutes a powerful tool in forensic science. It is important to notice, however, that due to the random characteristics of the quantity of emitted particles and the many factors that can affect the level of metals present on the hands of shooters, a rigorous procedure for sampling has to be established, including collection from a different body part of the suspect (the other hand, for example) to be used as a blank test.

TRACE ELEMENT ANALYSIS OF BLACK AND GREEN TEA BY
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

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Tea is a stimulant drink: Xanthines (theobromine, caffeine and theophylline) provide central nervous system stimulation and relaxation of smooth muscle. Other chemicals, such as phenolic acids, polyphenols and flavonoids provide significant antioxidant activity. Recently, trace elements in tea, especially iron, manganese and selenium, have been investigated for possible health benefits. Moreover, with the world-wide marketing of green tea as a beverage with possible health benefits, there is a need to establish not only the baseline of trace element levels, but whether they differ in terms of geographical location (influenced by soil type/chemistry, climatic conditions and growing methods), production and commercial processing. Sixteen trace elements (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Sn, Sb, Hg and Pb) were determined in tea samples (black, green and some flavoured teas) grown and marketed in Brazil and Argentina. Samples of brew infusions (produced by the Standard Infusion Method for Loose Leaf; 4.0g in 400 cm³, 3 min 55s infusion), acid digested leaf solutions and certified reference material solutions were analysed by quadrupole inductively coupled plasma mass spectrometry (ICP-MS) with internal standardisation (⁷²Ge, ¹¹⁵In, ²⁰⁹Bi), polyatomic interference correction and matrix-matched standards. Instrument stability was verified using responses from the analysis of the TMDA-54.3 water reference material standard. A wide range of trace element levels exist in black and green tea samples from the two South American countries, with overall elemental ranges being typical of those for such materials grown in many other countries. Green tea has very high levels of Al and Mn. The brewed infusion solutions contain good levels of several health-related trace elements (Cu, Zn, Fe and Se). Only very low levels of the non-essential elements, at below 1 mg/kg dry weight in the leaf material and 50 µg/l in infusions were found. The difficulties encountered in sample preparation and analysis (acid digestion, matrix effects and polyatomic interferences from Cl) and the potential health-benefits of tea drinking will be presented.

DEVELOPMENTS IN BIOLOGICAL AND ENVIRONMENTAL APPLICATIONS
OF LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS
SPECTROMETRY (LA-ICP-MS)

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Two decades have past since Gray published the first report of the use of ruby laser pulses to mobilise sample material directly from the solid for introduction to a quadrupole mass spectrometer for elemental and isotope ratio analysis. Since then successive developments both in affordable laser technology and more sensitive spectrometers, including high resolution and time-of-flight instruments, have propelled LA-ICP-MS into being a routine method of analysis, especially for many geological applications. The principal advantages of laser ablation are that it avoids the sample dissolution required for conventional solution nebulisation and permits spatially-resolved analysis (line or depth profiles). Several mainly wide-ranging reviews of LA-ICP-MS have appeared over the last five years, but the present work presents a critical assessment of recent developments in biological and environmental applications of this technique, considered broadly to include, for example, the elemental analysis of tree rings and bark, pollution monitoring via the analysis of coral, and fingerprinting of traffic-related metals in road sediments. Isotope ratio analyses relevant to environmental studies are discussed. The advantages and difficulties of LA-ICP-MS in conjunction with electrophoresis are also examined. Such combinations promise quantitative analysis of, for example, the binding of metals to various molecular size fractions in humic and fulvic acids.

BENEFITS AND OPERATING LIMITS OF A QUASI-DIRECT INJECTION
NEBULISATION (QDIN) SYSTEM IN USE WITH A THERMO FINNIGAN
ELEMENT II ICP-MS

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Benefits and operating limits of a Quasi-Direct Injection Nebulisation (QDIN) System in use with a Thermo Finnigan Element II ICP-MS.

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Following the torch integrated sample introduction system (TISIS) developed by Todoli and Mermet (1) we have made a simple device for quasi-direct injection of liquid samples, using a selection of concentric nebulizers at uptakes in the range 10 to 100 microlitres/minute. This QDIN device is a refinement of the low volume spray chamber of Cairns et al. (2), in that it was fitted with a heating sheath to suppress condensation.

Comparative measurements were made of memory effects with the QDIN and the Element II coaxial spray chamber, including several elements such as mercury and iodine that form volatile components in acidic matrices (EVC's).

It was found that the onset of visible regions of stored droplets in the QDIN correlated well with the persistence of some elements' memory effects. The amount of heating of the QDIN device that was required to prevent droplet storage was closely related to the nebulizer uptake in the range 30 to 100 microlitres/minute. For several EVC's the reduction of memory effects was striking.

The sensitivity of ICP-MS determinations with the QDIN was found to be similar to that of the standard Element II sample introduction system, but with the advantage of requiring less than a tenth of the usual sample quantity. Short-term stability of the QDIN, with sample both pumped to and aspirated by the nebulizer, was compared with the Element II standard system.

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IMPROVED ANION SPECIES ANALYSIS BY IC-ICP-MS USING ANALYTE-TO-GeO₂ SIGNAL RATIOING

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Ion chromatography on-line coupled to ICP-MS (IC-ICP-MS) is a powerful tool for speciation analysis. Ionic compounds are chromatographically separated by charge and size. The detection with ICP-MS yields low limits of detection and simplifies the identification of unknown species due to its element-specificity. By its elemental mass information it is possible to distinguish and quantify overlapping peaks. Chromatographic run times are reduced and/or more analytes are determined in one chromatogram.

One important application is the analysis of halogen anions in drinking water. For example, the potentially carcinogenic bromate is formed during the disinfection process with ozone. Traces of iodide result in a bad taste or odor, due to conversion to I₂ with air contact.

Germanium dioxide was found to be a well suited internal standard for IC-ICP-MS. GeO₂ has two important properties: The solubility in water is good enough and it remains uncharged at pH 4-6. This neutral molecule is added to an eluent as a continuous internal standard without interactions with anion or cation exchangers. The continuous Ge signal is a valuable monitor tool and indicates many different system failures in real time. The m/z 74 isotope is used as a “classical” internal standard for bromine and also iodine species because of its appearance in the same mass region. All kinds of non-spectroscopic interferences can be corrected. A fast semiquantitative quantification method was developed based on the ratios of analyte peak areas and GeO₂ signal height [1]. If the exact mass response of an ICP-MS is known, the capability of concentration determination of different elements with only one element standard is given. The ratio of analyte-to-GeO₂ for normalized concentrations turned out to be very stable over a long time and almost independent of ICP-MS instrumental settings. It was concluded, that changes of the mass response and ionization efficiency of Br, I and Ge are correlating. This stability allows to omit the classical calibration procedure and to perform a semiquantitative calibration simply by using the ratio of analyte-to-GeO₂. It is sufficient to determine the value of the ratio once a day with one calibration standard or if possible by calculating the mean value of previous measurements. Subsequently, the real time analyte-to-GeO₂ ratio is exploited for fast and simple concentration determination of bromine and iodine species. The GeO₂-ratioing method combines advantages of both continuous internal standardization and isotope dilution calibration.

The influence of several instrumental settings on the analyte-to-GeO₂ ratio was investigated, including tuning conditions, plasma temperature, different nebulizers, IC flow rate and quadrupole settings. A flow injection setup was installed to measure the transient signals of iodate/bromate and iodide/bromide using a large selection of varying parameters. Correlation will only apply for drastically changed settings which usually do not occur even if there is a relatively strong drift. The measurement of

analyte to GeO₂ ratios is well suited for fast semiquantitative analysis of bromide, bromate, iodide and iodate in waters and yields LODs at about 0.1 µg L⁻¹.

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IMPROVED SENSITIVITY OF THE NEW SHIP TORCH FOR ICP-OES

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A conventional inductively coupled plasma excitation source requires typically a gas flow of up to 20 L/min of Argon. This causes substantial analyte dilution, short residence times in the excitation zone of the plasma discharge and additionally high operating costs. Based on previous research [1] KLOSTERMEIER and BUSCHER developed a new torch design for inductively coupled plasma optical emission spectrometry with minimised gas consumption [2]. This was achieved with integration of an external air cooling system in the torch fastening and new torch geometry, inspired and closely related to geometry of enclosed plasma torches. Under optimised working conditions of the 27.12 MHz Ar plasma with 1.1 kW RF power, the total Ar gas flow was reduced to only 0.6 L/min.

Analytical figures of merit of the new SHIP (Static High Sensitivity ICP) torch were investigated [3]. Temperatures were determined to be at the order of 6,000 – 10,000 K for the excitation temperatures and 3,700 – 4,100 K for the rotational temperatures at total gas flow rates between 0.05 – 0.8 mL/min. The new torch was coupled with different sample introduction systems and the detection limits for several elements were found to be very close to the detection limits for the conventional ICP torch of a SPECTRO CIROS CCD spectrometer. From the presented data, it is possible to conclude that the new SHIP torch is a promising system for ICP-OES with minimum deterioration in analytical performance. Furthermore, it is an effective method to reduce the operating costs in ICP-OES significantly.

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DETERMINATION OF LOW LEVELS OF U AND TH ISOTOPES IN HUMAN URINE

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Because of their chemical toxicity, the determination of radionuclides uranium and thorium in environmental and biological samples is considered as a tool for assessment of exposure. Exposure to thorium and uranium can occur via food chain, mining and milling of elemental ore materials. Also the exposure to DU generated by nuclear and industrial applications that is demonstrated from the measurement of $^{235}\text{U}/^{238}\text{U}$ ratio.

ICP-MS has proved to be an excellent analytical tool for the determination of those radionuclides at low levels, combining excellent detection limits, multi-isotopic capabilities. However, uranium and thorium cannot be accurately measured in urine by ICP-MS because of the high content of total dissolved solids (TDS), that leads to signal suppression and salt built up on the cones and the torch of the ICP-MS instrument, after introduction of few millilitres sample. Therefore matrix separation is often required prior to analysis.

In this work a rapid and sensitive flow injection preconcentration and matrix separation technique coupled to HR-SF-ICP-MS has been developed and validated for the simultaneous determination of ultra-low levels of thorium and uranium in human urine. The method is based on the selective retention of U and Th from a urine matrix, after microwave digestion, on an extraction chromatographic TRU resin and their subsequent elution with ammonium oxalate. The U and Th contents in urine was found in the range 1.86-5.50 and 0.176-2.35 ng L⁻¹, respectively, well in agreement with levels considered normal for non-occupationally exposed subjects. The $^{235}\text{U}/^{238}\text{U}$ isotopic ratio in urine is measured on-line in FI transient signal with a precision of 0.82-1.04 % (RSD).

RAPID TECHNIQUES FOR THE DETERMINATION OF PU AND AM IN ENVIRONMENTAL MATRICES USING MICROWAVE SAMPLE PREPARATION, ON-LINE SAMPLE INTRODUCTION WITH APEX HIGH-SENSITIVITY SYSTEM AND ICP-DRC-MS DETECTION
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Plutonium and americium are important actinides from both environmental and occupational health perspectives. They are present in the environment as a result of nuclear weapons tests, reactor accidents, and reprocessing of nuclear fuels. In situations of either accidental or deliberate release, the rapid measurement of the long-lived isotopes of Pu and Am in environmental samples is important.

ICP-MS is one of the fastest methods for determination of long-lived radionuclides, and particularly for Am and Pu. The main Am and Pu isotopes are monitored in the mass range from 239 to 244 amu. Most studies have demonstrated that there are three main issues for the measurement of Am and Pu in environmental samples: (1) the high concentration of matrix constituents, such as Na, Ca, Mg, Si, organic matter etc; (2) the low level of Am and Pu in environmental samples; and (3) polyatomic interferences, such as $^{238}\text{U}^{1}\text{H}$ and $^{238}\text{U}^{1}\text{H}^{1}\text{H}$ that interfere with ^{239}Pu and ^{240}Pu , respectively, when high concentrations of U are present in samples. Therefore matrix-specific analytical approaches are required for particular combinations of environmental matrix and measured isotopes.

Three different environmental matrices were chosen: urine (which is the best medium to assess any human contamination), vegetation (which can be used for the urgent estimation of a sudden release of these actinides) and sediments (which are useful for long-term geochemical dating). Rapid and total microwave assisted digestion methods were developed for these three types of samples.

Different flow injection (FI) techniques based on on-line matrix separation and analyte preconcentration were developed. Rapid on-line separation was developed for each chosen sample types and actinides. It was found that the determination of Pu and Am in both digested and non-digested urine can be implemented simultaneously and using only one ion-exchange resin. The determination of Pu in more complicated matrices, such as vegetation and sediments require the use of two resins, because of the high level of Fe and rare earth elements (REE) in the samples. The APEX sample introduction system, which provides enhanced sensitivity, was implemented between FI system and ICP-MS instrument, providing an improvement in detection limit of between 5 and 10 times.

Carbon dioxide was used as a reaction gas to remove $^{238}\text{U}^{1}\text{H}$ for the determination ^{239}Pu , when samples contained a significant U concentration after on-line separation.

INTERFACIAL EFFECTS ON THE DEPTH RESOLUTION DURING THE
ANALYSIS OF MULTILAYERS METAL COATINGS BY RADIO FREQUENCY
GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY DEPTH
PROFILING

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In the analysis by radio-frequency glow discharge optical emission spectroscopy (rf-GDOES) techniques, the depth resolution mainly depends on the roughening induced during the sputtering and crater geometry. The shape of the sputtering crater (“edge effect”) has been found to be dependant on the experimental conditions. A reduction in the power and an increase of the pressure of the GDOES discharge reduced the crater edge contribution improving the depth resolution within the studied range. The roughening effects arisen during sputtering in depth profiling has been also analysed to evaluate the depth resolution function of the GDOES technique. Ultra thin chromium layers of 2.5 and 5 nm, buried at different depths in a titanium matrix up to a thickness of 3 mm, were properly resolved both near the surface and deeply embedded in the matrix.

The analysis of multilayer coatings consisting of 10 bilayers of 80 nm chromium and 140 nm titanium deposited on silicon confirms the importance of the crater shape and sputtering induced roughening effects. Reverting the order of the layers (10 bilayers of 80 nm titanium and 140 nm chromium) showed the effect of different sputtering rates of the materials in the depth profile. The profiles of materials with high sputtering rate (i.e. chromium in this study) become less affected than material with low sputtering rate (titanium) due to lower mixing of the layers.

DEVELOPMENT AND APPLICATION OF ISOTOPIC TAGS FOR
INVESTIGATION OF PROTEIN EXPRESSION AND PHOSPHORYLATION
USING LC-ICP-MS

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Two of the key challenges in proteomics research are: the quantification of changes in protein expression between normal and diseased tissue, which is important for the diagnosis of e.g. metabolic disorders; and determination and quantification of the degree and site of phosphorylation, and other post-translational modifications which determine protein function.

Recently, the isotope-coded affinity tag (ICAT) method has been developed by the Aebersold and Gelb[1], and used to determine the relative expression of peptides from diseased and un-diseased states. The ICAT method has proved popular because kits containing all the reagents necessary for labelling are commercially available, however a disadvantage is that excess reagents must be removed in order to prevent interference in the electrospray mass spectrum. We have been investigating the use of cyclic diethylenetriaminepentaacetic dianhydride (cDTPAA)[2] as an alternative approach. This compound is a bi-functional chelating agent which will react with an amine group and simultaneously chelate a metal ion. We have used this to tag bradykinin with In and Eu and will present results demonstrating how this can be applied to the relative quantification of peptides.

Phosphorylation of serine, threonine and tyrosine is probably the most important post-translational modification of proteins, and phosphorylation mapping is important for pharmaceutical research because diseases are often influenced by the phosphorylation pattern. We have been investigating the use of tris(2,4,6-trimethoxyphenyl) phosphonium propylamine (TMPP)[3] to tag simple carboxylic acids with a phosphonium group to improve ionisation efficiency in ESI-MS[4] and to make them amenable to detection by ICP-MS[5]. Recently, we have synthesised a brominated version of this compound and will report on results of using this to tag organic compounds and peptides to make them visible to Br-specific detection and for the determination of the degree of phosphorylation of peptides.

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DERIVATISATION OF PEPTIDES WITH A BROMINATED PHOSPHONIUM
DERIVATISING REAGENT TO DETERMINE THE EXTENT OF
PHOSPHORYLATION USING BROMINE AND PHOSPHORUS ISOTOPE
RATIOS

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It has now been recognised that reversible phosphorylation of proteins at serine, threonine, and tyrosine residues is probably the most important regulatory mechanism in gene expression and protein synthesis [1, 2]. Cell signalling controlled by protein phosphorylation regulates many cellular functions at receptors, ion channels, transcription factors, kinases and contractile proteins [3]. Therefore, the alteration of a single residue via reversible phosphorylation is capable of initiating complex cellular signals involved in almost all-physiological processes: metabolism, differentiation, and contraction etc [4-6]. This demonstrates the need to understand reversible phosphorylation qualitatively (i.e., the site where the modification is taking place) and quantitatively (to what degree the site is modified).

We have previously investigated the use of phosphonium salts as derivatising reagents for the analysis of carboxylic acids using LC-ESI-MS-MS [7] and LC-ICP-MS [8]. Recently we have synthesised Tris(3,5-dibromo-2,4,6-trimethoxyphenyl) phosphonium propylamine bromide (BrTMPP) as a derivatising reagent to facilitate the simultaneous detection of P and Br using ICP-MS. The addition of 6-Br atoms to each molecule of TMPP has resulted in increased sensitivity and made possible the application of isotope ratio techniques using this compound. This poster specifically reports on the use of BrTMPP for the determination of the degree of phosphorylation of phosphorylated peptides. Results will be presented showing the potential for this application.

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TRACE IDMS BY MULTIPLE ION COUNTING AND MC-ICPMS

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There is a growing demand from environmental, industrial and clinical laboratories for high accuracy reference values for trace elements at concentrations below 1ng/g. Multiple ion counting ICPMS coupled to the double IDMS technique is demonstrated to fulfil this demand.

A ThermoFinnigan Neptune MC-ICPMS has been modified to include four additional channeltron ion-counters positioned adjacent to the L4 and L3 faraday detectors. The spacing of the counters has been designed to optimise simultaneous ion measurements of isotope pairs from a range of elements that are frequently analysed at low levels. These include Cd, Ag and Pb.

The precision of ion counting pairs was evaluated using Cd and Ag solutions. Ratios of 1 yield internal precision of ~0.1% (RSD) for a measurement totalling <1 minute. The high sensitivity of the Neptune means that precise ratios of 0.1-0.2% can be obtained at signal intensities of 5000-10,000 cps equivalent to less than 5 pg/g. Analysis of lower concentration samples could be achieved using high efficiency desolvating nebuliser.

The double IDMS equation is shown to be a robust tool when applied to multiple ion counters. Drift in the sensitivity of different detectors is compensated by sample standard bracketing and spiking wherever possible to yield ratios close to 1. It is essential that samples and standards are closely matched.

The efficacy of the new technique was evaluated by measurement of Cd in the certified reference materials LGC6017 and LGC6019 (rain and river water) which contain 0.13 and 0.11 ng/g Cd respectively. Samples were spiked with ^{106}Cd so that the $^{106}\text{Cd}/^{111}\text{Cd}$ ratio is equal to 1. IDMS is therefore being measured upon an effective concentration of <20 pg/g (^{111}Cd comprising only 13% of Cd present). The combined uncertainty of the measurements is 1%, which compares favourably to a 10% uncertainty on the certificate derived from calibration measurements and inter-laboratory comparison

DO PLANTS FORM ARSENIC-PHYTOCHELATIN COMPLEXES? AN
APPLICATION OF THE PARALLEL AND SIMULTANEOUS USE OF ICP-MS
AND ES-MS FOR HPLC

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Plants are known to synthesis phytochelatin (PCs) of different chain-lengths in answer to heavy metal (As, Cu, Zn) challenge. Phytochelatin are derivatives of glutathione (GSH) with the general formula $(\gamma\text{-Glu-Cys})_n\text{-Gly}$, whereby $n = 2 - 11$. Until now mostly the increase in PC-concentration in plant cells was studied.

We developed an HPLC method which allows the direct determination of arsenic-phytochelatin complexes in plant extracts using ICP-MS (for arsenic) and ES-MS (for determining the characteristic m/z) in parallel. Using partially purified PCs mixed with arsenite, we determined that $\text{As}^{(\text{III})}$ can form complexes with PC_2 in form of $\text{As}^{(\text{III})}\text{-(PC}_2)_2$ with one "free" thiol"-group. $\text{As}^{(\text{III})}$ as well forms a mixed complex with PC_2 and GSH as $\text{GS-As}^{(\text{III})}\text{-PC}_2$ and preferential with PC_3 as $\text{As}^{(\text{III})}\text{-PC}_3$. All three complexes were identified by there characteristic ES-MS spectra and by detecting arsenic with ICP-MS at the same time.

Sunflower (*Helianthus annuus*), an arsenic tolerant strain of *Holcus lanatus* and the arsenic-hyperaccumulator *Pteris cretica* were used as model plants. In the later two plants only leaves were studied, whereas from *H. annuus* also the roots were studied. *H. lanatus* the $\text{As}^{(\text{III})}\text{-PC}_3$ complex was the dominant complex, whereas *P. cretica* did not contain any PC_3 , consequently not forming this complex. Instead *P. cretica* formed mainly the $\text{GS-As}^{(\text{III})}\text{-PC}_2$. In the leaves of *H. annuus* $\text{As}^{(\text{III})}\text{-PC}_3$ and $\text{GS-As}^{(\text{III})}\text{-PC}_2$ were as well the main complexes. Root cells of *H. annuus* contained/synthesised, in contrast, a whole range of As-PC complexes, including $\text{As}^{(\text{III})}\text{-PC}_3$, $\text{GS-As}^{(\text{III})}\text{-PC}_2$, $\text{As}^{(\text{III})}\text{-(PC}_2)_2$ and $\text{MA}^{(\text{III})}\text{-PC}_2$. There are several other as yet unidentified complexes present in *H. annuus* roots as well.

Ref.: Raab, A.; Feldmann, J.; Meharg, A.A. The nature of arsenic - phytochelatin complexes in *Holcus lanatus* and *Pteris cretica*
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ARSENIC SPECIES IN HAIR AND SKIN OF PRE-COLUMBIAN MUMMIES
USING XANES/EXAFS AND HPLC-ICP-MS

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Hair, like other keratinous tissues, does accumulate arsenic either during hair-growth or due to external contamination, a fact recognised early on in forensic medicine. The adverse health effects of arsenic on normal skin development (among others skin cancer) during or after prolonged ingestion of arsenic contaminated water or food are widely documented for regions like Bangladesh, Taiwan or Chile.

Despite this the arsenic species present in these tissues are rarely studied. For the study of arsenic species in hair and skin we used both extraction followed by HPLC-ICP-MS and a direct solid-state method x-ray absorption spectroscopy. The latter one is able to give information about the electronic environment (oxidation state) of the arsenic, the nature of ligands and the bond length by using EXAFS and XANES. We measured the arsenic in hair and skin of mummies found in the Atacama region of northern Chile and of people suffering from arsenic induced keratosis in central India. The same samples were used to determine the extractable arsenic species by HPLC-ICP-MS. Species determination by HPLC-ICP-MS showed that the dominant species in both hair and skin were inorganic arsenic with the majority of being arsenate. The XANES and EXAFS data however point to only one species that is the pentavalent arsenate. The latter fact is controversial, since it is widely established that arsenic binds to sulfur – however, no firm evidence are given in the literature. Additional dimethylarsenate ($\text{DMA}^{(V)}$) was a minor species present with traces of methylarsonate ($\text{MA}^{(V)}$). Those minor species would not be picked up by the XAS technique, due to the low sensitivity. The mummy hair and skin samples from Chile contained more arsenate than the Indian samples, while the amount of $\text{DMA}^{(V)}$ was about five-times higher in the hair and skin samples from central India. The hair and the skin samples from India contained about 10-times less arsenic than the samples from Chile. The higher total arsenic concentration, especially the much higher amount of arsenate, in the mummy samples might point to an external contamination post mortem during the funeral preparations.

Despite the combined use of solid state and solution speciation a distinction between internal and external arsenic was not possible, showing the problems faced by forensic analysts trying to determine post mortem whether arsenic played a part in a suspicious death.

NUCLEIC ACID DETERMINATIONS IN FLOWING STREAMS VIA CARBON
AND PHOSPHOROUS ATOMIC EMISSION

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A novel method for qualitative and quantitative nucleic acid determinations in flowing streams is presented. Particle Beam / Hollow Cathode Optical Emission Spectroscopy (PB/HC-OES) has been shown in the past to be very sensitive means of amino acid determinations through monitoring of carbon, hydrogen, and nitrogen atomic emissions [1]. The PB interface employs an effective nebulizer and desolvation system, a two-stage momentum separator, which removes solvent vapor. The resulting beam of dry analyte particles are introduced into the hollow cathode, atomized, and excited within the plasma. Advantages of PB/HC-OES include easy and rapid analysis, high sensitivity, low detection limits, and ready acceptance of liquid chromatography effluents. This relatively simple method of analysis has been extended to total-protein determinations. Jin et al. [2] have shown that single-nanogram limits of detection are possible in the monitoring of C(I) 193.0 nm for bovine serum albumin (BSA).

In this study we apply the PB/HC-OES method for the determination of nucleic acids through the monitoring of the resultant P (I) 177.5 nm and C (I) 193.0 nm optical emission. Detection limits for the full range of nucleic acids are the single-ng level, making PB/HC-OES very attractive for HPLC detection. Through monitoring of both the P (I) and C (I) responses, the empirical formula of each nucleic acid can be deduced, thus providing vital qualitative and quantitative information.

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STUDIES ABOUT THE IN-DEPTH PROFILE QUANTIFICATION OF THIN FILMS ON GLASSES BY RADIOFREQUENCY GLOW DISCHARGE-OPTICAL EMISSION SPECTROMETRY

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Radiofrequency glow discharge coupled to optical emission spectrometry (rf GD-OES) is becoming an important tool for the determination of compositional depth profiles of layered materials. Rf-GD-OES provides a rapid and sensitive depth profile elemental analysis of different types of coatings. The significant features of rf-GD-OES enabling such analyses arise from the nature of the rf glow discharge sputtering, where samples (both conducting and non-conducting) are sputtered very stably with Ar⁺ ions of low energies (<50 eV) and high current fluxes (of the order of 100 mA mm⁻²). The low Ar⁺ energy ensures that film sputtering proceeds without significant formation of altered layers, which is a prerequisite for successful depth profiling analysis of thin and ultra-thin films at high depth resolution [1].

In the last few years, Rf-GD-OES devices have been attempted for the depth profiling analysis of many different types of samples [2,3]; although, it should be mentioned that for the greatest part of these applications the samples are conductive. Rf-GD-OES has demonstrated to perform elemental depth profiling in non-conducting materials at a high spatial resolution down to the nano-scale, but the quantification of depth and concentration when investigating insulators still requires further work on normalization strategies to compensate for variations in elemental response factors between the different materials.

In this communication, the capabilities of the rf-GD-OES for the quantification of different types of thin films (conductors and insulators) on non-conducting glasses by resorting to the constant emission yield concept, and using for calibration a set of silicate glasses with a wide range of elemental concentrations and several conducting standard reference materials with different matrices, will be discussed.

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Certified Reference Materials for Speciation Analysis

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The importance of reference materials, and particularly, of certified reference materials as a tool for quality control in the analytical laboratory is uncontested [1]. For more than two and a half decades, the European Commission, through its Community Bureau of Reference (BCR), and later through its Standards, Measurement and Testing (SMT) program, have supported the development and production of reference materials [2]. The discontinuation of this policy has led to a gap that is only eventually closed by other producers of reference materials.

This situation is surprising and regrettable, since particularly the field of speciation analysis has a continuous and increasing demand for (certified) reference materials.

(Certified) reference materials are a primary tool in analytical method development and validation. They serve to monitor the efficacy of newly developed analytical methods throughout the many steps of the analytical procedure: extraction, digestion of the matrix, derivatisation of the analytes, (chromatographic) separation, and quantitative determination, often achieved by hyphenated techniques with element- or molecule-specific detection [3]. Furthermore, (certified) reference materials are an ideal tool to monitor the stability of an analytical procedure over time and with the modification of the analytical method.

It is thus just consequent that the importance of this market has been recognised by other players in this field, and that these increase the product portfolio of reference materials and substances. The most interesting additions to this product range are isotopically labelled compounds which, as an additional and unique feature, allow to monitor degradation and interconversion processes of organometallic species in the sample during the analytical procedure [4].

An overview over the currently available reference materials for speciation analysis will be given in this presentation, and new developments will be discussed.

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COMPARISON OF SOLID-PHASE MICROEXTRACTION COUPLED WITH GC-MS AND GC-ICP-MS FOR THE DETERMINATION OF ORGANOPHOSPHORUS PESTICIDES IN WATER SAMPLES

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As many of the organochlorine pesticides were banned in the 1970s, the agrochemical industry turned to the less persistent, but more acutely toxic organophosphorus (OPPs) compounds to control insect pests. Nowadays, OPPs are the class of agricultural insecticides most widely used in the world. They act as pesticides inhibiting acetylcholinesterase (AChE) insects, but they are also toxic to mammals existing regulatory limits for human exposure. Therefore, the development of sensitive and selective analytical methods for the determination of OPPs at very low levels in different environmental and/o biological samples is of great interest.

Solid-phase microextraction (SPME) is a novel solvent-free analytical technique, able to integrate extraction, preconcentration and sample introduction in a single step (1). Since its introduction in 1990 the use of SPME has been increasing for the extraction of organic compounds, including OPPs, from several matrices. Determination of SPME extracted pesticides can be carried out by gas chromatography coupled to various detectors like nitrogen phosphorus (NPD), photometric (FPD) and mass spectrometry (MS). On the other hand, the use of inductively coupled plasma mass spectrometry (ICP-MS) as detector for GC separation of OPPs can be an attractive alternative. ICP-MS possesses the advantage of an excellent selectivity in the presence of other compounds that may otherwise interfere.

Hence, the aim of this work was to investigate the feasibility of developing methods for the determination of OPPs in waters samples, based on SPME prior to gas GC-MS and GC-ICP-MS. Thus, the SPME process was studied in detail and important variables involving fibre type (PDMS, PA, PDMS-DVB), temperature effect, extraction time, desorption conditions, pH and ionic strength were optimised. Under optimized conditions, precision, intervals of linearity and detections limits were evaluated using SPME-GC-MS and SPME-GC-ICP-MS. The advantages and limitations of both methodologies are discussed for the determination of several OPPs in environmental water samples.

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DEVELOPMENT AND EVALUATION OF LOW PRESSURE LASER ABLATION COUPLED TO ICP-MS

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In laser ablation ICP-MS on-line ablation cells with He or Ar as ablation gas and gas condition determined by the sample gas flow, are commonly used as general setup. The use of reduced pressure conditions in the cell is limited due to the online coupling to the atmospheric ICP plasma.

However, in LIBS an increase of the signal intensity up to the factor 10 by reducing the pressure in the laser cell has been observed {1-3}. This indicates a significant change of the ablation conditions and thus reduced pressure in the cell could also have a positive impact in LA-ICP-MS. Studies on laser ablation with 581 nm excimer laser system showed a dependence of the amount of ablated material on pressure and ablation gas settings which is explained by the effect of reduced plasma shielding at low pressures {4}. Lowering the pressure from 1013 hPa to 13.3 Pa increased the amount of ablated material up to a factor of 25. A low pressure laser ablation process coupled to an ICP-MS could thus possibly also increase the signal intensity and may result in different aerosol composition compared to atmospheric conditions.

Therefore, a low pressure cell configuration was constructed and coupled to an ICP-MS. Most important, gas and pressure were independently selectable and adjustable to influence the sample density in the ICP. To study the particle agglomeration under reduced pressure conditions in various ablation gases (e.g. Ar, He and Ar/He) in comparison to atmospheric conditions, various samples like metals and silicates, were used.

Effects of reduced gas pressure on ablation yield, sensitivity and aerosol composition will be discussed.

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QUANTITATION OF QUENCHING EFFECTS ON ARGON METASTABLES IN PULSED GLOW DISCHARGE MASS SPECTROMETRY

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Pulsed Glow Discharge Mass Spectrometry coupled to separation devices such as gas chromatography can be employed to obtain real time elemental, structural and parent molecular information. This information is temporally segmented during the glow discharge pulse cycle and can be selected using the appropriate ion-extraction time {1,2}. Intact molecular ions are produced after pulse termination during the afterpeak by analyte collisions with long lived metastable argon atoms (Penning-ionization). Since plasma power is terminated, finite metastable atoms can be rapidly quenched by the introduction of organic vapors eluting from a separation method {3-6}. Every impurity or solvent molecule that co-elutes with the separated analyte competes for these available metastable atoms. This competition not only limits the dynamic range of hyphenated pulsed GD analyses, but also the possibility of solution based methods such as liquid chromatography, where large amounts of solvent co-elutes with each analyte. This contribution will demonstrate the quantitative quenching effects of the metastables during the afterpeak time regime. Quantitation is based on ion production of the sputtered cathode material (Cu⁺) during the elution of different amounts of organic vapors, which were introduced from a gas chromatograph.

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THE USE AND MISUSE OF HPLC/ICPMS IN SPECIATION ANALYSIS
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The determination of individual species of an element, speciation analysis, is no new analytical pursuit but in the last 3 decades it seems to have evolved into a small but distinct subspecies of analytical chemistry. The process began in the 1970s with the online coupling of separation systems to element selective detectors such as AAS. The field matured from the late 1980s with the introduction of ICPMS as a sensitive element selective detector which could be easily coupled to chromatographic systems, in particular to HPLC. For many applications, HPLC/ICPMS is a powerful tool for speciation analysis with the potential to provide quantitative data for “all” species of an element in a sample at the $\mu\text{g}/\text{kg}$ level, thereby providing an essentially complete speciation picture of the element. In this respect, HPLC/ICPMS might claim to be the only true speciation analysis method. But this potential to provide a complete speciation picture is not often realised. The talk will present successful applications of HPLC/ICPMS to speciation analysis, and discuss approaches to obtain better speciation data. In addition, examples of the poor application of HPLC/ICPMS in speciation analysis, in some cases resulting in wrong structural assignments, will be presented. The examples will be taken from the recent primary analytical literature, and focus on arsenic and selenium species.

DEVELOPMENT OF EXTRACTION PROCEDURES FOR THE
DETERMINATION OF ARSENIC IN TWO IN-HOUSE PEAT REFERENCE
MATERIALS

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There is an increasing interest in the use of ombrotrophic peat bogs as archives of atmospheric element deposition. To quantify the effects of human activities on the geochemical cycles of various elements, knowledge and understanding of pre-anthropogenic elemental sources, pathways, and fluxes are needed. One way to quantify the pre-anthropogenic fluxes of atmospheric trace elements is to study and interpret environmental archives. These may preserve not only the contemporary fluxes but also a chronological record of atmospheric fluxes of trace elements as they may have occurred prior to industrialisation, for comparison.

To evaluate the extraction yield of As in oven dried peat samples (105°C) compared to freeze-drying and to extraction from fresh peat samples, and to optimize a procedure for the extraction of As compounds from peat samples, two in-house peat reference materials were prepared. For this purpose two peat cores were cut frozen into 2*5 cm slides, which were homogenized by cryogenic milling. One aliquot of the homogenised frozen powder was dried at 105°C, another aliquot was freeze-dried, both to constant weight, respectively, and fresh, homogenised frozen material was used directly.

Common extractants for arsenic compounds in biological materials such as methanol, water, and methanol/water mixtures as well as different extraction procedures (microwave assisted extraction employing a high pressure autoclave, mechanical agitation, etc.) were checked for their ability to extract As compounds from these peat materials. The As concentrations in the extracts were determined by hydride-generation atomic fluorescence spectrometry (HG-AFS) and inductively coupled plasma-sector field-mass spectrometry (ICP-SF-MS) after microwave digestion with HNO₃ following the developed procedures for the determination of As in peat samples. An ultimate objective is to determine the dominant As species in peat bogs.

ABLATION STUDIES ON TITANIUM DIOXIDE POWDER SAMPLES WITH
TWO DIFFERENT LASER SYSTEMS (193 nm AND 266 nm)

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Titanium dioxide (TiO₂) in powder form is the most commonly used white pigment, because of its whiteness and opacity. It is appointed in various fields of technology, for instance as a coating material, especially for high-reflexion coatings, when it is deposited as a thin film on an optical component like a lens or a mirror. The reflectivity of such coatings is significantly affected by elemental impurities. It is essential to control the production process of such raw materials with an very sensitive, fast and accurate multielement method. LA-ICP-MS is a promising technique to detect and quantify the claimed specifications in the low ppm range of pure powder samples. For laser ablation, the powder has to be transformed into stable targets, that can be achieved using different sample preparation procedures as described in literature. [1 - 4]

In this study, pressed TiO₂ tablets and lithium-tetraborate fused TiO₂ samples were ablated with two different laser systems. In the first place, a 266 nm Nd:YAG (LSX-500, Cetac Technologies, Omaha, USA) was used, secondly an 193 nm ArF-excimer laser system (Geolas, Lambda Physik, Göttingen, Germany), supplemented with an 18 x 18 optical array, was used. As Ion source an ICP-MS (ELAN 6100 DRC, Perkin Elmer / SCIEX, On, Canada) was applied.

The results show a high reproducibility in lithium-tetraborat fused samples. However, significant differences in signal structures and ablation behaviour between both laser systems are observed. Quantitative results, intensities and limits of detection for trace elements were compared for both powder preparation procedures and laser systems. In addition severe interferences from polyatomic ions such as oxides and argides will be discussed.

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IDENTIFICATION OF DIMETHYLTHIOARSINIC ACID BY IC-ICP-MS AND
IC-ESI-MS/MS IN RICE SAMPLES

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Recently, sulfur analogs of well known arsenicals have been identified in biological and dietary matrices. In this presentation, the detection and identification of dimethylthioarsinic acid (DMTA) will be reported in rice samples after an enzymatic extraction. The enzymatic extraction is a synthetic two stage extraction; the first simulates the stomach and the second stage simulates the environment of the small intestine. The DMTA confirmation includes the co-elution of a DMTA standard and the DMTA in the rice extracts using two chromatographic separations and ICP-MS detection. In addition, the structure of this arsenical was confirmed using IC-ESI-MS/MS with a molecular ion of m/z 153 and fragment ions of m/z 138, 123, 105 (negative mode). Preliminary information will be provided with respect to the production of a standard and the stability of that standard in chromatographic mobile phase eluents. This identification of DMTA in rice and the report by other researchers of DMTA in sheep wool and urine may indicate a more widespread occurrence in nature.

Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

SELENIUM METABOLISM – ELUCIDATION OF SELENIUM METABOLIC PATHWAYS BY LC-ICP MS AND ESI-MS

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Selenium is an essential trace element with low intakes associated with deficiency symptoms and high intakes associated with toxicity symptoms. Furthermore, clinical trials have proposed an anti-carcinogenic activity of selenium. Selenium metabolism is not fully elucidated and there is a need for further research in this field in order to be able to understand the proposed anti-carcinogenic activity.

So far selenium excretion in human urine has been extensively investigated and the most important metabolites have been identified as selenosugars. The aim of this study is the investigation of earlier stages in the metabolic pathways.

The liver is the major metabolising organ for most compounds. Hence, metabolism studies are conventionally performed in liver preparations. To investigate if selenium compounds are metabolised in the intestine before they reach the liver, an in vitro experiment with a model of the intestine was performed.

Metabolism of various selenium standards was investigated based on their origin in nutritional sources. Standards of methylselenocysteine, selenomethionine, selenite and selenate were incubated with epithelial cells from pig small intestine and samples were analysed by LC-ICP-MS.

The selenium compounds were not metabolised to the same extent in the intestine model. Selenite was extensively metabolised and will probably reach the liver in a completely different chemical form. Attempts to identify the metabolites formed were performed by ESI-MS.

MULTI-PULSE LIPS SPECTROSCOPY USING A PASSIVE Q-SWITCHED ND LASER

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Laser induced plasma spectroscopy (LIPS) today can be considered as an established analytical technique useful for the rapid determination of the elemental composition of samples either in the solid, liquid or gaseous phase. LIPS offers several practical advantages over laser ablation ICP spectrometry, such as the possibility for remote or field measurements by using guided optics and/or portable instrumentation. As a result of these and other features, LIPS is finding more and more scientific and industrial applications almost every day.

A simple and cost effective LIPS instrumentation, which is gaining significant popularity in the analytical community in recent years, can be built around a microscope using a reliable Nd laser and a fiber optic non-intensified CCD spectrometer. These systems, that can be easily constructed in a laboratory or now be purchased from more than one commercial companies, have a somewhat limited analytical performance (mainly in terms of sensitivity and spectral resolution) but are portable, easy to use, long lasting and economical.

One of the possibilities to improve the signal-to-noise ratios of LIPS data is to use two laser impulses separated by some tens of microseconds for plasma generation. The use of this „double pulse approach” has been already demonstrated in the literature to produce a more intense plasma. However, an obvious disadvantage of this approach is that it uses a complicated setup based on two or more synchronized and aligned laser sources.

In our present work, we investigated the possibility to improve the precision and sensitivity of fiber optic spectrometer based LIPS systems by using a single laser source that produces multiple output pulses. The laser source used was a flashlamp pumped Nd:GGG laser equipped with a passive Q-switch. This laser, when set at the maximum pump energy, released 7-9 pulses s. By using this spreaded more or less evenly over a period of about 200 laser source and Al, Cu and Zn metallic targets, we performed time resolved LIPS measurements to assess the plasma lifetime, as well as the sensitivity and precision of the spectral data obtainable. The plasma lifetime was found s; significantly longer than that typical for to be several hundreds of single pulse LIPS. As expected, the sustained plasma also resulted in better precision (6-8% RSD based on 3-5 measurements) and 2-10 times higher signal intensities. The precision could be even further improved by using normalization based on the integrated continuum background. The success of this passive Q-switch approach means that the precision and sensitivity of LIPS systems can be improved in a cost effective way without sacrificing portability.

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ANALYSIS OF GEL ELECTROPHEROGRAMS AND BLOTTING MEMBRANES
VIA SPATIALLY RESOLVED GLOW DISCHARGE OPTICAL EMISSION
SPECTROMETRY

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Gel electrophoresis (GE) remains by a wide margin the most popular separation procedure in biochemical analyses, and is routinely employed in a number of disciplines for the resolution and purification of components in complex mixtures. As currently practiced, GE techniques can make use of a wide variety of support materials to facilitate separation based on a number of chromatographic mechanisms. One popular technique is known as 2-D gel electrophoresis, where separation occurs according to electrophoretic mobility in one direction, and isoelectric point along the second. This yields a 2-D map of biopolymers separated by mass and chemical composition. Once such a separation is complete, the gels can be stained or developed to reveal the location and quantity of the constituent biopolymers. Common techniques utilized for imaging include densitometry, phosphorescence, fluorescence, etc., or the gels can be dried to perform fluorography or autoradiography. In addition, the separated biopolymers are commonly transferred to membranes via blotting techniques to concentrate them and allow their probing, for example, via immunoassay methods. Atomic spectrometry has also made its way into gel detection for elemental analysis purposes. Some of the most popular techniques used for this aim are atomic fluorescence spectrometry (AFS), atomic absorption spectrometry (AAS), X-ray techniques and inductively coupled plasma mass spectrometry (ICP-MS). AFS, AAS, and ICP-MS are most commonly used with liquid sample introduction systems; thus, after proteins are stained for visualization, the regions of interest are excised from the gels and digested or the proteins electroeluted before analysis. A novel alternative is to use laser ablation (LA) coupled with ICP-MS. In this manner the gels are directly ablated and the resulting aerosol is swept into the plasma for analysis. LA-ICP-MS has also been applied to blotting membranes. Unfortunately, rastering of a complete 2-D electropherogram or blot is time consuming and the instrument components can prove quite expensive.

In our laboratory we have coupled a glow discharge (end-on viewing geometry) to a monochromatic imaging spectrometer to perform direct atomic emission spectrometry of gel electropherograms. In this fashion, one can rapidly obtain monochromatic laterally resolved atomic emission maps from entire electropherograms on dry gels or blotting membranes. For example, a common way of protein analysis (both non-specific and specific) on gels and blots is through metal-colloid staining. For proof-of-principle experiments, several blotting membranes containing Ag-stained samples have been imaged successfully (328.1 nm). Results with different metal particles, blotting membranes and dry gels will be presented as well as the current state of spatial resolution and sensitivity. Possible advantages and limitations of the proposed technique will also be discussed.

SELENIUM METABOLISM - QUANTIFICATION OF SELENIUM
METABOLITES IN HUMAN URINE. IS THE TRIMETHYLSELNONIUM ION A
CONSTITUENT OF HUMAN URINE?

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For several decades, trimethylselenonium, TMS_e has been considered an important metabolite in urine from rats as well as humans. Ingested selenium in form of inorganic as well as organic compounds is reduced to hydrogen selenide. The presence of TMS_e is based on the presumption that excess selenium is detoxified and excreted via successive methylation of hydrogen selenide to dimethylselenide and TMS_e, respectively. However, although the toxicity of dimethylselenide is more than 200 fold lower than the toxicity of inorganic selenium and selenoamino acids, the toxicity of TMS_e is about 30-fold more toxic than dimethylselenide, hence this further methylation does not contribute to detoxification of selenium.

In the last few years, several reports have shown that the major selenium metabolite in human urine is the selenosugar, Se-methylseleno-N-acetylgalactosamine. Recently, we identified the selenosugar, Se-methylseleno-galactosamine as a selenium metabolite in basal human urine. This selenosugar is a cationic species and previous experiments may have mistaken this metabolite for the trimethylselenonium ion.

The aim of this study was to quantify the seleno-sugars in basal human urine from individuals who were not supplemented with extra selenium.

Furthermore, different chromatographic systems previously used to indicate the presence of TMS_e were evaluated for their ability to separate TMS_e from the new cationic selenosugar.

ELEMENTAL ANALYSIS OF SOLUTION BASED ON PULSED GLOW DISCHARGE - TOFMS. INFLUENCE OF GAS FLOW RATE, POSITIVE DC CATHODE VOLTAGE DISPLACEMENT AND SAMPLER VOLTAGE ON ANALYTICAL PARAMETERS OF THE TECHNIQU

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The advantages of GD sources with pulsed discharge have been shown by several research groups. Glow Discharge -TOFMS and Pulsed Glow Discharge -TOFMS systems are effective tools for analysis of conductive and nonconductive samples and liquid samples. Glow discharge with pulse duration - 0.01-0.03 ms allows reaching high sputtering efficiency and high ionization degree of all samples types. But detection limits for PGD-TOFMS aren't sufficiently low for some applications.

New Pulsed Glow Discharge -TOF system with high flow rate of buffer gas, positive dc bias potentials on cathode and sampler was designed and investigated. Experimental system includes Glow Discharge Cell with Thin-Walled Metallic Hollow Cathode (TMHC) connected with capillary. Gases mixtures Ar-He and Kr-He (pumping rate $v = 20-300$ ml/min) were used in the discharge cell. Discharge voltage was changed from $U_d = 1000-2000$ V negative during the pulse up to 10-100 V positive bias (U_c) after the pulse. Sampler potential was in range $U_s = 0-50$ V. TOFMS resolution was $M/DM = 1200$. Values of U_c , U_s and v were optimized in experiment. A new low memory sampling system (without Cell opening) was used in experiment. The sampling system includes quartz capillary, sample port, port for gases mix, clamp, furnace (for sample drying and quartz cell. The sample injects through capillary in TMHC. After drying in a ceramic furnace (1 – 2 min) TMHC was moved to sampler and pulsed discharge (current – up to 2.5 A, voltage – 1000-2000 V, pulse duration – 5 – 100 us, frequency – 100 – 4000 Hz, cathode temperature – up to 2400 C, time of measurement – 1 – 20 sec) started. Cathode was made from Nb. Memory effect for this system was tested for Cd standard solution – it didn't exceeded 1.5%.

It was found in the experiment that appropriate values of sampler potential U_s and pumping rate v have considerable influence on analytical signal. At the same time influence of cathode potential U_c on analytical signal is a more weak. These data are compared with theoretical estimations based on pulse discharge model with Monte-Carlo simulation.

LASER ABLATION-INDUCTIVELY COUPLED PLASMA MASS
SPECTROMETRY FOR THE DIRECT ANALYSIS OF
DIFFERENT PLASTIC MATERIALS

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There is an obvious need to implement fast and reliable procedures for the analysis of polymers, in accordance with the current regulations, and laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) can be very suited for this purpose, taking into account its multi-element capabilities, excellent sensitivity and high sample throughput.

It is the goal of this work to evaluate the performance of state-of-the-art LA-ICPMS instrumentation for the direct determination of heavy metals As, Cd, Cr, Hg, Pb, Sb in different polymeric materials of commercial interest (polyethylene bags and ABS pieces), paying special attention to the following aspects:

- i) the possibilities to achieve chemical resolution in the dynamic reaction cell (DRC), in order to alleviate the interference of $40\text{Ar}^{12}\text{C}^+$ on 52Cr^+ ;
- ii) the possible effect of the use of the DRC on the multi-element possibilities of the technique;
- iii) the performance of the available polymer reference materials (BCR CRM 680 & 681) for calibration;
- iv) the need to use an internal standard for the analysis of polymers of different composition.

COUPLING OF A MICRO-FLOW IONIC CHROMATOGRAPHY WITH A HIGH RESOLUTION SECTOR FIELD ICPMS

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In the scope of speciation analysis, it is mandatory to develop highly sensitive and specific instruments which allow to show the existence of possible highly toxic species even at ultra-trace levels. The coupling of liquid chromatography to inductively coupled plasma mass spectrometry (LC-ICPMS) has been adopted in the recent years as a prime method to answer these needs.

While liquid chromatography ensures the separation of the analytes it also induces a dilution which dramatically lowers the overall sensitivity of the coupled system. The dilution increases with mobile phase flow and consequently with column diameter. A significant improvement can be achieved by the use of micro flow liquid chromatography. In this case, the dilution factor is typically improved by a factor 20 compared to an analytical column. But micro flow chromatography implies a very strict control of dead volumes and memory effects in the spray chamber.

The present study shows results from the coupling of a micro flow ionic chromatography and a high resolution sector field ICPMS (μ IC-HR ICPMS). The mobile phase in which flow reaches 40 μ l/min, is introduced into the plasma torch via a low uptake concentric nebulizer and a cyclonic spray chamber. The chamber incorporating three flow spoilers as calculated by computational fluid dynamics [1], is designed to wash out in only 2.4s. The analytical performances are characterized by the speciation analysis of rhodium on a mixed bed resin (CS5). The asymmetry factor measured at 5% of the elution peak height varies between 0.96 and 1.5. The peak efficiencies exceed 5000 plates and the detection limit is about 0.6 pg of injected rhodium.

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LASER ABLATION ICP-MS U-TH-PB DATING OF COMPLEX ZIRCON: APPLICATION AND LIMITS

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Among applications for laser ablation ICP-MS (LA ICP-MS) the U-Th-Pb analysis of zircon is still one of the most challenging ones in terms of the required spatial resolution, precision and accuracy. Worldwide more than 15 laboratories have installed the LA ICP-MS zircon dating method. However, the actual number of the peer-reviewed papers applying this technique is still low compared to studies using conventional techniques (e.g. ID-TIMS, SHRIMP). Nearly half of the LA ICP-MS papers published over the last decade dealing with various aspect of improving the technique, showing the need for further developments.

Zircon belongs to the key minerals for unravelling many processes during earth history.

The U-Th-Pb systematic in most zircon grains is complex due to alteration processes, such as dissolution, recrystallization and new zircon growth. A spatial resolution of 5 to 40 μm are commonly needed to resolve the different age pattern in complex grains. Therefore, at present many zircon grains remain still undateable for LA ICP-MS. Only few studies have shown that they are capable to analyse 30 μm areas and to precisely detect low Pb contents, which are relative common e.g. for younger and detrital zircon grains.

The U-Th-Pb zircon dating technique was developed in our lab over the last year using an UV 213 and -since recently- an UP 213 Merkantek laser systems attached to a Thermo-Finnigan Element II. The spatial resolution, limited by signal intensity of Pb-207, is usually between 20-35 μm . A relative simple approach was used to correct for within-run U-Pb fractionation before normalisation to a repeatedly analysed reference zircon. The internal and external precision (over 4-8 hrs) generally achieved for the Pb-206/U-238 (0.5-1%, 1-2%, 1s) and the Pb-207/Pb-206 (0.5-1.5% 1s) is comparable to or even better as precision reported by other laboratories. Although up to 30times less material is consumed. The main controlling factor for the error is counting statistic in case of the Pb-207/Pb-206 and the reproducibility of the ablation process and sample heterogeneity for the Pb-206/U-238. We will present data of different studies currently completed at our department. Analysed grains spanning a wide range of magmatic, metamorphic and detrital zircon, demonstrating their natural complexity. The results of the studies are encouraging and illustrate the ability but also the limits for LA ICP-MS dating of complex zircon.

PRECISE DETECTION OF U-236 AND PU ISOTOPES IN HUMAN URINE AT
PPQ TO SUB-PPQ LEVEL

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Sensitive methods are needed for monitoring and understanding the pathway of artificial long-lived radionuclides in the biosphere and the human body. Multi-collector Inductive Coupled Plasma Mass Spectrometry (MC-ICPMS) is a powerful tool for monitoring environmental contamination, because it allows precise detection of long-lived radionuclides at ultra trace levels even in very small amounts of sample material. The double-focusing MC-ICPMS Neptune, equipped with a retarding potential quadrupole lens and a secondary electron multiplier (SEM) for ion counting, allows simultaneous detection of up to 9 isotopes over a large dynamic range of up to 10 orders of magnitude. For homogeneous samples the concentration (from microgram to 0.5 femtogram/sample) and isotope composition can be determined with a precision and uncertainty of usually 0.1 to 5 % using the isotope dilution method, e.g. isotope measurements relative to a well characterised U-233 or Pu-242 tracer.

Using a method recently developed at our department it is for instance possible to detect urinary excretion of Depleted Uranium (DU) in the low picogram/litre range or at fractions below 0.2% of the total urinary uranium concentration. This allows to monitor the inhalation of up to a few microgram of insoluble non-natural uranium particles in the lung several months or even years later.

Sample preparation includes matrix separation and purification of the U or Pu fraction using standard ion-exchange chromatography. For sample introduction a Cetac autosampler and Aridus desolvating nebuliser are used. Signal sensitivity for Pu and U is 0.3-0.45 V/ng/ml using an uptake rate of 50 and 100 microlitre. The effect of U-238 tailing and hydride formation is about 4 to 7 E-7 at m/z 239 and about 2 to 4 E-8 at m/z 236. Isotope abundance and stability of faraday-SEM gain are the main controlling factors for the internal and external precision. Reproducibility of the U-235/U-238, U-234/U-238 and U-236/U-238 (0.5 femtogram/ml U-236) for a 8ppb SRM950a solution per day is about 0.1, 0.3 and 2%, respectively. Current detection limits for Pu isotopes and U-236 are below 0.1 femtogram per sample or below 1 E-19 g/ml urine using an enrichment factor of 500.

Different examples of the analyses of U and Pu isotopes in urine of non-exposed to somewhat exposed humans will be discussed.

ANALYSIS OF ALUMINA-BASED CATALYSTS BY LA-ICP-AES
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Direct analysis of solid sample is an important challenge in elemental analysis as the sample preparation step is time and reagent consuming with a risk of error through the contamination of reagents or loss of volatile elements during the preparation step.

Alumina-based materials are employed in catalyst preparation and are a matrix difficult to solubilize. Besides, there is a demand from the manufacturer for a fast analysis. Therefore, the possibility of determination of platinum and tin was studied using LA/ICP-AES hyphenation. The laser ablation system is a LINA Spark[®] Atomizer, based on a Nd:YAG laser operated at 1064 nm with the laser beam focused relatively deep behind the sample surface. A laser-induced microplasma created close to the target surface enhances the production of vapor/aerosol.

The samples were presented for the ablation as pressed pellets to obtain a regular surface of the sample likely to be ablated. Comparison of supports (Teflon, boric acid) is discussed and effect of the pressure and of the granulometry of the initial catalyst on signal stability is evaluated.

Powdered materials offer the possibility of adding analytes to apply a standard addition method. Calibration methods including standard addition method are then discussed. Accuracy is evaluated through a comparison with samples analyzed by X-ray fluorescence spectrometry. Except for a few samples, analytical results were found satisfactory. It remains to understand what could be the role of parameters such as the specific surface.

A NEW APPROACH FOR QUANTITATIVE SELENOPROTEOMICS BY
NANOHPLC – ICP-MS WITH ON-LINE ISOTOPE DILUTION ANALYSIS

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Proteins and peptides are an essential part of all living systems from the most elementary to the most complex. They are concerned with all physiological processes and in this connection are of considerable interest in biochemical and clinical research. Some of the therapeutically important proteins most relevant to the pharmaceutical industry include for example selenoproteins. To date the biggest unmet need in proteomics is a method for the quantitative measurement of protein, an important prerequisite for an elucidation of protein expression and function with diagnostic and therapeutic relevance. Several mass spectrometric techniques may be capable of providing sequence information but there are no solutions to the inherent difficulty to generate results with quantitative quality. For improved protein quantification and by electrospray or MALDI mass spectrometry a class of deuterated tags was developed, which are termed isotope-coded affinity tags (ICAT®) but they show a limited applicability and insufficient sensitivity, and the quantitative results have a relatively poor precision.

This poster discusses a new approach for the quantification of selenopeptides from selenium containing proteins by nanoHPLC-ICP-MS with on-line isotope dilution analysis. Technical details of the development of the nano HPLC – ICP-MS coupling will be presented and the system will be characterized with respect to precision, detection limits and calibration. Selenopeptides from a tryptic digest of selenized calmoduline protein are separated on a reversed phase nano column (i.d. 75 µm). Post-column addition of a species-unspecific ⁷⁶Se spike allows the quantification of the selenopeptides. The use of a collision cell in ICP-MS allows the elimination of detrimental interferences on selenium detection as a prerequisite for a correct isotope dilution analysis. Furthermore the part of non-digested protein could be detected and thus the efficiency of the tryptic digestion be estimated.

RECENT ADVANCES IN ARSENIC SPECIATION ANALYSIS
USING HPLC-ICPMS

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Arsenic is certainly one of the best investigated elements with respect to its speciation. Not only the necessity for speciation analysis itself but also the stability and the 'simplicity' of the arsenic compounds might have been the driving forces for many research groups to work in this area. Most of our knowledge obtained about the arsenic speciation in the marine environment was obtained without ICPMS. With all this knowledge and available standards it was only a matter of time before the detection power of ICPMS was employed for arsenic speciation analysis in the terrestrial environment. The intensive use of ICPMS as arsenic-selective detector revealed that terrestrial samples contain more or less the same arsenicals as do marine samples, although the concentrations are generally much lower. In return previously well characterised samples of marine origin have been reinvestigated with HPLC-ICPMS and minor arsenicals have been detected and identified with molecule-selective detectors.

In the last four years the detection of the two highly toxic trivalent organoarsenic compounds, methylarsonous acid and dimethylarsinous acid, in human urine samples was certainly one of the highlights in the arsenic speciation field. The second big issue that emerged in the last two years was the detection and identification of sulphur-containing arsenic compounds in various samples. Besides these two major issues several arsenic compounds have been detected in terrestrial samples albeit at ultratrace levels (sub $\mu\text{g}/\text{kg}$) in the last year. In all these cases ICPMS played a substantial role due to its selectivity and detection power.

The presentation will cover and discuss the recent findings and developments in the 'arsenic speciation business'.

METALLOPROTEIN IDENTIFICATION AND CHARACTERIZATION IN
ORANGE JUICE BY 2D-PAGE, ICP-Q-MS AND MASS SPECTROMETRY
(Q-TOF-MS).

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Juice industry has a great economical importance due to the year-round consumption of fruit juice that converts elaborated products and fruit concentrates, in valuable semi-finished stuff that can substitute the fresh juices. The juices from the markets use different types of fruits but the most habitual one is elaborated with sweet oranges (*Citrus sinensis*).

The authenticity of orange juice has a great interest to check its quality level avoiding adulterations. Different chemical parameters can be used for this purpose, and the analytical methods are usually based on profile analysis of specific compounds, e.g., of sugars, amino acids, organic acids, carotenoids, flavour components, limonoids, flavonoids and phenolics. The increasing information available about chemical composition of orange juice has allowed more refined methods of adulteration. Thus, it is necessary the development of analytical methodologies to evaluate more specific parameters for this purpose.

The protein content of orange provides very specific information about the type of fruit and the changes that it can suffer: diseases, maturity, origin, and others. The traditional methods reported in literature for protein presence evaluation in complex matrices are based on second dimension-polyacrilamide gel electrophoresis (2D-PAGE), followed by spot scissions and their tryptic digestion. The peptide mixture obtained is usually evaluated by mass spectrometry (MS) to achieve the protein identification. Besides, the use of ICP-MS can be used to detect the presence of metallo-proteins.

In the present study, 2D-PAGE followed by ICP-MS has been used for rapid Cu, Zn and Fe metalloproteins identification. Latterly, mass spectrometry system (Q-TOF) was applied to the characterization of these selected metalloproteins after tryptic digestion. The procedure has been applied to protein evaluation in fresh hand-squeezed orange juice.

HPLC-ICP-MS AND HPLC-ESI-Q-TOF STRATEGIES FOR THE ANALYSIS AND CHARACTERIZATION OF IODINE SPECIES IN MILK

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Iodine is an essential element for life since it is a constituent of the thyroid hormones and its deficiency can produce mental disease and poor physical development in children and goiter in adults. For these reasons the introduction of iodine dietary supplements is a common practice. Selenium intakes present a basic interest during infant nutrition, since iodine level in breast milk is known to be affected by the maternal diet and formula milk need to be supplemented with iodine. In addition the more known bioactive iodine molecules: iodo-tyrosine (MIT), diiodo-tyrosine (DIT), diiodothyronine (T2), triiodo-thyronine (T3), thyroxine (T4) and others, have chiral centers, and the different enantiomers forms have shown differential biological effectiveness. Finally, a recent study about the iodine speciation in fish tissues (1) reveals that unknown species of this element are present in these samples. Therefore, additional studies related to new iodine species characterization are necessary.

Different analytical approaches have been proposed for iodine speciation, generally based on the use of HPLC and UV detection, for pharmaceutical formulations and serum samples (1,2), but they suffer of low sensitivity and the use of HPLC-ICP-MS has been the method of election (1, 4), especially for biological and food samples in which iodine concentration is low and critical. Finally, LC-MS system has also been proposed for T3 and T4 characterization (5), although no information is provided about real samples application.

In this work, an analytical strategy based on parallel use of HPLC-MS/MS and HPLC-ICP-MS has been used for chiral speciation of iodine in milk samples. In the case of unknown species, an alternative approach involving three analytical steps: (i) 2-D gel electrophoresis, (ii) screening for iodine-containing spots by ICP-MS, and (iii) tryptic digestion followed by HPLC-ES-MS/MS, has been performed- metallomic analytical approach (MAA) (6,7).

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A SENSITIVE METHOD FOR ANALYSIS OF HALOANISOLES IN WINES BY
ON-LINE EXTRACTION USING PERVAPORATION AND DETERMINATION
BY GAS CHROMATOGRAPHY COUPLED TO ICP-MS

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The majority of cork-related taints are the so-called “musty” taints, principally due to volatile organic compounds at low levels such as chloroanisoles, of which 2,4,6-trichloroanisole (TCA) is very well known. TCA is not the only one that produces this effect, but is the most commonly off-flavour compound occurring in this type of sample. Some authors reported that TCA was present in 62% of the tainted wines they analyzed, which affects a significative percentage of the European bottled wines [1], and has important economical consequences.

Several approaches have been proposed for the extraction of anisoles from wine, such as liquid-liquid extraction (LLE) [2] and solid-phase extraction [3]. Solvent-less solid-phase microextraction (SPME) has also been applied to isolate TCA from wines [4]. E. Anticó et al. [2] evaluated soxhlet, ultrasound assisted and shake-flask extraction as extraction methods from cork stoppers. More recently, the use of stir bar sorptive extraction (SBSE) [5], pervaporation [6] and pressurised liquid extraction [7] have been reported for the same purpose. These techniques have been used as a previous step prior to the determination by gas chromatography either with Electron Capture Detector (ECD) or mass spectrometry.

In the present study we propose the coupling of gas chromatography-inductively coupled plasma-mass spectrometry (GC-ICP-MS) for haloanisoles determination in wine in order to improve the sensitivity of the recently published methods. Haloanisoles were extracted from wines by pervaporation (PV) directly coupled to the GC-ICP-MS, which really simplify the sample treatment and allows to the selective and sensitive determination of musty compounds in only one step.

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COMBINED USE OF ICP-Q-MS AND MASS SPECTROMETRY (Q-TOF-MS)
FOR SELENOPROTEINS IDENTIFICATION AND CHARACTERIZATION IN
FORMULA AND COW MILK AFTER SEPARATION BY 2-D PAGE

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Milk is an important food from birth, and as much formula milk for newborns as cow milk for adult require a careful quality control to assure their authenticity and the absence of fraud. Several instrumental approaches have been proposed for food authentication, but mass spectrometry is becoming a prominent importance. Proteins can be used as biomarkers of food quality and authenticity, and their characterization and quantification using mass spectrometric detectors coupled to single or multidimensional liquid chromatography constitutes a powerful tool for this purpose. In addition, some bioactive molecules in this food are metalloproteins, and the use of sensitive atomic detectors such as ICP-MS, can assist to a fast identification of these compounds.

Generally, a separation step is necessary to characterize the numerous proteins present in these types of samples, and multidimensional devices involving different chromatographic columns or two-dimensional polyacrilamide gel electrophoresis are the systems under election.

The proteins of milk are classified into two groups: caseins and whey proteins (α -lactalbumin, β -lactoglobulin and serum albumin). These proteins constitute practically the entire protein mass of sweet and acid whey. However, other minor proteins and metalloproteins have also important roles for health.

The purpose of the present research is to characterize low-abundance proteins, such as selenoproteins, in formula and cow milk. Peptide mass fingerprinting of in-gel tryptic digests has been used for minor selenium proteins identification. A previous selection of selenium-tagged spots was performed by fast analysis with ICP-MS.

SIMULTANEOUS SPECIATION OF MERCURY AND SELENIUM BY HPLC-
MAD-AFS/AFS AND HPLC-MAD-ICP-MS

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Mercury and selenium are two critical elements due to their toxicity. However, at some concentrations selenium is essential. The behaviour and action of these elements is strongly dependent of their chemical species. Organomercury species are the most toxic species of this element, being methylmercury (MeHg⁺) the most common one in environmental samples. The higher toxicity of MeHg⁺ is related to the high solubility of this compound in lipids. Therefore, methylmercury crosses the cellular membranes very easily, getting to the target organs, where it is bioaccumulated. Finally, mercury is biomagnified, reaching higher levels on the top of the food chain [1].

On the other hand, selenium has the double face of benefit and harmful effects [2]. It has been demonstrated that selenium has positive effects when it is present at appropriate levels, especially when it is associated to aminoacids, peptides and proteins. In addition, many of these proteins have protective roles for all major forms of life. A typical example of selenium importance is glutathione peroxidase (GPX), an antioxidant enzyme which contains this element in its structure. Anyway, Se also has damaging effects when is present at too high concentrations, becoming then a toxic element.

Some of the defence mechanisms of living organisms under mercury presence are related with antioxidant enzymes, and the increase of total selenium levels with mercury has been demonstrated [3]. Therefore, the study of these two elements and their chemical species is required when cause-effect behaviours are investigated.

In the present study two couplings for the simultaneous speciation of mercury and selenium in marine biota are proposed and compared. The first one is based on liquid chromatography coupled to two atomic fluorescence detectors connected in series, previous online microwave assisted digestion and hydride generation. The second one uses ICP-MS for the detection of the elements after their separation by liquid chromatography. Interferences related to polyatomic species were avoided using hydride generation.

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DEVELOPMENT OF A NOVEL PASSIVE SAMPLING SYSTEM FOR THE
TIME-AVERAGED MEASUREMENT OF ORGANOTIN COMPOUNDS IN
AQUATIC ENVIRONMENTS

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Environmental concern about organotin compounds has considerably increased in last years owing to their wide industrial use as pesticide formulations and biocides in antifouling paints. Their direct introduction into the marine and freshwater environment and their high toxicity towards non-target organisms at very low levels (ngl-1) has led to include triphenyl and tributyltin compounds in the European Union Pollutant list (EU, Directive 76/464) [1].

In order to control the effectiveness of this legal regulation several sampling methodologies (most of them based on spot sampling) are being developed in recent years to control these priority water pollutants at very low levels.

In this work a new passive sampling system for the measurement of time-average concentration of these organotin compounds and their degradation species has been developed.

The passive sampling device comprises a solid membrane, as diffusion limiting membrane, and a receiving phase-membrane both held in a PTFE body [2]. Sampling rates are dependent on the rate of permeation through the diffusion limiting membrane, the surface area of the exposed system and the affinity of receiving membrane for target compounds in accordance with the Fickian diffusion law.

Different combinations of receiving and diffusion limiting membranes have been tested for these analytes. The best results have been obtained with C18 EMPORE™ discs as receiving phase and polysulphone and also cellulose acetate as diffusion membrane. Organotin compounds accumulated in both membranes are extracted with an ultrasonic bath using acetic acid and methanol (3:1) as eluent. Determination of all species is performed by gas chromatography with a flame photometric detector (GC-FPD) and by gas chromatography coupled with ICP-MS detection (GC-ICPMS) [3] after ethylation with sodium tetraethylborate. The prototype has been calibrated in a laboratory flow-through tank that reproduced field conditions.

Calibration data under controlled temperature and turbulence conditions will be reported for sampling periods ranging between 7 and 14 days. On the one hand, this system provide a continuous monitoring of the levels of organotins compounds in the aquatic environment, so provides information on fluctuating analyte concentrations; and on the other hand, pollutants are accumulated in the receiving phase to levels exceeding those in waters minimizing the risks of degradation between sampling and analysis. So this methodology could be a good alternative to traditional spot sampling which provides only an instantaneous estimation of the concentration of pollutants.

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ACCUMULATION AND SPECIATION STUDIES OF BASED-Pt
ANTITUMORAL DRUGS IN RAT ORGANS

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Cisplatin (cis-diamminedichloroplatinum (II)) is the most important of the platinum containing antitumoral drugs. It is used in treatments of a variety of cancers, but this drug present several side effects as nephrotoxicity and ototoxicity. Similar side effects has been observed in experimental rats. The carboplatin and oxaliplatin drugs has been introduced to avoid the cisplatin side effects. The toxicity mechanisms of these drugs are not well known but it is believed the Pt accumulation in tissues and its interaction with tissue-proteins are responsible of the problem (1).

In this work the Pt accumulation in target organs such as kidney, cochlea, brain, or liver of laboratory rats (2) has been studied. Results obtained for Pt distribution among the different organs show a high dependence on time, dose and type of Pt-drug administrated.

Results for extraction studies carried out for the target organs will be presented for the point of view of both total and species content. Also Pt-containing drugs evolution in the organs will be afford (3).

Parallel studies of Pt-methionine and Pt-Gluthatione interactions (3) will be presented as an attempt to study in depth posible protective mechanisms for side effects.

Cisplatin transformation and Pt-drug adducts formed by the drug bonding to the citoplasmid faction of tissues has been studied by the coupling of Liquid Chromatography (LC) and Inductively Coupled Plasma Mass Spectrometry, LC-ICP-MS.

In the near future the comparison results from the analytical and clinical point of view and the metallomics studies, will allow elaborating a model for prevention and treatment of the Pt-drugs side-effects.

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PLUTONIUM ATOM RATIOS IN SEDIMENTS FROM BALLSTON LAKE, NEW YORK: CONTINENTAL TRANSPORT OF 1950's NEVADA TEST SITE DEBRIS?

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The US conducted over 100 above-ground nuclear tests at the Nevada Test Site (NTS) between 1951 and 1962. Most of these low-yield tests are known to have dispersed actinides and fission products in neighboring regions of the western US. The quantities of NTS fallout that were deposited in more distant locations such as the eastern US have received less attention. However, one test, Simon, conducted on April 25, 1953, apparently resulted in localized, heavy deposition of fallout in the vicinity of Albany and Troy, New York; the Simon cloud was transported some 3000 km, across the continental US, where it collided with a large thunderstorm in upstate New York. This deposition was first noticed accidentally by a researcher at a local university, who later described the findings in the literature (Clark, 1954).

The objective of the present study is to examine high-resolution aquatic sediments from a lake in the vicinity of this 1953 deposition, namely Ballston Lake. Ballston Lake is an abandoned channel of the Mohawk River; two dated cores were obtained from basins in the lake during the 1997 and 2002 field seasons. One of the cores, obtained from a meromictic (undisturbed) basin exhibits lamination with discernable annual or sub-annual strata. Our work is focusing on determination of the $^{239+240}\text{Pu}$ activity profile and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios. It is expected that recent aquatic sediments will exhibit a 1963/1964 "global fallout maximum" with a characteristic $^{240}\text{Pu}/^{239}\text{Pu}$ signature of 0.180 ± 0.014 . However, 1950's NTS deposition in this system is expected to produce additional $^{239+240}\text{Pu}$ activity maxima, and lower $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios.

In our work, sediments are treated with several different preparation procedures: acid leaching, fusion with potassium pyrosulfate, and fusion with potassium hydroxide. Pu is separated and preconcentrated from the sample solution using extraction chromatography with TEVA resin, and is determined using sector ICPMS. ^{242}Pu is used as a spike for isotope dilution.

Reference: H.M. Clark, Science, May 7, 1954, pp. 612-622.

SIMULTANEOUS DETERMINATION OF ARSENIC, MERCURY AND SELENIUM IN FOODSTUFFS BY HG-ICP-OES

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The increasing demand for quality in food production and distribution continues to stimulate the development of sensitive and selective analytical methods for trace elements determination in foodstuffs. Arsenic and mercury are highly toxic elements and their presence in food composites is a matter of concern to the well being of both humans and animals. Selenium may be classified either as essential or toxic depending on the ingested amount and accurate quantification is needed due to the narrow concentration range between its detrimental and beneficial function.

In this work, a new analytical procedure for the simultaneous determination of As, Hg and Se in foodstuffs has been developed. After sample dissolution, the determination was based on the use of simultaneous ICP-AES equipped with a vapor generation accessory, in order to obtain high sensitivity and selectivity as well as multi-element capability.

The study included the following steps: (a) multivariate investigation of the effect of operating conditions on the vapor generation and transport; (b) evaluation of the analytical figures of merit; (c) optimization of the pre-reduction step, taking into account the presence of all the analytes; (d) interference study; (e) application to real samples.

Under the optimized conditions (sodium borohydride concentration: 1.6% (w/v), sodium borohydride flow rate: 0.7 ml/min; carrier gas flow rates: 230 and 500 ml/min, before and after the gas-liquid separator, respectively), vapors of all the analytes were efficiently generated and transported to the plasma source. Due to the increased sample introduction efficiency, the emission intensities at various analytical wavelengths were significantly higher than those obtained with pneumatic nebulization, allowing to obtain g/l for arsenic, mercury instrumental detection limits of 0.6, 0.5, 1.0 and selenium, respectively. RSD%-values were 1-5% at ppb-concentration level. Concerning the pre-reduction step, only the reduction of Se(VI) to Se(IV) was performed, while arsenic was determined as As(V), with a decrease of sensitivity lower than 15%. Reaction conditions were optimized in order to avoid losses of mercury.

Finally, the procedure was applied to certified reference materials (rice flour and spinach leaves from NIST) and real samples (natural and Se-enriched rice samples). Accurate results were obtained, proving that the developed method is suitable for As, Hg and Se determination in foodstuffs at very low (natural) concentration levels.

DETERMINATION OF RARE EARTH ELEMENTS IN BONES USING
LA-ICP-MS

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During the degradation of metal implants in bone the dissolved alloy components are incorporated into the surrounding bone tissue or are transported into other organs. For a deeper understanding of the dissolving process of the implants it is an essential requirement to use a method with a high spatial resolution for qualitative and quantitative analysis of the dissolved alloy components.

New implant alloys, which are nowadays tested in animal studies, contain a huge diversity elements a multi element technique like ICP-MS is well suited for the determination of main, minor and trace elements of the degrading alloy in the matrix of bone tissue. The required spatial resolution is achieved by Laser Ablation as a sample introduction technique. To obtain quantitative results matrix matched standards are crucial.

After optimization of the preparation procedure of the matrix matched standards the first biological samples were quantitatively determined. The results obtained by matrix matched standards are compared to NIST and other glass standards.

Finally, the quantification results are used to characterize the degradation and the transport processes of the dissolved components of the degrading metal implant in-vivo.

SIMULTANEOUS ANALYSIS OF CADMIUM, LEAD, MERCURY AND
ARSENIC IN FOODSTUFFS BY ICP-MS AFTER CLOSED VESSEL
MICROWAVE DIGESTION: METHOD VALIDATION

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Except for occupationally exposed individuals, food is usually the most important source of toxic trace element intake. Exposure to toxic metals is associated with many chronic diseases and recent research has found that even low levels of cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg) can cause a wide variety of health problems. Therefore, the content of these cumulative toxic metals in food should be carefully checked in order to prevent possible toxicological risks. Many countries have established limits for the toxic trace elements in dietary products, including seafood. Commission Regulation (EC) No 466/2001, as amended by Commission Regulation (EC) 221/2002, setting maximum levels for the heavy metals Pb, Cd and Hg in foodstuffs.

Atomic Absorption Spectrometry (AAS) is the most commonly used technique for heavy metals quantitation in a large variety of food samples but recent possibilities for human nutrition and toxicology were offered by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), which allows the analysis of small samples with low analytes concentration, the simultaneous determination of many elements, with a large dynamic range, high sensitivity, characterized spectral interferences, rapid mass scanning and short time of analysis. Consequently, ICP-MS has become the instrument of choice for even routine trace metal analytical applications in a growing number of laboratories. These attributes combined with a single sample preparation, such as closed vessel microwave digestion, allow quantitative analysis with high accuracy. Indeed, a closed system minimizes the dilution times and the sample contamination because smaller amounts of reagents are needed and atmospheric exposure is limited. Moreover, the possible loss of volatile elements is considerably reduced during closed vessel digestions.

In order to propose an alternative to SAA analysis currently practiced, a method validation of the analysis of these elements by ICP-MS after closed vessel microwave digestion, were realized by our laboratory, National Reference Laboratory (NRL) - heavy Metals. In our knowledge, there is no reference method on ICP-MS techniques in foodstuffs. Due to the lack of validated method, the French AFNOR guidelines NF V03-110 untitled “intralaboratory validation procedure for an alternative method compared to a reference method – case of quantitative analysis methods” was used for the evaluation of this method. Thus, several criteria considered as compulsory (linearity, specificity, precision under repeatability conditions and trueness) have been estimated and discussed in addition to intermediate precision reproducibility, the limit of detection and the limit of quantitation.

The aim of this work was to give evidence that this method, based on a closed vessels microwave digestion prior to the ICP-MS determination, can be used in the laboratory

for the routine determination of total Cd, Pb, Hg and As in foodstuffs with adequate analytical performance. A comparison with in-house methods, using Electro-Thermal-AAS techniques, was performed using external proficiency testing scheme and food samples.

DIETARY EXPOSURE ESTIMATES OF SEVERAL ELEMENTS FROM THE 1ST FRENCH TOTAL DIET STUDY

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Performed part of the initiative of France's General Food Directorate (DGAL), attached to the Ministry of Agriculture, Food, Fishing and Rural Affairs, and the National Institute on Agronomic Research (INRA) and with the collaboration of the French Food Safety Agency (AFSSA), this Total Diet Study of French consumers is the first major study covering exposure to trace elements and minerals presented in "as-consumed" foods. It provides a first panorama of intakes and exposure to these food components for the French population.

Total Diet Study (TDS) consists in combining individual quantitative consumption data with the measured contamination levels of foods as they are actually eaten. Compared to exposure studies based on the contamination of raw materials, the TDS yields more realistic data and avoids overestimating risks.

To estimate the dietary exposure of main minerals and trace elements from purchased and cooked food by French population, approximately 1080 individual food samples were collected and analysed for 18 elements (arsenic, lead, cadmium, aluminium, mercury, antimony, chrome, calcium, manganese, magnesium, nickel, copper, zinc, lithium, sodium, molybdenum, cobalt and selenium). Intakes were calculated from different food behaviours found in France for average and high consumers among adults and children. Dietary exposures of those consumers estimated from the France 2000 Total Diet Study (FTDS) are reported, and compared with existing nutritional reference values (Lowest threshold intake, LTI) or toxicological reference values (Provisional Tolerable Weekly Intakes, PTWI or Upper Level, ULs) of the respective element and from previous French studies. This study confirms for the populations concerned, the low probability of nutritional or health risks due to food consumption. However, certain consumer groups are subject to a non-negligible risk of nutrient intake below the recommended minimum levels or to exposure to contaminants exceeding the reference toxicological values.

A LASER ABLATION ICP-MS SYSTEM FOR THE ANALYSIS OF RADIO-ACTIVE SAMPLES

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Laser ablation in combination with ICP-MS is established as a versatile and powerful method for the analysis of solid samples. The simple sample preparation and the high spatial resolution in combination with relative short analysis time and the quantification possibilities increased the interest in this method for the analysis of radio-active materials.

The handling of such radio-active samples like fuel rods from nuclear power plants is difficult and time consuming. The companies running nuclear power plants are interested in manifold characteristics like the local burn up within the fuel rods. Other possible samples are the cladding tube and any other activated material. So far, in the hotlab of the PSI, such samples were analyzed using ICP-MS and HPLC-ICP-MS after digestion, SIMS and radio spectrometric methods. The laser ablation system will simplify the sample preparation, and local quantitative analysis will be possible. Other projects include the quantitative radial element and isotope distribution, depletion and enrichment of fission products, especially the noble gases in inclusions.

Such high radio-active samples have to be handled within a glove box to exclude contamination of the environment. Additionally, there has to be always a lead shield of several centimeters to minimize the radiation dose of the operators. This inevitable safety makes the use of manipulators necessary and simple things like the transport and positioning of the sample in the ablation cell become difficult. Dedicated procedures to handle the samples and involved parts like the ablation cell with a simple manipulator have to be developed and tested.

Due to possible contamination only the ablation cell, xyz stage and few optical elements are located in the shielded box. The laser itself, aperture, camera and all electronics remain outside. The laser beam and the visualization enter the box through small quartz windows. For ablation, a 266 nm Nd:YAG laser was chosen for his robustness, simple of use and high energy. The samples of interest are not transparent. Therefore we do not expect fractionation problems from large particles within the ICP. The ablation system will be combined with a MC-ICP-MS.

In this work the design of a laser ablation system for samples with a very high activity is described. Results of the establishment and optimization using inactive or low active samples will be presented and discussed.

IN SITU LASER ABLATION SAMPLING FOR INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Aerosol transport efficiency in laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been determined to be less than 10% [1] which is caused by aerosol deposition in the ablation cell and in the transport tubing [2]. Therefore, inspired by a study using LA-ICP-atomic emission spectrometry (AES) [3], an in situ laser ablation system was built for ICP-MS in order to reduce loss or modification of the aerosol during transport. In this setup the sample is placed right in front of the ICP and the laser beam is focused orthogonally through the quartz torch onto the sample surface.

The optics for laser focusing and sample observation were mounted on a movable stage. This setup allows ablation of material with the same laser source and optics from samples inside the torch as well as from samples placed in a cell outside the ICP-MS (conventional). The laser used for the experiments was a Q-switched Nd:YAG laser at a wavelength of 266nm (1 to 20Hz).

The laser system was coupled to an ICP quadrupole mass spectrometer (Elan6000, Perkin Elmer, USA). The sample was mounted in front of the inductively coupled plasma at the tip of the injector tube made of stainless steel. The gas flow through the injector tube was directed over the sample surface that the entire aerosol is directly transferred into the plasma.

The resulting signals have durations of about 5 to 50ms depending on the sample matrix and the number of laser pulses as used in single hole drilling. The reduction in signal duration from seconds in conventional laser ablation to milliseconds for in situ laser ablation leads to a 100 fold increase in signal to background ratios.

For conventional and in situ laser ablation the number of ions counted in the spectrometer strongly depends on the number of laser pulses as well as on the gas composition used for ablation. The gas dependency of the detection efficiency (counts per laser pulse) is different for the two techniques. However, all investigated parameter settings led to more counts per laser pulse for the in situ configuration.

The technique of in situ LA-ICP-MS offers a promising approach to study transport effects in conventional LA-ICP-MS. A major limitation working with quadrupole MS is the fact that the signals are very fast and therefore a multi element approach is with the present configuration limited.

A detailed description of the setup will be shown and a comparison of the signals of conventional and in situ LA-ICP-MS will be given. Furthermore signal to background sensitivity and detection efficiency will be extensively discussed.

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FROM ALAN GRAY UNTIL TODAY -
20 YEARS OF LASER ABLATION-ICP-MS
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Recent progress in laser ablation-inductively coupled plasma mass spectrometry techniques is related to the continuing development of lasers and ICP-MS instrumentation.

The first publication by Gray [1] in the mid 80's, already highlighted the potential of laser ablation for sample introduction with the newly developed ICP-MS. The work of Gray followed from many earlier studies which used laser ablation sample introduction into an ICP-OES or direct emission measurements of the laser induced plasma using a Ruby laser [2]. With the introduction of the ICP-MS, where sensitivities were initially more than 100 times better than in OES and have since then improved even more, LA-ICP-MS is an important analytical technique today.

Seven years after the first report using LA-ICP-MS, a landmark paper showing that quantitative results can be obtained using LA-ICP-MS, was published [3]. This report attracted the attention of the geological community and led to a large number of applications. Typical geological samples contain several phases of sub mm size for which the LA is an ideal sampling tool.

Fundamental studies in LA have been stimulated by the work of Russo et al. [4]. Within these studies, the ablation behaviour as a function of laser wavelength, energy density, and pulse width has been evaluated in detail. However, the influence of the ICP has gained increasing interest in fundamental studies [5], which further elucidate the relevant parameters in laser ablation ICP-MS.

After 20 years of research and development, it is now clear that the particle size and the composition of the particles sizes produced during the ablation process are of fundamental importance and the processes involved need further investigation.

One of the recent steps in laser ablation ICP-MS is the introduction of femtosecond lasers [6-8]. Initial results suggest that these lasers will further improve performance of LA-ICP-MS. Fundamental studies and validation in real-world application are yet required to demonstrate the capability of these lasers and to justify the cost of these systems.

Several strategies in LA-ICP-MS have been developed that allow spatially resolved quantitative analyses and produce precise and accurate data.

New applications in biology and medicine have been demonstrated using ns lasers. This work could become the driving force in the near future [9].

Thanks to Alan Gray laser ablation as sample introduction has helped to avoid time consuming and contamination-prone wet chemical methods and led to an established,

invaluable analytical technique for micro and bulk analysis today, which will be discussed in the presentation.

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SIMULTANEOUS DETERMINATION OF CR(III) AND CR(VI) WITH ION CHROMATOGRAPHY AND AN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER AS ELEMENT-SELECTIVE DETECTOR

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Due to its extensive use in industrial processes (e.g. steel industry, for dyes and pigments, for chrome-plating, and leather tanning), large quantities of chromium compounds are discharged into the environment. The new EC regulations for the maximum concentration are: in water and wastewater (< 50 mg Cr/L), cement [< 2 mg Cr(VI)/kg], electrical and electronic equipment [no Cr(VI) from 1. July 2006] and automobiles [max. 2g Cr(VI) per vehicle].

Although chromium can exist in several oxidation states from 0 to +6, only the trivalent and hexavalent species are stable in the environment. The mobility, bioavailability, and as a consequence the toxicity of chromium, depend on its chemical form. Whereas Cr(III) is classified as an essential trace element (responsible for the control of glucose and lipid metabolism in mammals) and hardly soluble in water, Cr(VI) is a confirmed human carcinogen and highly soluble, mobile, and hence more easily bioavailable. Thus, information about chromium speciation is necessary to evaluate properly physiological and toxicological effects.

In aqueous solutions Cr(III) exists as trivalent cation Cr^{3+} and/or its hydrolysis products [$\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3$]. In contrast Cr(VI) is mainly present as CrO_4^{2-} or HCrO_4^- . From this it is obvious that speciation analysis is always an analytical challenge, because either way one elutes with the solvent front when ion-exchange chromatography is employed.

For the determination of Cr(VI) an anion-exchange column (Dionex IonPac AS 14A, 2x150) was used. A 50 mM KOH solution served as mobile phase. To keep the contamination from the chromatographic system as low as possible a metal free DX320 ion-chromatograph was used. With this method we obtained a determination limit of 0.1 $\mu\text{g Cr(VI)/L}$ by using an anion self regenerating suppressor (ASRS 4mm) and ICPMS (Agilent 7500cs) as element-selective detector with an injection volume of 25 μL . Under these conditions Cr(III)-species could not be directly determined.

Therefore, we implemented a Shodex RSpak NN 414 and NN 614 column for the simultaneous separation of both chromium species. According to the manufacturer the stationary phase of this column is a polyhydroxymethacrylate bonded with trace amounts of sulfo groups. With HNO_3 and H_2SO_4 (1×10^{-2} M- 1×10^{-3} M) as mobile phases the two Cr-species did not elute from the column. Increasing the elution strength by adding NH_4NO_3 was partly successful but the total separation time was unacceptable long (60 min.). Pure $(\text{NH}_4)_2\text{SO}_4$ (80mM) separated both chromium species within 15 minutes but the signal from Cr(VI) showed a strong tailing. After further optimising the mobile phase composition we found a 40 mM NH_4NO_3 / 60 mM $(\text{NH}_4)_2\text{SO}_4$ at pH 3.5 adjusted with HNO_3 as optimum. With these conditions a determination limit of $\sim 0.5 \mu\text{g/L}$ for both chromium species with an injection volume of 25 μL was obtained.

In the presentation the optimisation as well as the application of the developed methods for the determination of the chromium speciation in water samples (mineral-, tap-, waste-) and cement samples are discussed.

SECTOR FIELD ICP-MS FOR THE DIRECT DETERMINATION OF
SEMICONDUCTOR RELEVANT INORGANIC CONTAMINANTS AND
MATRICES

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With the introduction of new high-k materials replacing SiO₂ as gate dielectric and metal gates instead of polycrystalline Silicon semiconductor devices will shrink < 45 nm. Subsequent the detection power of analytical instrumentation has to be increased and new materials have to be analyzed. Typical sample preparation steps such as evaporation and digestion bear the risk of contamination and/or loss of volatile elements and should be avoided. Beside that such steps are too time consuming for close production control. Sector field ICP-MS allows direct determination of almost all typical semiconductor matrices while guaranteeing separation of the analyte from matrix induced spectral interferences. The presentation will demonstrate detection limits in semiconductor matrices, with emphasize on new materials, such as organometallics.

IS ICP-MS AN OPTION FOR QUALITY CHECKS IN FOOD PRODUCTS?
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For quality checks in food products major elements such as Ca, Mg, and Fe are measured using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) or Atomic Absorption Spectrometry (AAS). For safety assurance minor elements such as heavy metals are monitored using AAS and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Principally ICP-AES and ICP-MS are both capable to measure major and minor elements, but ICP-AES is limited by its sensitivity for heavy metals, which are present in foods only in trace amounts. In order to increase sample throughput and consequently decrease costs per sample it would be of great interest to measure all elements by one single equipment.

In our work we focused on the analysis of Ca, Cu, Fe, K, Mg, Mn, Na, P, and Zn by ICP-MS in order to extend the applicability of this analytical tool. A method was set-up on an ICP-MS Elan DRC II using the least interfered isotopes and if applicable the least sensitive ones in order to avoid high counts on the sensitive detector. The influence of remaining potential interferences was checked for each chosen isotope by adding the interferent to the analytical solution. 10-point calibration curves were measured and their linearity was checked through residual plots. In lack of appropriate certified reference materials six in-house food products were used for the validation of the established method. These foods were digested using nitric acid under high pressure (high pressure asher) and were analyzed by an accredited in-house method based on ICP-AES (Optima 3000). The measured concentrations were compared to the results obtained by the ICP-MS. Each sample was analyzed under simple repeatability (8 replicates, same day), duplicate repeatability (difference between duplicates, 7 different days) and intermediate reproducibility conditions (mean of duplicate, 7 different days).

Precision in terms of simple repeatability and intermediate reproducibility was comparable between the two methods. For the duplicate repeatability ICP-MS seemed to be less precise than ICP-AES.

Trueness was determined on the same set of analysis that had been used for precision evaluation. No significant difference between the two methods in the case of Ca, Cu, Fe, K, Na, and P was found. For Mg, Mn, and Zn a small but significant bias was detected. Future work will focus on these three analytes, which still give unsatisfying results in terms of trueness.

For the time being it can be concluded that ICP-MS offers a great potential of application for quality checks in food products besides the already known good performance in trace element analysis. This is important for laboratories that are specialized in trace element analysis but want to enlarge their field of application without necessarily investing into an additional equipment such as ICP-AES.

ICP-MS FOR ENVIRONMENTAL AND BIOMEDICAL ANALYSIS OF PLATINUM GROUP ELEMENTS

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Platinum group elements (PGE) have attracted considerable interest in recent years in environmental and biomedical research. The authors will discuss the complexity of problems encountered in three exemplary applications of PGE analysis by ICP-MS. The examples involve analytical approaches with increasing complexity: (1) elemental analysis, (2) speciation analysis by LC-ICP-MS and LC-ESI-TOF-MS and (3) 2D-HPLC-ICP-MS. Analytical challenges and future trends will be illustrated.

(1) Elemental analysis at ultratrace levels

The development of methods for the determination of Pt, Pd and Rh in environmental samples was triggered due to the continuous spread of these elements from cars fitted with exhaust catalyst. The discussion is centred on the development of sensitive ICP-MS methods suitable for quantification of platinum group elements at pg g⁻¹ concentrations levels in environmental (airborne particulate matter) and biological samples (human tissue samples, urine). Accurate quantification is often compromised due to unwanted spectral interferences, especially in the case of Rh and Pd. Present and future concepts for elimination/correction of such problems are illustrated.

(2) Speciation analysis by HPLC-ICP-MS and HPLC-ESI-TOF-MS

The use of cancerostatic platinum compounds (CPC) has gained undisputed importance in the antineoplastic chemotherapy. In the context of clinical pre-approval studies all compounds have been well characterized under physiological conditions, but only little is known about the degradation pathways of the parent drugs in different compartments of the water cycle. Speciation analysis is a prerequisite for fundamental understanding of the environmental relevance of CPC emission. A method will be presented allowing to determine the three relevant CPC and major metabolites within one chromatographic run. In this context the potential of species specific IDMS will be discussed for both ICP-MS (ICP-DRC-MS, ELAN DRC II, PerkinElmer SCIEX, Canada) and ESI-TOF-MS (LC/MSD TOF, Agilent Technologies, Germany)

(3) 2D-HPLC-ICP-MS

Ruthenium coordination compounds as indazolium trans-[tetrachlorobis(1H-indazole)ruthenate(III)] (KP1019) are promising alternatives to established metal-based anti-cancer drugs. A 2D-HPLC-ICP-MS study which supports elucidation of the pharmacological mode of action of the drug is presented.

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RELATIONSHIPS BETWEEN AERODYNAMIC PARTICLE SIZE AND METAL
CONCENTRATIONS IN URBAN DUST SAMPLES USING INDUCTIVELY
COUPLED PLASMA MASS SPECTROMETRY, X-RAY FLUORESCENCE, AND
A MICRO-ORIFICE UNIFORM DEPOS

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The study is designed to test the hypothesis that element concentrations in airborne particulate matter decrease as aerodynamic particle size increases. Teflon filters are loaded with re-suspended particles (certified reference materials) using a micro-orifice uniform deposit impactor (MOUDI). This is a cascade impactor which divides samples into 10 size fractions, ranging from 0.057 μm to 9.9 μm in aerodynamic diameter. Elemental concentrations are first determined using non-destructive ED-XRF, after which the elements are extracted using high pressure microwave-assisted digestion followed by ICP-MS analysis. Two different microwave digestion systems and two different ICP-MS instruments at Health Canada and Environment Canada were used to test the digestion method for the loaded filters. Preliminary results confirm that, between 9.9, 6.2, 3.1 and 1.8 μm , there is a tendency for Fe, Sand Pb concentrations to decrease as aerodynamic particle size increases; however, the relationship is less clear in the smaller particle size range (between 0.32 and 0.057 μm).

THERMAL IN-LINE SEPARATION OF ELEMENTS IN LASER ABLATION
ICPMS – A Rb-Sr CASE STUDY

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Spectral interferences from elemental or polyatomic ions are a significant problem for the analysis of mono-isotopic elements and isotope ratio determinations using LA-ICPMS, where all isotopes of interest should be interference free. In general, however, this is not the case and different approaches are used to account for these interferences. In cases, where the abundance of the interference relative to the analyte ions is sufficiently low, numerical corrections can often be used, even though the correction will increase the uncertainty of the results. When the interference is of high abundance, however, chemical separation is required.

Since any modification of the sample composition before laser ablation analysis would ultimately destroy advantages of LA-ICPMS, especially its high spatial resolution in the solid sample and reduced sample preparation, the only approach to reduce the abundance of potentially interfering elements is the modification of the sample aerosol before introduction to the ICPMS.

Even though ion-molecule reactions, using collision or reaction cells can often provide an effective means to eliminate or alleviate such interferences, this requires a suitable reaction gas with high discrimination efficiency.

Sr isotope ratios are important geological and biological indicators, where precision and accuracy for the isotope ratio measurement are limited by the variable abundance of Rb in the samples. Isobaric ^{87}Rb and ^{87}Sr cannot be resolved by sector field instruments, while ion molecule reactions were applied successfully [1], although the dynamic reaction cell appears to be sensitive to the sample matrix [2], limiting the applicability of this approach.

In this study, vaporization has been used to selectively remove Rb from the laser generated aerosol. The aerosol is passed through an electrically heated graphite tube where selective vaporization occurs, based on the thermodynamic properties of the elements and the sample material [3]. Easy to vaporize elements are removed from the sample aerosol, probably by condensation on the cold tube end. The set-up and optimization for Sr-isotope ratio measurements will be discussed in detail.

Discrimination of Rb from Sr in the aerosol, determined from the measured ion signals, is in the first instance a function of the tube temperature. Results obtained using a quadrupole-based ICPMS show that this approach allows a suppression of the Rb interference by two orders of magnitude, when ablating a NIST 610 glass reference sample, which significantly improves the accuracy and precision of the isotope ratio determinations.

[1] L. J. Moens, et al.; *J. Anal. At. Spectrom.*, 16, (2001), p. 991

[2] F. Vanhaecke, et al.; *J. Anal. At. Spectrom.*, 18, (2003), p. 1060

[3] T. Vaculovic, et al.; Canadian J. Anal. Sci. Spectroscopy, (2004), subm.

STUDIES ON ANALYTE RESPONSE AND POLYATOMIC ION FORMATION IN DEPENDENCE ON OPERATING PARAMETERS IN LA-ICPMS

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In this study, the dependence of the analyte sensitivity, background signals and the formation of polyatomic ions during laser ablation sampling in inductively coupled plasma mass spectrometry, (LA-ICPMS) was investigated. The influence of the ICP operating parameters were studied for solid sample introduction. A 193 nm ArF-excimer and a 266 nm Nd:YAG laser system, respectively, were used for the ablation of a NIST SRM 610 using 10 Hz laser repetition rate at a fluency $> 15 \text{ J/cm}^2$. Signal intensities for different m/z strongly depend on plasma conditions. Under all conditions, the signal intensities decrease at smaller sampling depths. The dependency on gas flow and rf-power, on the other hand, is significantly affected by the presence of a shield and its operation electrically grounded or floating. Sensitivity maximizes in dependence of rf-power at different carrier gas flow rates for the grounded shield and increasing rf-power shifts the optimum gas flow rates to higher values. With floating or non-shield, the maximum is observed for much smaller gas flow rates and sensitivity is reduced by an average factor of 5 to 6. This is, however, accompanied by a significant reduction of spectral and non-spectral background signals and higher signal-to-noise ratios can be obtained. Oxide formation (measured as the ThO^+/Th^+ ratio) is mostly affected at low rf-power settings, where increasing carrier gas flows above a certain threshold leads to sharply increasing values. A constant level is obtained for increasing sampling depth and decreasing carrier gas flow rate.

U^+/Th^+ intensity ratios are used as an indicator of robust plasma conditions in LA-ICPMS. Any significant deviation of the measured intensity ratio from their concentration ratio in the sample is attributed to incomplete vaporization, atomization and ionization of the laser-generated aerosol inside the ICP.[1] Robust operating conditions also depend on the ablation system and the carrier gas used. The U^+/Th^+ ratio approaches the concentration ratio of the sample with increasing sampling depth and decreasing carrier gas flows. Above 1200 W, there is only little dependence on rf-power indicating that residence time becomes the dominating factor for efficient atomization in the ICP. The increase in the ratio at increasing carrier gas flow rates is steeper for operation with grounded shield and floating shield, compared to the non-shield torch.

This presentation will demonstrate the complex dependence of ICP-MS parameters (sampler distance, rf-power, carrier gas flow rate and composition, operation of the shield) on the operating conditions for laser ablation using different wavelength and gas environment when optimizing the ICP-MS system for quantitative analysis.

Reference

[1] Guillong, M., Günther, D., J. Anal. Atom. Spectrom., 2002, 17, 831-837.

THE USE OF COLLISION CELL ICP-MS FOR THE DETERMINATION OF A
SUITE OF ELEMENTS IN CLINICAL FLUIDS

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The analysis of metals in biological fluids (whole blood, serum and urine) has been used for many years to provide information on toxicity, work-place exposure, nutrient information and as a diagnostic tool for a number of ailments.

When analysed by ICP-MS, many of the elements of interest suffer from mass spectral interferences derived from the sample matrix. In the past, these have been overcome by the use of high resolution mass spectrometry or by non-mass spectral techniques such as atomic absorption. These techniques can be expensive, time-consuming and/or less suitable for high sample through-put. It is the author's intention to test the ability of collision cell technology to provide a faster, more robust alternative.

A method has been developed that requires only simple dilution of the biological matrix before measurement of a range of elements in a single run. Analytical data for several problematic elements in several different biological matrices will be represented. These elements include As, Cd, Cr, Fe, Mo, Pb, Se and Zn.

A direct comparison of results obtained using magnetic sector ICPMS and collision cell ICPMS has been made that has confirmed the ability of the collision cell to overcome polyatomic interferences. The ability of the method to measure large numbers of samples overnight without detrimental affects on stability or accuracy will be demonstrated.

EXPLOITING THE BENEFITS OF MULTI-COLLECTOR ICP-MS FOR NOVEL ISOTOPE DILUTION TECHNIQUES

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Isotope dilution is now a familiar technique for high accuracy analysis by mass spectrometry. It involves the addition of an isotopic analogue (often called a “spike”) of the analyte of interest to a sample followed by the measurement of the ratio of analyte to spike. In the authors’ laboratory, an exact matching double IDMS technique is used in which the spike is added to a standard as well as the sample such that the ratios in both are the same[1]. Wherever possible the samples and standards have been spiked such that the ratios are approximately unity.

In many instances, it would be useful to employ a ratio greater than unity. This is particularly true where the analyte is at a very high concentration and/or where the cost of the spike material is prohibitive. In these cases, it is desirable to add a relatively small amount of spike material to the sample resulting in only a small change in isotope ratio. The precision of single-collector ICP-MS is such that small deviations in the isotope ratio cannot be distinguished. Multi-collector ICP-MS has the capability to measure the isotope ratio with precision of <0.01% (one standard deviation) and thus the difference in the ratio can be used in the IDMS equation.

Non-unity matched IDMS has been used for the quantification of sulfur in a high purity compound – dibutylsulfide. This is often used as the calibrant for sulfur determinations in many routine laboratories and, as such, there is demand for certification with improved uncertainty. In addition, sulfur is of particular interest in proteomics applications where this method could be used for the quantification of peptides.

A comparison of data provided for standard solutions using a range of isotope ratios will be presented together with the quantification data for dibutylsulfide. The implications on the uncertainty of the analysis are also discussed.

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MINERALIZATION OF ANCIENT BONES AND HAIR AND THEIR ANALYSIS
BY PLASMA SPECTROMETRY METHODS

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ICP atomic emission spectrometry (Ultrace 170, Jobin-Yvon) and ICP mass spectrometry (Agilent 7500ce) were used for a determination of Zn, Pb, Cu, Ca, S, Al, As, Sb, Se and Hg in bones and hair of the members of noble family of Dietrichstein from the 17th and 18th century. The hydride-forming elements (As, Sb, Se) were determined by means of hydride generation technique (hydride generator designed by Labtech Brno, Ltd., Czech Republic) coupled with ICP spectrometers and Hg was determined by the cold vapour technique. Comparison results were obtained using atomic absorption spectrometry.

The samples were taken from human remains buried in the Dietrichstein family crypt, located in the town Mikulov (Region South Moravia, Czech republic). The burials were moved to this crypt from the St. Anna Church, destroyed by fire in the middle of the 17th century.

The samples were taken to plastic bags and stored at dry and dark place. The hair samples were cleaned by washing procedure before the mineralization. The first step consisted in washing in distilled water, then three times in acetone and for the last again in distilled water. Then the samples were cut into small pieces and dried in drying box using the temperature of 100°C during the night. The amount of 0.5 g of the sample was mineralized in the mixture of acids (HNO₃, HClO₄, HCl). The samples of bones were cleaned from mechanical contamination and 0.5 g of the sample was dissolved in 5 mL of concentrated nitric acid.

Generally, results of analyses of these ancient samples of human remains show the post-mortem chemical changes that substantially influence the information value of material. Details will be discussed.

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DETERMINATION OF SULFUR SPECIES IN FOSSIL FUELS BY SPECIES-SPECIFIC AND SPECIES-UNSPECIFIC ISOTOPE DILUTION GC-ICP-MS

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The main source of anthropogenic sulfur emissions into the environment is the combustion of sulfur containing fossil fuels. In the atmosphere the generated sulfur oxides are converted to sulfuric acid and sulfates. These sulfur species can influence atmospheric processes and they are also hazardous contaminants so that it is aspired to strongly reduce sulfur emissions. Also the reduction of sulfur in gasoline is necessary because modern car engine catalysts are affected by sulfur compounds. According to the EU directive g/g in 2005 for sulfur in gasoline \square 98/70/EC there will be a legal limit of 50 and diesel fuel. However, so called "sulfur-free" gasoline with sulfur contents of $<$ g/g is already available. This leads to the necessity of further \square 10 improvements in the desulfurization steps by the refineries. To optimize these processes the concentration of the different sulfur species must be routinely determined in corresponding samples by sensitive and accurate analytical methods.

In the past, inductively coupled plasma isotope dilution mass spectrometry (ICP-IDMS) was often used for sensitive and accurate determinations of trace elements in different matrices, for example, for the determination of sulfur traces in fuel samples (1). In this work species-specific and species-unspecific GC-ICP-IDMS methods are developed for the determination of sulfur species in gasoline and diesel fuel. Because thiophene is the main sulfur compound of "sulfur free" gasoline a species-specific GC-ICP-IDMS method using a ^{34}S -enriched spike was developed. A micro-scale synthesis of a corresponding isotope-labeled thiophene spike was carried out. For diesel fuel and heating oil the main sulfur compounds are benzothiophene and dibenzothiophene. Spike syntheses for these species are under investigation to also allow corresponding determinations by species-specific GC-ICP-IDMS.

In the future the development of a method for species-unspecific GC-ICP-IDMS analyses is also planned. This system will use the continuous addition of a definite amount of a spike compound to the separated sulfur species (post-column isotope dilution technique) by a permeation tube. This species-unspecific GC-ICP-IDMS will allow the determination of all sulfur species using only a single ^{34}S -enriched spike. First results with this system will be presented.

This work is carried out in cooperation with the Interdisciplinary Research Training Group Program (DFG-Gratuiertenkolleg 826) Trace analysis of elemental species: Development of methods and applications.

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SYNTHESIS, SEPARATION AND QUANTIFICATION OF GOLD-NANOPARTICLES USING ICP-MS HYPHENATION TECHNIQUES

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Nanoscopical structures like nanotubes and nanoparticles (NPs) show properties differing from that of the bulk material and over the last years they have been object of intensive investigation. Colloidal gold forms the most stable metal NPs and it is manifold used.

The particles' size and size distribution play a major role in many of their widespread applications: nanoparticles are currently used to investigate size dependent electronical, magnetical and optical properties, they are applied as catalysts for organic synthesis and as protein markers in biology.

Normally, the determination of gold NPs' size is carried out through TEM (transmission electron microscopy) where pictures are taken and the individual particles are measured. A simple alternative is a size dependent separation by liquid chromatography techniques. Additionally, coupled to a powerful element-specific detection method like ICP-MS, quantification can be carried out.

In this work we present an HPLC-ICP-MS method and a GE-ICP-MS hyphenation for the separation and quantification of gold nanoparticles. Synthesised colloidal gold is characterised and quantified using an external calibration with standard solutions. The obtained results are compared to size determinations with microscopical methods.

Papercategory:

p

Topic(s):

Instrumentation (ICP-MS, ICP-AES, MIP-AES, etc.) - Applications
Elemental speciation - Applications

APPLICATION OF MICROWAVE INDUCED PLASMA ATOMIC EMISSION
SPECTROMETRY AS ELEMENT SPECIFIC DETECTOR FOR Cr(III)/Cr(VI)
SPECATION ANALYSIS

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Coupling of a low power helium microwave induced plasma atomic emission spectrometry (MIP-AES) with ion-pairing HPLC separation of Cr(III) and Cr(VI) species will be described and evaluated. Interfacing of HPLC and MIP was performed by hydraulic high-pressure nebulization and radiative-heating water-cooling desolvation system. The influence of the Cr-species form, the TBA ion-pairing reagent, the methanol content of the eluent and the recovery of the TBA-Cr(VI) complex from the RP-18 column on the Cr-signal formation and calibration were evaluated. The volume of the sampling-loop was optimized both for peak-height and peak area measurement. A signal depression in the case of Cr(VI) injection can already be experienced in aqueous medium and that is more significant if organic reagents (complexing agent and/or methanol) are present. This depression is not the consequence of the incomplete recovery of TBA-Cr(VI) complex from the HPLC-column and it can also be observed in the inductively coupled plasma, too. Therefore, species dependent calibration is required using both ICP or MIP plasmas for element specific detection.

CAPILLARY ELECTROSPRAY MASS SPECTROMETRY AND HR-ICP-MS FOR
THE DETECTION AND QUANTIFICATION OF BPA FOR
BORON NEUTRON CAPTURE THERAPY

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Boron Neutron Capture Therapy (BNCT) is a promising binary treatment for cancer. It is based on the emission of an alpha particle when natural ^{10}B isotope of boron captures thermal neutrons. Sulphydrilborane (BSH) and boronophenylalanine (BPA), or a combination of both has been used as boron carriers in patients. BPA is currently used in phases II/III clinical trials in Japan and Europe.

Studies on BNCT are dependent on precise and accurate measurements of boron concentrations (i.e. 100pg/g to 100µg/g) in specimens and biological samples of limited sizes, i. e. 10µg to 500 µg.

Moreover, the rapid and accurate determination of boron concentrations is mandatory for biological experiments on new compounds, predictive tissue dosimetry, toxicology and pharmacology studies as well as clinical investigations.

In this presentation, a new analytical approach for the separation and detection of BPA performed by coupling capillary electrophoresis to electrospray mass spectrometry is described: this allows in a short time with an efficient separation the quantitative analysis of BPA . Total boron content is then measured by high resolution inductively coupled mass spectrometry.

ON THE PRODUCTION OF LASER GENERATED AEROSOL PARTICLES

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LA-ICP-MS, which is today's most suitable technique for direct solid analysis, is still suffering from a number of drawbacks, which are related to the ablation process, the aerosol transport and the vaporization, atomisation and ionisation of the laser generated aerosol within the ICP. Understanding and ultimately modelling the related fundamental processes will help to localize such drawbacks and to design strategies to overcome these restrictions.

Beside the direct ablation process - the interaction of the laser with the sample - the laser generated aerosol has been experimentally proved to be one of the major sources of these problems. The size distribution of particles and the size dependent chemical composition causes a discrimination of certain elements during transport to and vaporization in the ICP. The question arises how the aerosol particles are produced and what parameters are influencing the chemical composition and physical emergence of the aerosol. It will be shown that the basic features of a laser-generated aerosol can be directly related to the fundamental chemo-physical processes governing the growth and production of particles. Influence of certain parameters (e.g. pulse duration: fs/ns) will be given.

SPECIES-SPECIFIC AND SPECIES-UNSPECIFIC MULTI-SPECIES ISOTOPE
DILUTION ANALYSIS OF ORGANO-ELEMENTAL COMPOUNDS BY ICP-MS

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Since the first species analyses in 1994 by isotope dilution ICP-MS (1,2) many other investigations in elemental speciation have been carried out with the isotope dilution (ID) technique. The reason for the increasing importance of ICP-IDMS in elemental speciation is the fact that this method is highly sensitive but also a primary method of measurements resulting in accurate analytical data. Species-specific and species-unspecific ICP-IDMS methods have been established (3), where for the first mentioned technique isotope-labelled spikes of the analyte must be used whereas for the second one any isotope-labelled compound of the element of interest can be applied. Species-specific ICP-IDMS can also be used to validate sample preparation steps for possible species transformations, a problem which often occurs in species analysis but cannot easily be identified by other analytical methods.

The relatively stable organometallic compounds monomethylmercury (MeHg⁺), trimethyllead (Me₃Pb⁺), and the butyltin compounds Bu₂Sn²⁺ and Bu₃Sn⁺, which are all highly toxic and must therefore be determined even in low concentration ranges in the environment and especially seafood samples, are traditionally analysed by species-specific GC/ICP-IDMS after conversion into volatile compounds. Because the same reagent (NaBEt₄ or NaBPr₄) can be used for this derivatisation step, it is also possible to determine all these elemental species within one analytical run by an optimised GC temperature program. Spike solutions of the mercury and tin species are commercially available since a short time, which will promote this multi-species determination to become soon a routine method. However, the corresponding trimethyllead spike must still be synthesised at the moment, but we developed a successful method for the production of labelled Me³²⁰⁶Pb⁺ in the micro-scale range.

The determination of organo-sulfur species in gasoline, diesel fuel and heating oil is of actual interest with respect to the world-wide trend to reduce sulfur in this type of samples. Thiophen and benzothiophen derivatives are the most abundant sulfur species in gasoline and diesel fuel, respectively. Species-specific GC/ICP-IDMS methods were therefore developed for the accurate, sensitive and fast determination of these sulfur species in such samples. However, for the determination of a large number of other sulfur species with minor abundance a species-unspecific GC/ICP-IDMS is under development using a permeation tube for spiking after sulfur species separation.

For species-specific ICP-IDMS determinations it is an important precondition that no isotope exchange takes place between the spike compound and other elemental-species. This problem became obvious when we tried to analyse iodinated hydrocarbons by the corresponding ¹²⁹I-labelled spike compounds. An isotope exchange occurred within a few minutes so that this prevented correct determinations by GC/ICP-IDMS. On the other hand, analogous bromine species could be

determined by species-specific GC/ICP-IDMS because no isotope exchange took place, which could be explained by the different binding energies of the halogens to carbon.

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LASER-SCATTERING PLASMA DIAGNOSTICS FOR THE TIME AND
SPATIALLY RESOLVED CHARACTERIZATION OF A MILLISECOND-
PULSED GLOW DISCHARGE

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Glow discharges have become increasingly attractive due to their ability to perform direct spectrochemical analysis of solid samples. As of late, glow discharges operated in pulsed mode have drawn especial attention because better analytical figures of merit have been observed. In addition, a pulsed glow discharge enables fast speciation analysis to be performed because of the rapid changes in plasma ionization conditions that occur. However, pulsed glow discharges have not been widely studied, in contrast to their dc or rf counterparts, and thus we are still far from completely understanding the behavior of the different plasma species. In order to improve the analytical performance of the pulsed glow discharge it is imperative to gain a better knowledge of the temporal behavior of the plasma fundamental parameters. For this purpose we have utilized laser scattering techniques that, as opposed to other diagnostic methods, do not assume local thermodynamic equilibrium, are non-invasive, and offer inherent temporal and spatial resolution. A previously described instrument was used to obtain axial profiles of the pulsed GD plasma gas-kinetic temperature (T_g) via Rayleigh scattering [1]. When a 5ms square-wave pulse (-920Vp, 60Hz) is applied to the GD, the maximum T_g values observed go from ~700K to ~1000K, depending on the pressure (1Torr vs 3Torr Ar) and peak current. At 3Torr the maximum T_g is reached faster and in both cases it is observed that T_g close to the cathode does not return to room temperature, a fact that may have implications on the stability of the plasma with respect to the frequency and length of the pulse. Furthermore, the electron number density (n_e), electron energy distribution function (EEDF) and the electron temperature (T_e) were observed via Thomson scattering. For this purpose, the detection optics were modified and a photon-counting imaging technique was employed to allow the simultaneous observation of Thomson scattering from multiple spatial positions. Experimental observations on the temporal behavior of electron fundamental properties in a pulsed glow discharge will be reported as well.

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STRATEGIES FOR SIMULTANEOUS MEASUREMENT IN PLASMA SPECTROMETRY

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The ability to measure species in a truly simultaneous fashion affords many important opportunities in all branches of chemical analysis. From the simplest standpoint, simultaneous measurement shortens analysis time, and is therefore critical in high-throughput analysis. The gain is, of course, related to the number of channels (analytes) that must be determined. Further, if a fixed measurement time exists, simultaneity provides a higher signal-to-noise ratio, since all species can be examined during the full measurement interval. This gain, in turn, yields better detection limits and precision. Also, in many instruments, particularly plasma spectrometers, a large fraction of the observed signal fluctuation is correlated; that is, all signals vary as a function of time in much the same fashion. If the various signals are examined exactly at the same moment, they can therefore be ratioed to reduce the noise, often to the point where precision is limited by fundamental events (the arrival of photons or ions). In the same way, background correction is improved if signals and the adjacent background can be determined at the same instant.

In this presentation, a number of strategies will be described for performing simultaneous measurement in plasma spectrometry, with particular emphasis on plasma-source mass spectrometry. The first examples will involve mass spectrometers that provide simultaneous measurement of a broad range of mass-to-charge ratios at once. Recent work with a time-of-flight mass spectrometer (TOFMS) will illustrate how this form of simultaneous spectrometer can be used to advantage with sequential-injection analysis and with a modulated ICP. In both applications, the ability to monitor several isotopic peaks at once is critical and can be employed to reduce both isobaric overlaps and matrix interferences. A second form of simultaneous spectrometer, consisting of a Mattauch-Herzog double-focusing sector-field unit and a second-generation focal-plane camera (multichannel array detector), will also be highlighted. This system, with a greater number of channels (128) and larger detector elements than the first-generation instrument, offers higher resolution, better sensitivity, faster readout rates, and computer-selectable gain on a channel-by-channel basis. To illustrate its capability, it has been coupled to an electrothermal vaporizer, so multi-element and multi-isotope analysis can be performed even on microliter samples.

Simultaneous analysis is being exploited also in the area of source design. In one conception, two sources are being extracted at the same time into a single TOFMS, so

elemental speciation or metallomics can be performed more efficiently and with less likelihood of error. In a second arrangement, metal-containing proteins separated by two-dimensional gel electrophoresis are being quantified simultaneously, by means of a monochromatic imaging spectrometer.

HIGH-PRESSURE ELECTROSPRAY IONIZATION SOURCE (HPESI) FOR ELEMENTAL SPECIATION

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Electrospray ionization (ESI) is currently one of the most widely employed means of ionization in mass spectrometry. In ESI, a high electric field generates a liquid jet from a solution surface, resulting in the formation of charged droplets, and eventually the production of gas-phase ions. ESI is used widely in elemental speciation analysis because of its ability to produce from solution ions ranging from bare metals to large biomolecules, and under gentle conditions. Unfortunately, ESI suffers several shortcomings. It is often complicated by large differences in sensitivity among analytes caused by chemical composition, surface activity, or gas-phase basicity/acidity. ESI is also susceptible to severe matrix effects and varying response among different solvent systems, making quantitation difficult in many instances. Further, the application of ESI is limited by the formation of electrical arcs or corona discharges, restricting application to solvent systems within a range of surface tensions and conductivity.

In this presentation we describe a novel ESI source aimed at overcoming these limitations. High-pressure electrospray ionization (HPESI) employs elevated ambient gas pressures in order to enhance the mechanisms of conventional electrospray ionization. It is well known that the breakdown potential (the voltage that can be applied across a spatial gap before an electrical discharge forms) of a gas depends on pressure in accordance with Paschen's Law. That is, raising the gas pressure above atmospheric conditions permits higher voltages to be applied across a known distance before electrical discharge occurs. Thus, operation of ESI at an elevated gas pressure, as occurs in HPESI, permits greater electric fields to be employed without the formation of an electrical arc or corona discharge. In turn, stronger electrostatic fields allow greater numbers of electrical charges to be deposited on the surface of droplets, ensuring that the Rayleigh instability limit is more quickly reached, and thus that less desolvation is needed before ions are formed from the progeny droplets. A higher number of surface charges (and consequently a stronger electric field) on the droplet surface also suggests an increased probability of ion formation, and thus greater efficiency of ionization. HPESI also permits greater force to be applied to the liquid surface without electrical discharge, permitting solvents of high surface tension (such as pure water), low conductivity, or high viscosity to be sprayed successfully. Operation of ESI at high gas pressures also significantly modifies desolvation mechanisms, permitting ESI to be accomplished more efficiently. Studies aimed at characterizing this novel source will be described, and current analytical figures of merit examined.

AN INDUCTIVELY-COUPLED PLASMA/ELECTROSPRAY IONIZATION
DUAL-SOURCE TIME-OF-FLIGHT MASS ANALYZER FOR
COMPREHENSIVE ELEMENTAL SPECIATION.

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Many applications at the forefront of atomic spectrometry require determination of the chemical forms or non-covalent complexes associated with elements of interest, as well as the quantity and identity of the atoms that constitute a sample. Overwhelmingly, elemental speciation analysis is currently accomplished by hybrid techniques comprised of a chromatographic separation followed by some form of atomic spectrometry. In this approach, the chemical form of each component in a mixture is identified by its chromatographic elution time, while the quantity and identity of the elements associated with each eluent is established by atomic spectrometry. Unfortunately, this approach is limited in that the chemical form of each element is established indirectly based upon its retention time, and thus with a certainty limited by the resolution and reproducibility of the chromatographic separation. Also, because identification is often achieved by retention-time matching, limited chromatographic resolution can lead to misidentification of components, and little can be ascertained as to the identity of unknown or unexpected components within a mixture. This is especially problematic in bioanalytical applications, where the elements under study might be associated with any number of unknown species in complex biological mixtures, over a wide concentration range.

One solution to such problems lies in pursuing a more comprehensive method of elemental speciation, establishing the chemical identity and elemental composition of each eluent simultaneously. In our work, comprehensive elemental speciation is accomplished through a unique dual-source time-of-flight mass spectrometer (TOFMS) capable of simultaneously monitoring ions produced by two distinct ionization sources. The sources take the general form of one atomic source (e.g. ICP) and one molecular source (e.g. ESI), the first being responsible for determining element identity and concentration, while the second provides information concerning chemical form and molecular association. Because both are analyzed by a common TOFMS, complete atomic, isotopic, and molecular mass-spectral information is available simultaneously. Further, since two dedicated sources produce the two different types of information, each can be independently optimized. Overall, simultaneous, direct, and rapid determination of elemental speciation can provide unambiguous identification of target analytes, facilitate the discovery of previously unknown or unexpected ones, simplify determination of the stoichiometry of metals and bound species, and permit fast screening without spectral artifacts common to other instrumentation. When coupled to existing chemical and physical separations in a hybrid technique, comprehensive speciation of components within multielemental mixtures can be accomplished in a single step. Design criteria, current experimental capabilities, and future embodiments of this novel instrument are discussed.

ENVIRONMENTAL ANALYSIS BY ICP-AES / ICP-MS: OBTAINING MORE
INFORMATION FROM THE SAME DATA

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Modern analytical instrumentation offers the analyst the opportunity to collect vast amounts of data. In addition to quantitative data on specific elements using multi-element analysis, information on spectral background and potential interferences is often collected via multi-wavelength and multi isotope data. Software algorithms are used to help the analyst select the data required for the selected task, but much of the information potentially available from the data is not used.

This presentation will discuss some of the chemometric methods used in the authors laboratory utilising data obtained by atomic spectroscopy (ICP-AES / ICP-MS). The focus will be on practical applications of these approaches rather than the detailed mathematics. Examples will be presented for a range of environmental applications involving experimental design, calibration, signal processing and pattern recognition in order to show how chemometrics can be used to save time, optimise systems and reveal hidden trends.

USE OF A NOVEL SEQUENTIAL EXTRACTION PROCEDURE WITH
CHEMOMETRIC DATA TREATMENT AND ICP-AES ANALYSIS TO ASSESS
THE METAL DISTRIBUTION WITHIN THE PHYSICO-CHEMICAL
COMPONENTS IN SEDIMENTS FROM THE GALICI

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A study of the trace metals distribution in sediment samples from the Galician coast (Spain) has been performed. A multielement extraction method optimised via experimental design has been employed. The method uses centrifugation to pass the extractant solution at varying pH, through the sediment sample. The sequential leaches were collected and analysed by ICP-AES. Chemometric approaches were utilised to identify the composition of the physico-chemical components in order to characterise the sample. The samples collected at different sites could be classified according to their differences in metal bioavailability. The method proved to be quick and reliable to evaluate different sediment samples. It offers a new tool for environmental geochemistry analysis and might also be useful as fast screening method for the bioavailability of metals in the environment.

A NOVEL ON-LINE SEQUENTIAL EXTRACTION PROCEDURE FOR METAL
PARTITIONING IN SOILS AND SEDIMENTS

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A new rapid and reproducible extraction method for the evaluation of trace metal distribution in soils and sediments has been developed. This approach combines the results obtained from atomic spectroscopic measurements with chemometric data processing. Following optimisation, the method was evaluated on a range of different reference materials using a simple sequential extraction procedure. The physico-chemical phases of the samples and their percentage elemental composition were obtained and the results were found to correlate well with those obtained using Tessier extraction procedure¹. The method has also been used to study the effect of humic acids on the bioavailability of trace metals in soils and sediments and applied to the characterisation of areas of trace metal contamination.

The method has been further developed to enable the rapid on-line sequential extraction of geological samples with direct coupling to the detection instrument (ICP-AES). The construction of the system will be described and its application demonstrated with reference to a range of soil and sediment samples.

1. Santamaría-Fernández, R.; Moreda-Piñeiro, A.; Hill, S. J.; J Environ. Monit., 2002, 4, 330-36.

CHARACTERISATION OF SELENIZED YEAST SUPPLEMENTS FOLLOWING
IN VITRO GASTROINTESTINAL DIGESTION

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Since recent studies have shown that selenium supplementation with selenized yeast can reduce the risk of several forms of cancer in humans,(1) there has increased the use of selenized yeast in human food supplements, raising a demand for analytical methods capable of identifying and determining selenium species. On important aspect of the problematic concerning selenized yeast is related to quality control and safety of marketed preparations available. The most common method of quality control is the determination of the selenomethionine (SeMet) content after enzymatic hydrolysis with proteolytic enzymes (protease) or non-proteolytic enzymes (driselase) or during simulated gastrointestinal digestion processes.(2)

In vitro enzymolysis showed the lowest SeMet extraction recovery (between 25 and 35% of the total Se) in spite of its high Se solubilisation efficiency (approaching 100%). So, the aim of this study was to identify the other selenocompounds that could be present in those enzymatic extracts. For this purpose, different separation procedures were analysed in combination with both ICP-MS and ESI-MS/MS detection. Selenized yeast prepared in our laboratory using both natural abundance selenium and ⁷⁷ enriched selenium were studied.

(1)L.C. Clark, Jr.G.F. Combs, B.W. Turnbull, E.H. Slate, D.K. Chalker, J. Chow, L.S. Davis, R.A. Glover, G.F. Graham, E.G. Gross, A. Krongrad, Jr.J.L. Leshner, H.K. Park, Jr.B.B. Sanders, C.L. Smith, J.R. Taylor, J. Am. Med. Assoc., 1996, 276, 1957.

(2)L. Hinojosa Reyes, J.M. Marchante-Gayón, J.I. García Alonso, A. Sanz-Medel, In preparation.

PERFORMANCE CHARACTERISTICS AND APPLICATIONS OF A NEW
GLOW DISCHARGE SECTOR FIELD MASS SPECTROMETER

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Glow discharge mass spectrometry is established as the high-end tool for the solid analysis of high purity metals. However, the sector field instruments which are currently in use suffer slow scan speed and consequently low sample throughput.

The presentation will introduce a new glow discharge mass spectrometer based on a fast flow grimm type source combined with a state of the art sector field analyzer as detector. The performance characteristic of the instrument as well as application examples will be shown.

MEASUREMENT OF MERCURY ISOTOPE RATIOS IN ENVIRONMENTAL SAMPLES USING MC-ICP/MS

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Recent measurements have suggested that isotope signatures of mercury in different environmental compartments and among mercury ores from various sources may vary. However, it is still debated whether mercury from anthropogenic sources is isotopically different from geogenic mercury, which would allow tracing of mercury sources according to their isotopic fingerprint.

This presentation describes the use of an on-line mercury cold vapor technique to generate a continuous steady signal, which can be processed for precise isotope ratio measurements by multi-collector (MC)-ICP/MS. Special attention has been paid to ensure optimal MC-ICP/MS conditions allowing highly precise measurement of ratios (1 SD < 50 ppm, 0.005 ‰), enough to be able to detect the anticipated small differences in mercury isotope ratios in nature.

The extent of mercury fractionation has been investigated in a variety of sediments from different locations, for which sources of mercury have been identified. The samples consisted of (1) certified sediment reference materials obtained from natural or anthropogenically contaminated environments, (2) well characterized and dated sediment profiles from the Lake-658 of the Experimental Lakes Area, and (3) river catchments affected by gold or mercury mining.

An internal precision of 10 to 70 ppm (1SE) was obtained for all ratios and across the various sediment samples investigated. The external precision of the measurements for replicate sample digests ($n \geq 6$) was between 0.02 and 0.24 ‰ (1 SD), depending on the certified reference material. The range of δ values observed extended from 0.15 to 5.93 ‰ for the certified sediments and from 0.51 to 1.52 ‰ for the sediment profile (ELA, Lake-658). The magnitude of the mercury fractionation per amu was constant within one type of sample.

The measurements demonstrated the ability of the proposed method to detect significant differences in mercury isotope ratios within one type of samples (e.g. between different sediments) and so far have unequivocally shown that natural variations in mercury isotope ratios exist in nature. Future research will focus on the differentiation between natural and anthropogenic sources in the global mercury cycle. There is a need to get better understanding of the range of mercury isotope fractionation that can be expected in nature, i.e. among matrices (air/water/sediment/biota) and a single matrix (sediment cores). This information needs to be reconciled with observed differences to ultimately assess, whether variations in mercury isotope ratios are caused by natural fractionation processes or are a result of anthropogenic activity.

ARSENIC SPECIATIONS OF MARINE SAMPLES BY HPLC-ICPMS

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Arsenic speciation of the extracts from marine organisms performed by HPLC-ICPMS with two different columns. One is a Capcell Pak C18 (Shiseido, Japan) reverse phase column and the other is a Hamilton PRP X-100 anion-exchange column. Seven arsenic species (AsV, MMA, AsIII, DMA, AsB, TMAO, and TeMAs) were detected in the extracts from algae by a Capcell Pak C18 column. The detection limits for 8 arsenic species by HPLC-ICPMS were in the range of 0.03-0.23 mg L⁻¹ based on 3s of blank response (n=5). The repeatability was in the range from 2.2 to 15.2% for all eight species. The method was validated by analyzing a certified reference material DORM-2 (dogfish muscle) and then successfully applied to several marine samples e.g., oyster, fish muscle, shrimp and marine algae. For the extraction of arsenic from seafood products, the low power microwave digestion was employed. Also, four arsenosugars and one unknown arsenosugar were detected in the extract from Hijiki by a Hamilton PRP X-100 column.

FRACTIONATION OF ELEMENTS FROM AEROSOL, SEDIMENT AND FLY ASH SAMPLES

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The aim of the research was to apply a simple operationally defined sequential leaching procedure for the determination of the distribution of elements in atmospheric aerosol, sediments, and fly ashes. For fractionation by particle size, aerosol was sampled in 8 different fractions using Berner-type cascade impactor. For fractionation by chemical bonding a simple 3-stage sequential leaching procedure was applied to establish the distribution of metals between environmentally mobile (1), bound to carbonates and oxides (2), and environmentally immobile, (bound to silicates) (3) fractions in aerosols. The concentration of main and trace elements was measured by atomic spectrometric method with an RSD of <5 % from solutions. Wet and dry depositions were calculated. The aim of collecting precipitate and aerosol samples in the same site at the same period was to determine the distribution of elements in two depositions. The soluble fractions of depositions (Ddrymobile+Dwet) were compared to the total depositions (Ddry+Dwet) and it has been found that 50-94 % of elements were dissolved in the water.

Sediment samples were collected from the top 10 cm layer of the bottom of the Lake Balaton. A 4-step sequential leaching procedure was applied for the determination of the distribution of elements. Results of the sum of 4 fractions of bottom sediments of the lake, rivers on its catchment area and harbors were compared to sediment quality values (SQVs) and sediment background values (SBVs). Data showed that the average concentration of elements was usually less than that of SQVs and other background data for soils and geochemical values.

A five-stage sequential leaching procedure was successfully optimized for analysis of fly ash samples. The sequential leaching experiments together with solid phase examinations carried out by X-ray powder diffraction provide information on the possible environmental impact of substance associated pollutants. Results of the total elemental analysis and the sequential leaching method were compared and good agreement was found for most of elements. Uncertainty of the leaching method is reasonable, even when experimental parameters are strictly fixed and the analysis is quite tedious. The ratio of environmentally mobile fractions was compared to the conventional test method and reasonable conformity has been found. This characterization method can be used to interpret leaching behavior in terms of element species and mode of binding to the matrix. The methodology opens a new aspect to understand the behavior of toxic metals released from fly ashes into the nature.

DETERMINATION OF THE DISTRIBUTION OF ELEMENTS IN SEDIMENTS
COLLECTED IN THE LAKE BALATON

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It is recognized that the distribution, mobility and biological availability of chemical elements depend considerably upon the chemical and physical associations which they undergo in natural systems. The sequential extraction procedures are commonly used to isolate metals associated with the exchangeable, reducible, oxidisable and residual fractions of elements.

The aim of the research was to apply a simple sequential leaching procedure for the determination of the distribution of elements in sediments. Samples were collected from the top 10 cm layer and up to the 80 cm depth of the bottom of lakes at 17 different points in the Lake Balaton. The sample was dried at room temperature then stones and plant fragments were removed in and 2 mm sieves. A 4-step leaching by passing the dried sample through a 63 method was developed and validated for analysis of sediment samples: 1. exchangeable elements and elements bound to carbonates, 2. elements bound to Fe/Mn oxides, 3. elements bound to sulfide compounds, 4. acid-soluble elements. The concentration of elements was determined by atomic spectrometric method with an RSD of <5 %. Standards were prepared from ultra pure chemicals.

Particular attention was paid to distinguish between environmentally mobile and environmentally immobile fractions because these represent the two extreme modes by which the metals are bound to the solid matrices. Based on the results model has been developed for calculation of the fraction of metals adsorbed on the surface of Fe(OH)₃ and MnO₂. Data collected during the 8 years monitoring were evaluated by chemometric method. Comparing the average concentration values for international findings, it can be definitely confirmed that the quality of the sediment in the Lake Balaton is satisfactory. The sediment is not polluted and its disposal on the soil is feasible.

SUITABILITY OF COATINGS CONTAINING HYDROGEN AS CRM FOR GDS
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The development of certified reference materials (CRMs) for hydrogen is an essential task for a reliable GDS quantification. Despite the very large offer of analytical methods existing, there still are severe limitations as far as the quantitative analysis of hydrogen in (layered) solid samples is concerned, e.g. maximal investigated depth or no localized information at all. The combination of quick qualitative analysis ($\mu\text{m}/\text{min}$) of layered materials up to a depth of $\sim 100 \mu\text{m}$ and low detection limit of hydrogen ($\sim 1 \mu\text{g}/\text{g}$) makes GD-OES a powerful technique for the analysis of hydrogen. Nevertheless, the quantification of hydrogen by GD-OES is not possible yet due to the lack of CRMs necessary for calibration. At present there is still no CRM suitable for the GDS calibration of hydrogen (www.comar.bam.de).

Many trials of production of bulk materials (charged with hydrogen) or hydride pellets have failed mainly due to the poor stability of the concentration of hydrogen over longer periods of time even at room temperature. The reliable alternative has been proven to be in form of thick coatings containing hydrogen in bound form and hence unable to diffuse out from the sample even at higher temperatures. Different matrices (coatings) are requested to perform a matrix independent calibration.

Electroplated thick coatings like Zn(H) have provided a homogeneous and stable hydrogen concentration under various conditions. WC(H) hard coatings have established a second class of coatings where the homogeneous H concentration keeps stable. Another suitable candidate of H-CRM is Si(H), unfortunately the existent coatings were destined to Nuclear Reaction Analysis (NRA), so that the coating thickness is rather low for GD-OES.

The homogeneity of the hydrogen concentration in the selected coatings is checked by qualitative GD-OES depth profiling. The stability of the hydrogen concentration is periodically checked out over the topmost $1\text{-}2 \mu\text{m}$ by quantitative Elastic Recoil Detection Analysis (ERDA) and NRA.

Different concentrations of H could be defined for each selected type of coating. A certification of the hydrogen concentration in the selected sample is the next goal of the present work.

HIGH SPEED HIGH THROUGHPUT ANALYSIS OF ENVIRONMENTAL SAMPLES USING ICP-OES

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ICP-OES has been used for the analysis of environmental samples (soil digests, wastewaters, etc) for many years and has proven to be a reliable tool. The results do comply with most of the requirements. The bottleneck in the analysis for many (commercial) laboratories is the speed at which samples en QC's can be measured. The speed of analysis becomes more and more a critical item. When the analytical performance (limit of determination, precision, reproducibility and repeatability) is being compromised. In order to increase the analytical speed (sample throughput) the following items need optimization:

- 1) The sample introduction plays a major role in the optimization of the speed: the need to minimize memory effects, stability of aerosol generation (nebulization)
- 2) Optimization of plasma conditions
- 3) Finding the minimum acceptable integration times(s)
- 4) Optimization of software

The above items were investigated using two different spectrometers employing both Echelle configurations, but equipped with different detectors: PMT-based and a solid-state detector based optical system (L-PAD) large format programmable array detector. The results are presented and discussed.

THE SIMULTANEOUS ANALYSIS OF ARSENIC, SELENIUM AND MERCURY
IN FOODSTUFFS USING ICP-OES

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The elements Arsenic, Selenium and Mercury are relatively insensitive for the analysis with ICP-OES. In order to improve the limits of determination for Arsenic and Selenium, hydride generation techniques have been used and many hardware variations have been used for hydride generation. Often hardware becomes a limiting factor as the use of it becomes cumbersome. Also the repeatability of the hardware has been limited in many cases.

The direct analysis of Mercury by ICP-OES is being limited by the sensitivity (L.O.D.'s in the range of 2-4 ppb) and in many cases not good enough for analysis. Dedicated mercury-analyzers are being employed with cold-vapor generation (and pre-concentration by amalgamation) and fluorescence detection obtaining detection limits in the sub-ppt range. In several applications, e.g. foodstuffs, limits for the above elements are in the range of 10-20 ppb in the solid. The sample preparation (digestion) of these samples have to take place in closed vessels (microwave digestion) or at low temperature to avoid loss of mercury. The sample digestion results in many cases in a dilution factor in the order of 50. This means that the instrumentation needs to provide a limit of determination in the range of 0,2-0.4 ppb.

This paper presents and dicusses the results of a study where the aim was to simply the necessary hardware for As and Se-hydride and Hg-cold vapor generation for introduction into the ICP and the simultaneous analysis of those 3 elements.

In the sample preparation, care was taken that the final samples were also suitable for the analysis of other major and trace elements.

EMISSION YIELD RELATED RESEARCH AT IFW DRESDEN
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Quantification in GD-OES is applied in different manner.

The most accurate quantification is used at bulk analyses with matrix specific calibration and results in a relative precision and accuracy of about 0.1 % in the best cases. Hereby, analysis and calibration must be done at the same conditions, which are usually constant voltage and current in the dc mode. In the rf mode constant power and pressure are very useful, if the impedance of plasma does not change between the samples used for calibration and analysis. Another option exists, if conductive samples are analysed. By an active pressure control it is also possible to maintain a constant effective rf voltage or dc bias voltage together with constant power.

It is assumed that other parameters, like pressure, when working at constant electrical conditions, temperature, sample reflectivity and real structure of the sample are less important or constant. Mostly this prerequisite is valid, because similar samples are used for calibration and analysis. Additionally, an intensity ratio is often used, which compensates for those changes, which are linear correlated.

In the case of matrix independent calibration the use of constant discharge conditions is preferred too. However, there are drastical changes of the physical properties between the set of calibration samples and the unknown sample to analyse possible.

The determination of the matrix independent emission yields requires furthermore the exact determination of sputtering rates. Up to now there is no standardised method for their determination existing and the accuracy of the analytical result depends on the used values. All sputtering rates (absolute and relative) are determined at defined discharge conditions (e.g. 700 V and 20 mA for a 4 mm anode) but must be used at the parameters, which are ideal for the analysis. Hence, for quantification it is essential, if the relative sputtering rates depend on the discharge parameters.

We will present an overview about developments and results of our research related to this topic.

PULSED GLOW-DISCHARGE TIME-OF-FLIGHT MASS SPECTROMETRY FOR
ELEMENTAL AND MOLECULAR ANALYSIS

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Glow discharge (GD) is a highly specialized source that especially meets the requirements for accuracy, simplicity and speed for content depth profiling and bulk analysis in both Optical Emission and Mass Spectrometry. The pulsed radio frequency GD source has the potential for both elemental and molecular analysis. To exploit the information delivered by pulsed rf-GD sources fast sampling is required. In terms of mass spectrometry this is available only through time-of-flight mass spectrometry (TOFMS). The presented new rf-GDTOFMS system is a successful combination of a commercial high end glow discharge instrument and an extremely fast and high resolution time-of-flight mass spectrometer. Compared to optical glow discharge (GDOES) instrumentation, a GDTOFMS system show much simpler spectra, lower background signals, and detection limits are up to 2 orders of magnitude better. First results obtained with the GDTOFMS are compared with measurements from a GDOES instrument for conducting and non-conducting materials.

PREPARATION OF POWDERED SAMPLES FOR LA-ICP-OES
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Inductively coupled plasma with optical emission spectrometry (ICP-OES) was used for the analysis of powdered samples with different characteristics. The problems of a long dissolution procedure necessary for the nebulisation technique of the powders sampling were solved by using the direct sampling technique of laser ablation (LA). Powdered precursors of WC/Co sintered hardmetals, soils and dry milk were presented for the analysis as pressed or poured pellets.

Q-switched Nd:YAG laser with the wavelength of 1064 nm was used for ablation of prepared pellets. Samples were placed into an ablation cell which was connected with XY-translator allowing a sample moving during ablation. The ablated mass was transported by Ar through a polyamide tube to ICP spectrometer Jobin Yvon 170 Ultrace (laterally viewed).

The good homogeneity, hardness and cohesion are the most important properties of prepared pellets. The pellet quality is mostly influenced by the sort and amount of binder material. Metal powders (Ag, Al), urethan resin, cellulose or vax were studied as a binders suitable for pellet preparation. The advantages and disadvantages of pressed pellets without any binder were discussed. The emission signal-time dependences of selected analytical lines were studied. The conformation of the ablation craters were recorded using optical microscop, scanning electron microscop (SEM) and profilometer.

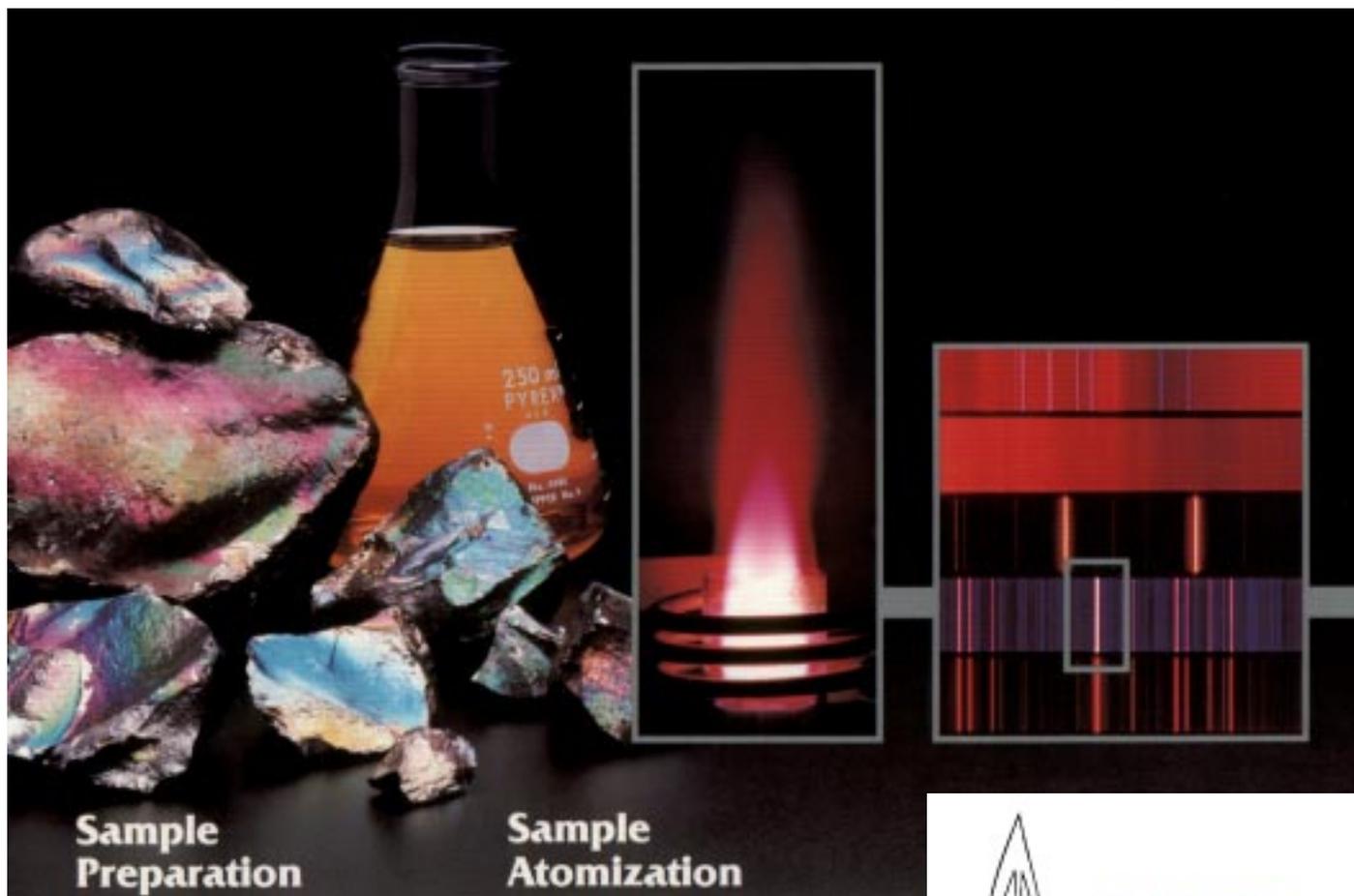
This work was supported by project J07/98: 143100003 of the Ministry of Education, Youth and Sports of the Czech Republic

ICP Information *NEWSLETTER*

INDUCTIVELY COUPLED PLASMA DISCHARGES FOR SPECTROCHEMICAL ANALYSIS

Ramon M. Barnes, *Editor*

Volume 30, June 2004 - May 2005



**2006 Winter Conference on
Plasma Spectrochemistry**

Tucson, Arizona, January 8 - 14, 2006

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2005 Asia-Pacific Winter Conference on Plasma Spectrochemistry

Chiang Mai, Thailand, April 25-30, 2005

The first biennial Asia-Pacific Winter Conference will be held at the Lotus Hotel Pang Suan Kaew (www.lotuspskhotel.com) in Chiang Mai, Thailand (www.tourismthailand.org). More than 300 scientists are expected, and over 200 papers on modern plasma spectrochemistry will be presented. Six plenary lectures and 22 invited speakers will highlight critical topics in 12 symposia.

Symposium Features

- Elemental speciation and sample preparation
- Excitation mechanisms and plasma phenomena
- Flow injection and flow processing spectrochemical analysis
- Glow discharge atomic and mass spectrometry
- Inductively coupled plasma atomic and mass spectrometry
- Laser ablation and breakdown spectrometry
- Microwave atomic and mass spectrometry
- Plasma chromatographic detectors
- Plasma instrumentation, microplasmas, automation, and software innovations
- Sample introduction and transport phenomena
- Sample preparation, treatment, and automation; high-purity materials
- Spectrochemical chemometrics, expert systems, and software
- Spectroscopic standards and reference materials, databases
- Stable isotope analyses and applications



Also

- Continuing Education Short Courses, Saturday - Sunday, April 23-24
- Manufacturer's Seminars, Saturday - Sunday, April 23-24
- Spectroscopy Instrumentation Exhibition, Monday - Thursday, April 25-28
- Provocative Panel Discussions, Daily
- Workshop on New Plasma Instrumentation, Tuesday - Thursday, April 26-28
- Conference Excursion and Dinner

Information

For program, registration, hotel, and transportation details, visit the Conference website at <http://www-unix.oit.umass.edu/~wc2005>, or contact Ramon Barnes, ICP Information Newsletter, Inc., P.O. Box 666, Hadley, MA 01003-0666, telephone: 413-256-8942, fax 413-256-3746, e-mail wc2005@chem.umass.edu.

2005 Asia Pacific Winter Conference on Plasma Spectrochemistry

Monday - Saturday, April 25-30, 2005, Chiang Mai, Thailand

Schedule of Activities

Call for Papers, Abstracts Due; Early Bird Registration	Monday, January 3, 2005
Exhibitor Booth Reservation and Pre-Registration Due	Monday, January 3, 2005
Final Abstracts for All Papers Due	Friday, January 28, 2005
Exhibitor Reservation Deadline	Friday, January 28, 2005
Conference Pre-Registration	Friday, January 28, 2005
Hotel Pre-Reservation	Friday, March 25, 2005
Late Pre-Registration Deadline	Friday, March 25, 2005
Winter Conference Short Courses	Saturday – Sunday, April 23 – 24, 2005
Manufacturers' Seminars	Saturday – Sunday, April 23 – 24, 2005
Winter Conference on Plasma Spectrochemistry	Monday – Saturday, April 25 – 30, 2005
Workshop on New Plasma Instrumentation	Tuesday – Thursday, April 26 – 28, 2005
Instrument Exhibition	Monday – Thursday, April 25 – 28, 2005
Conference Dinner	Friday, April 29, 2005
Conference Manuscripts Final Deadline	Thursday, June 30, 2005

Tentative Program

Monday, April 25, 2005

08:00 **Opening and Welcome**
08:10 **PL01 Plenary Lecture 1**
09:10 **IL01 Invited Lecture 1**
09:40 **IL02 Invited Lecture 2**
10:10 Break
10:30 **IL03 Invited Lecture 3**
11:00 **CL01 Contributed Lecture 1**
11:30 **CL02 Contributed Lecture 2**
12:00 Lunch and Exhibition Opening

Afternoon

**Parallel Sessions: Plasma Spectrochemistry and
Non-plasma Atomic Spectrometry
Exhibition and Poster Session**

Tuesday, April 26, 2005

08:00 **PL02 Plenary Lecture 2**
09:00 **IL04 Invited Lecture 4**
09:30 **IL05 Invited Lecture 5**
10:00 Break
10:30 **IL06 Invited Lecture 6**
11:00 **CL03 Contributed Lecture 3**
11:30 **CL04 Contributed Lecture 4**
12:00 Lunch

Afternoon

**Parallel Sessions: Plasma Spectrochemistry and
Non-plasma Atomic Spectrometry
Poster Session and Exhibition**

Wednesday, April 27, 2005

08:00 **PL03 Plenary Lecture 3**
09:00 **IL07 Invited Lecture 7**
09:30 **IL08 Invited Lecture 8**
10:00 Break
10:30 **IL09 Invited Lecture 9**
11:00 **IL10 Invited Lecture 10**
11:30 **IL11 Invited Lecture 11**
12:00 Lunch

Afternoon

**Parallel Sessions: Plasma Spectrochemistry and
Non-plasma Atomic Spectrometry
Poster Session and Exhibition**

Thursday, April 28, 2005

08:00 **PL04 Plenary Lecture 4**
09:00 **IL12 Invited Lecture 12**
09:30 **IL13 Invited Lecture 13**
10:00 Break
10:30 **IL14 Invited Lecture 14**
11:00 **CL05 Contributed Lecture 5**
11:30 **CL06 Contributed Lecture 6**
12:00 Lunch

Exhibition Closes

Afternoon Excursion

Friday, April 29, 2005

08:00 **PL05 Plenary Lecture 5**
09:00 **IL15 Invited Lecture 15**
09:30 **IL16 Invited Lecture 16**
10:00 Break
10:30 **IL17 Invited Lecture 17**
11:00 **CL07 Contributed Lecture 7**
11:30 **CL08 Contributed Lecture 8**
12:00 Lunch

Afternoon

**Parallel Sessions: Plasma Spectrochemistry and
Non-plasma Atomic Spectrometry
Poster Session**

Conference Dinner

Saturday, April 30, 2005

08:00 **PL06 Plenary Lecture 6**
09:00 **IL18 Invited Lecture 18**
09:30 **IL19 Invited Lecture 19**
10:00 Break
10:30 **IL20 Invited Lecture 20**
11:00 **IL21 Invited Lecture 21**
11:30 **IL22 Invited Lecture 22**
12:00 **Closing and Lunch**

2006 Winter Conference on Plasma Spectrochemistry

Tucson, Arizona, January 8 - 14, 2006

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Symposium Features

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- Inductively coupled plasma atomic and mass spectrometry
- Laser ablation and breakdown spectrometry
- Microwave atomic and mass spectrometry
- Plasma chromatographic detectors
- Plasma instrumentation, microplasmas, automation, and software innovations
- Sample introduction and transport phenomena
- Sample preparation, treatment, and automation; high-purity materials
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- Spectroscopic standards and reference materials, databases
- Stable isotope analyses and applications



Also

- Continuing Education Short Courses, Friday - Sunday, January 6 - 8
- Manufacturer's Seminars, Friday - Sunday, January 6 - 8
- 6th Annual Golf Tournament, Sunday, January 8
- Plasma Spectroscopy Instrumentation Exhibition, Tuesday-Thursday, January 10-12
- Six Provocative Panel Discussions, Daily
- Workshop on New Plasma Instrumentation, Tuesday-Thursday, January 10 - 12

Information

For program, registration, hotel, and transportation details, visit the Conference website at <http://www-unix.oit.umass.edu/~wc2004>, or contact Ramon Barnes, ICP Information Newsletter, Inc., P.O. Box 666, Hadley, MA 01003-0666, telephone: 413-256-8942, fax 413-256-3746, e-mail wc2004@chemistry.umass.edu.

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ICP Information NEWSLETTER

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Objective

The *ICP Information NEWSLETTER* is a monthly journal published by the ICP Information Newsletter, Inc., a nonprofit organization, and is devoted exclusively to the rapid and impartial dissemination of news and literature information related to the development and applications of plasma sources for spectrochemical analysis.

Background

ICP stands for **inductively coupled plasma** discharge, which during the past 30 years has become the leading spectrochemical excitation source for atomic emission spectroscopy and ion source for inorganic mass spectrometry. The popularity of this source and the need to collect in a single literature reference all of the pertinent data on ICP stimulated the publication of the *ICP Information NEWSLETTER* in 1975. Other plasma sources, such as microwave induced plasmas, direct current plasma jets, and glow discharges, have grown in popularity and are also included in the scope of the *ICP Information NEWSLETTER*.

Scope

As the only authoritative monthly journal of its type, the *ICP Information NEWSLETTER* is read in more than 40 countries by scientists actively applying or planning to use the ICP or other types of plasma spectroscopy. For the novice in the field, the *ICP Information NEWSLETTER* provides a concise and systematic source of information and background material needed for the selection of instrumentation or the development of new methodology. For the experienced scientist, it offers a single-source reference to current developments and literature.

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Editorial

The *ICP Information NEWSLETTER* is edited by Dr. Ramon M. Barnes, Professor Emeritus of Chemistry, University of Massachusetts at Amherst, with the assistance of a 17-member Board of National Correspondents composed of leading plasma spectroscopists. The international Board members report news, viewpoints, and developments. Dr. Barnes has been conducting plasma research on ICP and other discharges since 1968. He also serves as chairman of the Winter Conference on Plasma Spectrochemistry, also sponsored by ICP Information Newsletter, Inc.

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- Original submitted and invited research articles by ICP and plasma experts.
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Conference Activities

The *ICP Information NEWSLETTER* has sponsored 12 international meetings on developments in atomic plasma spectrochemical analysis since 1980 in San Juan, Orlando, San Diego, St. Petersburg, Fort Lauderdale, Kailua-Kona, and Scottsdale. Meeting proceedings have appeared in special issues of *Spectrochimica Acta, Part B, Analytical and Bioanalytical Chemistry*, and *Journal of Analytical Atomic Spectrometry*. The 2006 Winter Conference will be held in Tucson, Arizona on January 8-14, 2006. Contact wc2004@chemistry.umass.edu for details.

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SIMPLE ELIMINATION OF MEMORY EFFECT ON THE DETERMINATION OF
TOTAL MERCURY IN SEDIMENT AND MARINE BIOLOGICAL SAMPLES BY
ISOTOPE DILUTION ICP-MS

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Mercury is an important element for the assessment of environmental pollution because of its high toxicity to human being as well as small being things. Sediment and marine biological samples are frequently analyzed to monitor Hg dynamics and pollution in water environment.

Inductively coupled plasma mass spectrometry (ICP-MS) has often been applied to measure Hg in sediment and marine biological samples due to its high sensitivity. In addition, isotope dilution technique that has the potential of a primary method of measurement is also applicable. However, the ICP-MS measurement of Hg is subject to memory effect in a sample introduction device. The memory effect can lead to a high background and a long wash out time, and thus would cause a significant error in the measurement.

We propose a simple and reliable elimination method for the memory effect of mercury in a sample introduction device of ICP-MS. First, a small volume sample introduction device that consisted with a self-aspirate type micro-flow nebulizer (100 mL min⁻¹) and a small volume cyclonic spray chamber (20 mL inner-volume) was utilized to restrict a sample carry-over and accelerate the wash out. Second, aqua-regia was used for a sample digestion and the wash out solution for the sample introduction device. Aqua-regia can decompose organomercury species and dissolve mercuric sulfide (HgS), which is major species in sediment sample and resists to acid attack. Aqua regia can also prevent a reduction of mercuric ion to Hg(0) by the formation of an anionic chloride complex ([HgCl₄]²⁻), and thus 10 % aqua-regia solution, which is the same solution condition as the digested sample solution, was used as the wash-out solution. The wash out time required to reduce the steady state signal of 50 ng mL⁻¹ standard solution to 0.1% of the signal was less than 90 s, in spite of a conventional sample introduction device and 0.1 M HNO₃ solution as the washout solution requires over 10 min for washing. Furthermore, a spurious transition of the signal intensity caused by the difference of the solution condition, so call the transient effect, was not observed when the sample solution was measured after the wash out. The analytical results obtained for Hg in sediment certified reference materials, PACS-1 and MESS-3, and marine biological certified reference materials, BCR 464 and DOLM-2 were all in good agreement with their certified values together with small uncertainties. The proposed approach is simple and reliable for the determination of Hg in sediments and marine biological samples by ID-ICP-MS.

USE OF N₂-AR MIXED GAS PLASMA FOR THE DETERMINATION OF AS
AND SE IN SEDIMENT AND BIOLOGICAL SAMPLES BY ICP-MS WITH A
COLLISION/REACTION CELL

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Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most powerful techniques for trace elements analysis. However, in the case of As and Se measurement, ICP-MS is subject to severe spectral interferences of polyatomic species produced from Ar and concomitant elements in the sample.

Recently, an ICP-MS equipped with a collision / reaction cell system (ICP-CRCMS) have been utilized to eliminate the spectral interferences of argide based polyatomic species. The collision/ reaction system can greatly improve signal to background ratio(S/B) for As and Se, while the systems also follows the loss of the sensitivity of As and Se.

In this study, we propose a method for enhancement of the sensitivity of As and Se in the ICP-CRCMS measurement, where a N₂-Ar mixed gas plasma was investigated to enhance the sensitivity for As and Se. When N₂ gas was added into the outer or the intermediate gas flow, the plasma tends to shrink, which is plasma volume reduces, by the pinch effect. This volume reduction of plasma can lead to increase the proportion of analyte ions in the central canal. In addition, it can also lead to improve the ionization efficiency of As and Se whose ionization potentials are rather high. As a result, the analytical response of As and Se would increase by using the N₂-Ar plasma than all Ar-plasma. When N₂ was mixed into the intermediate Ar gas flow up to 10%, the signal intensities of As and Se maximally four and three-fold increased although those of ArAr⁺ and ArCl⁺ less increased with the same operating condition. Thus, the S/B of As and Se could be three to four-fold improved by using the mixed gas plasma. We also applied this method to the determination of As and Se in sediment and biological certified reference materials, PACS-1 and MESS-3, and NIST SRM 1577b and DOLM-2. Isotope dilution analysis was also applied to Se determination. The analytical results obtained for each CRM were all in good agreement with those certified values and information value with good precision. The mixed gas plasma was very useful to improve the precision of the analytical results for As and Se in sediment and biological samples obtained by ICP-CRCMS.

SELENIUM-SPECIFIC DETECTION AND IDENTIFICATION OF METHYL-
SELECYSTEINE-CONTAINING COMPOUNDS IN YEAST-BASED Se-
ENRICHED SUPPLEMENTS BY HPLC WITH ICP-MS AND ELECTROSPRAY
MS/MS DETECTION

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Selenium (Se) is a crucial nutrient for higher organisms (including humans) since it is an essential component of a number of Se-containing proteins and enzymes, some of which have important nutritional functions. Recent studies have shown that Se supplementation in the diet can reduce the risk of cancer and other human diseases¹. Thus interest in Se and marketing of Se as a food supplement has increased in recent years.

The anti-carcinogenic effects of Se have been associated with certain Se-metabolites such as methylselenol (CH_3SeH). However, the relationship and mechanism by which Se supplementation may reduce certain cancer risks is not fully understood. Absorption, tissue distribution, bioavailability, and cancer prevention properties depend on the chemical species of Se present in supplements. The lack of information on the concentration and identity of the chemical species in which Se occurs in food and supplements demands for analytical methods that allow quantification and identification of the Se-compounds in such complex matrices.

Se-yeast has probably been the most widely investigated food supplement as it is the only form of Se to date to have shown efficacy in human anticancer intervention studies¹. Despite a large number of studies, information available on the identity of the molecules incorporating or binding Se in yeast is still scarce², mostly because of the complexity of the matrix and the low concentration of the Se-compounds. Although the major component of Se-yeast has been identified as selenomethionine (SeMet), the recent verification of other Se-species with highly potent cancer-preventative activity and higher bioavailability than SeMet (e.g. methyl-Se-cysteine (SeMC) species)³ in this dietary Se supplement offers a continuing challenge for the speciation analysis of high Se-yeast by MS techniques.

Reversed-phase HPLC methods combined with on-line ICP-MS and electrospray MS/MS are evaluated for Se speciation analysis of water-soluble selenocompounds in high selenium yeast. Extraction of the Se-compounds from the complex matrix in water was achieved using accelerated solvent extraction (ASE). Verification of gamma-glutamyl-SeMC in the water-soluble extract, on the basis of retention time, molecular mass determination for the $[\text{M}+\text{H}]^+ {}^{80}\text{Se}$ ions (m/z 313) and detection of its product ions, is reported here for the first time. The mass spectral confirmation for gamma-glutamyl-SeMC in yeast is of interest, as this species is believed to serve primarily as a carrier of SeMC, which has been demonstrated to be metabolised in animals and humans to methylselenol, an anti-carcinogenic Se-metabolite.

(1) M. P. Rayman, *Br. J. Nutr.*, 2004, **92**, 557-573.

(2) P. C. Uden, H. T. Boakye, C. Kahakachchi, R. Hafezi, P. Nolibos, E. Block, S. Johnson and J. F. Tyson, *J. Anal. At. Spectrom.*, 2004, **19**, 65-73.

(3) H. Goenaga Infante, G. O'Connor, M. Rayman, R. Wahlen, J. Entwisle, P. Norris, R. Hearn and T. Catterick, *J. Anal. At. Spectrom.*, 2004, in press.

THE 1ST SWIFT-WFD PROFICIENCY TESTING IN SUPPORT OF THE
IMPLEMENTATION OF THE WATER FRAMEWORK DIRECTIVE
IN THE EUROPEAN LABORATORIES

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The project Screening methods for Water data Information in support of the implementation of the Water Framework Directive (SWIFT-WFD), funded by the European Commission (Contract no: SSPI – CT – 2003 – 502492) for 3 years started on the 1st of January, 2004. The main objective of the project is to support the successful implementation of the WFD which strongly depends on the quality of monitoring data and their comparability from river basin to river basin. This objective requires primarily, but among others, the development, validation and dissemination of rapid, affordable and user friendly measurement techniques. One of the activities of the project is the production of 3 sets of Reference Materials (RM) and the corresponding calibrants for the quality control of the analysis of priority pollutants listed in the Directive, and the organization of 3 Proficiency Testing (PT) schemes among European laboratories experienced in the analysis of these analytes.

The first set of materials consist of 4 river water reference materials (two at natural and two at fortified analyte levels) for several metal and major components. The batch sample was taken from the river Meuse, the Netherlands, and transported to IRMM for the preparation of RMs. The spiking solutions, to prepare the RMs at fortified levels, and the calibrants were prepared by the University of Barcelona.

National Contact Points were invited from all the countries of Europe and to individuate a small number of analytical laboratories in their country to participate in the 1st SWIFT-WFD PT.

The 1st SWIFT-WFD PT was organized with the participation of 55 laboratories from 21 European countries that received the RM samples in September 2004. The results were due the beginning of November. After the statistical evaluation of the measurement data, a technical discussion meeting was held in Rome at the beginning of December 2004.

The results of the 1st SWIFT-WFD PT, together with the introduction of the main conclusions of the Rome meeting, will be presented and briefly discussed.

LA-ICP-MS STUDIES IN NICRALY-BASED COATINGS ON HIGH TEMPERATURE ALLOYS

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In many technical applications metallic construction materials are subject to corrosive/oxidated environments at high temperatures. The most commonly used system are overly coatings of MCrAlY type (M=Ni, Co). These materials are characterized by relatively low chromium contents and substantial additions of titanium, tantalum, tungsten, etc., which frequently results in poor oxidation resistance of the materials [1]. Development and application of coating systems which guarantee reliable component protection during long term services is a crucial requirements for this type of materials in industrial gas turbines. With LA-ICP-MS the element distribution after oxidation in air at temperature 980 °C after 300, 1000, 5000, 15000, 20000 hours were determined. The laser ablation system was coupled to a double-focusing sector field ICP-MS. Experiments were performed using line scan measurements. The surface of the samples was scanned with a focused laser beam (diameter of laser crater – 15 µm, wavelength - 213 nm). The quantitative determination of Ni, Co, Cr, Al and others elements in order to study diffusion processes in coatings and alloys was performed using a standard reference material with the similar element composition.

[1] W.J.Quadakkers, “Coating system development for future, high efficiency gas turbines”, 7th Polish Corrosion Conference, KOROZJA 2002, 17-21 June 2002, Krakow, Poland

SPECTROSCOPIC DIAGNOSTICS OF A CONTINUOUS POWDER
INTRODUCTION MICROWAVE INDUCED PLASMA ATOMIC EMISSION
SPECTROMETRY SYSTEM

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Spectroscopic diagnostics is useful for evaluation of excitation conditions of different elements in the plasma and for improvement of analytical measurements. Fundamental studies on the analysis of inorganic and organic powder materials by continuous powder introduction microwave induced plasma atomic emission spectrometry (CPI-MIP-AES) are presented. In this experimental study we have used spectroscopic methods to characterize both argon and helium plasma obtained by means of a TE101 integrated cavity. This device produces very stable plasma that can withstand up to 10 mg min⁻¹ of a powdered sample load. Spectroscopic diagnostics and the analytical potential of a CPI-MIP-AES system are evaluated and compared with those of a solution nebulization MIP-AES. Radial profiles of electron number density and electron temperature as well as excitation temperature are obtained. To study the analyte vaporization capacity of the MIP the radially resolved rotational temperatures are determined. Emission profiles and limits of detection for some elements are reported. Also the influence of operating conditions as microwave power, gas flow rates and sample feed on plasma parameters is investigated. They are found to affect the spatial distribution and some changes in the plasma parameters values can be observed in the range 120-200 W and at a powder loading of between 0.5 to 5.0 mg min⁻¹. Remarkable differences in fundamental plasma parameters are observed when inorganic (glass powder, soils, R.U. powder) or organic (activated carbon) samples have been introduced to the plasma. It was found that in the presence of AC a uniform spatial distribution of electron number density is observed and the value exceeds 10¹⁵ cm⁻³. Comparison with other microwave plasma devices already described in the literature is made in terms of the electron density and the electron and gas temperature.

ALTERNATIVE PLASMA SOURCES FOR ATOMIC SPECTROSCOPY.
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Various plasma sources for atomic spectroscopy operating at atmospheric as well as at reduced pressure are described in literature. Among these, the inductively coupled plasma is the most successful one due to its ability to dissociate even strongly bound molecules and to excite or ionise all elements of the periodic table uniformly. Although designed for liquid analysis even solid materials can be directly analysed for instance by use of a laser ablation system. In this lecture some new plasma based approaches for emission and mass spectrometry will be discussed, which differ significantly from conventional ICP arrangements.

Most of the ICP/AES and ICP/MS work described so far in literature is more or less related to conventional torches operated at high forward generator power and high cooling gas flow rates. A novel torch design has been recently developed by KLOSTERMEIER and BUSCHER for inductively coupled plasma atomic emission spectrometry, which allows to operate the plasma discharge at very low gas flow rates of less than 1 L/min in total. [1]. Cooling of the torch is achieved by external cooling. Due to the low flow rates the residence time of the analyte atoms is drastically increased resulting in improved sensitivities, so that it is justified to give this design a new name: SHIP (Static High Intensity ICP). This new torch, which allows also operation at lower generator powers, has now been coupled to an ICP-MS via an ultrasonic nebulizer. The optimisation of power and gas flow rates will be shown and first analytical figures of merit will be discussed.

For ultra-trace analysis of solid samples direct current (DC) and radio frequency (Rf) driven glow discharges are powerful sources for atomic emission (AES) as well as for mass spectrometry. The same set of metallic multi-layer samples has now been investigated by Rf-GD-AES as well as Rf-GD-SFMS. Results from extremely thick (>50 μm) and ultra-thin (atomic) layers [2] will be discussed.

Both approaches, SHIP and GD plasmas, excel by lower gas flow rates and power consumption, which are pre-requisites to reduce the size of the plasma without losing the analytical benefits. Some new trends to miniaturise plasma sources for emission and mass spectrometry will be discussed including first analytical applications.

[1] A. Klostermeier, PhD thesis, University of Muenster, Germany, 2003.

[2] K. Shimizu, R. Payling, H. Habazaki, P. Skeldon, G. E. Thompson, J. Anal. At. Spectrom. 2004, 19, 692 – 695.

DIRECT ATOMIC SPECTROMETRIC ANALYSIS OF METAL OXIDE
SAMPLES BY CONTINUOUS POWDER INTRODUCTION INTO MICROWAVE
INDUCED PLASMA

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A continuous powder sampling microwave induced plasma atomic emission spectrometry (CPI-MIP-AES) procedure for analysis of metal oxide samples has been investigated. A laboratory-made fluidized-bed sample introduction system for the direct plasma spectrochemical analysis of solid samples has been evaluated. Studies were carried out on Al₂O₃ and MgO as model compounds for optimization of the system's parameters, such as the gas flow, power and feed rate. The effect of operating conditions and sample particle size on the analytical performance was evaluated. A study of the effect of the particle size indicated that when the powder particles were less than 63 μ m, detection limits of some volatile impurities were comparable to those obtained with solution nebulization. The matrix effect on vaporization and excitation efficiency of trace elements of different volatility was studied. Test samples of Al₂O₃, La₂O₃, MgO, SnO₂ and ZnO were carried as a dry particle aerosol to the MIP. Calibration was performed using samples of individual metal oxides with a known (certified) content of some trace elements. The limits of detection for CPI-MIP-AES determination of Cd, Cu, Hg, Mg, Pb, Zn were in the range of 0.1-90 ng g⁻¹. The argon plasma did not have a sufficiently high heat transfer capability to ensure complete sample vaporization under continuous sample loading conditions. The addition of activated carbon as a conductive material to the samples for improving the analytical potential of the method used has been investigated and discussed.

The proposed method has been applied to determining of some elements in the lead crystal glass BCR-126A certified reference material. The standard addition technique was used to ensure good accuracy of the results. The results obtained were mostly within the 95% confidence intervals of the certified values, and the precision, expressed as relative standard deviation, was between 4 and 12%.

EVALUATION OF CONTINUOUS HYDRIDE GENERATION MICROWAVE
INDUCED PLASMA ATOMIC EMISSION SPECTROMETRY SYSTEM FOR
SIMULTANEOUS DETERMINATION OF TRACE ELEMENTS IN SOILS
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A method of continuous introduction of volatile hydrides and mercury into an argon microwave induced plasma sustained in a TE101 cavity has been optimized for the simultaneous determination of the trace elements in soils. A conventional gas/liquid separator was used for direct coupling of HG unit with MIP without separation of excess hydrogen. For determination of total element contents, soil samples have been decomposed by heating in a mixture of acids using a pressure bomb. The contents of element extractable fraction were examined after recommended leaching procedures. Matrix interferences in the liquid phase were observed. Interferences from relatively small amounts of Cu and Fe on the generation of the hydrides were minimized by increasing of acid concentration of sample solution, decreasing of NaBH₄ concentration or masking with EDTA. At higher interferent concentrations the analytes could be effectively separated by a reductive preconcentration technique with palladium as a collector. Then palladium should be removed by precipitation with dimethylglyoxime.

The optimum acidity using hydrochloric acid and NaBH₄ concentration for simultaneous generation of hydrides were studied. The method involves an off-line pre-reduction of SeVI to SeIV by HCl. The mutual interferences from the hydride-forming analytes were observed and considered when the analytical procedure has been developed. The effect of the carrier gas flow rate and microwave power on signal intensities was also investigated.

Analytical characteristics include detection limits in the range from 3 to 15 ng ml⁻¹, linearity of three orders of magnitude and signal stability of between 0.8 and 2% under compromise conditions. The proposed method has been applied to determining of some elements in Czech Loam 7004 and Chinese soil GBW-07405 certified reference materials. The standard addition technique was used to ensure good accuracy of the results. The results obtained were typically within the 95% confidence intervals of the certified or reference values, and the precision, expressed as relative standard deviation, was between 3 and 12% depend on the analytical procedure used.

CE–ICP-MS – AN EFFICIENT TOOL FOR THE INVESTIGATION OF
ANTICANCER METALLODRUG ACTION

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In clinical treatment of cancer diseases a significant and constantly increasing role play platinum coordination compounds. Among them, cisplatin and its analogues take unquestionably leading position due to their specific cytotoxic action against certain kinds of malignancies. The fundamental challenge created by the needs of the contemporary chemotherapy is development of new generation drugs, possessing a wider spectrum of action and a lesser toxicity. Biological activity of newly designed and established metallodrugs can be estimated, among other functions, by the characterization of their interactions with plasma transport proteins, e.g., albumin and transferrin. For such investigations, various techniques have been applied, but the necessity for off-line separation of the components of the reaction mixture made the existing analytical methodology rather time-consuming and inefficient. Therefore, techniques with a higher separation ability and minor impact on the original species distribution become of major concern. One of these is capillary electrophoresis (CE) that being hyphenated with inductively coupled plasma (ICP-MS) or electrospray ionization mass spectrometric detection offers great potential in metallodrug investigation.

In this presentation, the hyphenated CE–ICP-MS technique has been proposed for the identification and characterization of free and protein-bound fractions in model systems comprising various platinum group metal complexes and human serum proteins. Recent results on monitoring the kinetics of binding reactions at various metal/protein molar ratios (important for revealing the degree and rate of metallodrug binding), determination of the number of metal atoms attached to the protein molecule, evaluation of the platinum metal complex-protein binding constants (allowing for quantitative estimation of the differences in binding strength for individual complexes and proteins), as well as on the elucidation of structures of the adducts formed, will be presented and critically discussed.

DETERMINATION OF METHYLMERCURY IN TUNA FISH IN THE FRAMEWORK OF
CCQM P-39 INTERCOMPARISON AND INVESTIGATION OF THE LIMITATIONS OF
ETHYLMERCURY AS INTERNAL STANDARD

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Mercury is considered one of the most toxic elements depending on the species it is found in the environment. The main source of human intake of mercury contaminants originates from methylmercury in fish and fishery products. Methylmercury is particularly interesting due to its high toxicity compared to inorganic mercury and its high proportion among organomercury species in the environment.

CCQM-P39 was an activity of the Inorganic Analysis Working Group (IAWG) of CCQM and was organised by the Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) of the European Commission (EC). In CCQM-P39 As, Hg, Pb, Se and Methylmercury in tuna fish muscle were the measurands under investigation. Organomercury was included for the first time in a pilot study in view of its toxicity. We have been participated in the CCQM P39 interlaboratory comparison as invited expert laboratory and our purpose was to demonstrate the measurement capability of our newly developed analytical method.

In our study a hyphenated SPME-GC-pyrolysis-AFS method was applied for the determination of methylmercury in CCQM P39 tuna fish material. Me-Hg was extracted from the samples by sonication in an alkaline mixture of KOH and methanol (3 h, 75°C), then it was derivatised with NaBPh₄ followed by headspace SPME sampling (10 min) and GC-pyrolysis-AFS detection. All steps of the sample preparation were characterised and optimised. The optimised method was validated by applying BCR 464 certified reference material.

According to the literature ethylmercury as an internal standard is often used for the quantification of methylmercury. It is applied as an internal standard because it has not generally been found in marine animal samples, and the analytical attributes of methylmercury and ethylmercury are very similar. On the other hand however, according to our experiment the stability of ethylmercury seemed to be less than of methylmercury under the applied conditions, therefore its use as an internal standard would have led to misquantification of methylmercury. Eventually, in our presented methodology it was rejected to be used as an internal standard.

DETERMINATION OF ^{210}Pb AND ^{210}Po IN LARGE SEDIMENT SAMPLES BY HR-ICP-MS AND RADIOMETRIC METHODS

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Naturally occurring radionuclides which can stem also from technologically enhanced sources, such as phosphate and fertilizer manufacture and use, are important due to their contributions to the natural radiation dose in the environment.

^{210}Pb and its daughter nuclide ^{210}Po (half-lives 22.3y and 138.4d, respectively) are of particular interest because in natural environments such as oceans they, above all ^{210}Po , contribute to the collective exposure by about two orders of magnitude more than anthropogenic radionuclides.

Bulk analysis of ^{210}Pb can be done with gamma spectrometry, however, as ^{210}Pb has a low energy gamma line (46.5 keV, gamma yield 4.25%) there is a need for attenuation correction in the analysis. In addition, and as a consequence of this, there is a sample volume limitation. Beta counting of ^{210}Bi is used to determine ^{210}Pb after an ingrowth period of 30 days, which is necessary for ^{210}Bi to reach equilibrium with ^{210}Pb . Also ^{210}Po can be used for ^{210}Pb determination. After the measurement of polonium, the sample solution has to be stored for at least one year after which the ^{210}Po that has ingrown from the ^{210}Pb present in the sample is measured again.

In the present paper a method with a fast response time for the analysis of ^{210}Pb and ^{210}Po is described. Sediment samples (10g) are leached in acid. Polonium and lead are separated from the solution with Eichrom Pb.Spec resin. ^{210}Po is deposited spontaneously onto silver disc along with a conventional ^{209}Po yield tracer and measured with an alpha spectrometer. As for ^{210}Pb a faster and more accurate analysis method based on the use of a sector field ICP-MS is presented. These results are compared with those obtained by beta counting of ^{210}Bi .

A NEW THIOARSENOSUGAR IDENTIFIED WITH HPLC-ICPMS AS A
SIGNIFICANT COMPOUND IN THE KIDNEY OF
THE CLAM TRIDACNA DERASA
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Arsenosugars are present in marine animals but their origin is usually attributed to their food, namely marine algae. Among marine animals the giant clam *Tridacna derasa* is the champion with respect to arsenic speciation. In the kidney of this species 15 arsenic compounds have been reported [1].

In the present work we investigated a freeze-dried kidney from a cultured *Tridacna derasa* ground to a homogenous powder. The arsenic compounds were extracted with water using ultrasonic agitation for 10 minutes.

Anion-exchange chromatography on a Hamilton PRP-X100 polymer-based column (4.1x 100mm) with an aqueous 20 mM carbonate buffer solution, pH 10.3 at a flow rate of 1.5 ml/min and an Agilent 7500c ICPMS were used for the determination of the arsenic compounds. Under these chromatographic conditions we observed more than 10 signals in the chromatogram of which the last eluted after 60 minutes. Because of a recent report by Schmeisser et al. we speculated that this signal could be a new thioarsenosugar [2]. When the extract was treated with H₂O₂ the signal at 60 minutes disappeared completely and the signal for the known sulfate-arsenosugar increased. When the extract was treated with a saturated aqueous solution of H₂S the signal for the sulfate-arsenosugar disappeared and the signal at 60 minutes increased.

Then a standard solution of a sulfate-thioarsenosugar was prepared by adding an aqueous H₂S solution to our sulfate-arsenosugar standard. When this new standard was spiked to the kidney extract a clear increase of the signal at 60 minutes was observed.

In order to shorten the retention time for this new compound to find a compatible mobile phase for the electrospray MS detection we increased the concentration of methanol in the mobile phase up to 40% (v/v) and reduced the flow rate to 0.4 ml/min. Under the new chromatographic conditions the standard sulfate-thioarsenosugar eluted in 12 minutes.

Electrospray mass spectra of the kidney extract showed a [M+H]⁺ protonated molecular ion at m/z 425 at a retention time of 12 minutes.

All these investigations verify the sulfate-thioarsenosugar as a new arsenic compound in a biological sample.

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ICP-MS WITH COLLISIONAL INTERFACE, ION MIRROR ION OPTICS AND
LOW NOISE QUADRUPOLE
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The Varian ICP-MS instrument is designed to deliver superior sensitivity and very low background count rates. An “interlaced coils” plasma is sampled by a high-brightness Collisional interface. The ions are focused by an efficient “Ion Mirror” ion optics and separated by a low-noise quadrupole. Until now, only a few design concepts of the instrument have been revealed.

The principles of the plasma, interface, ion optics, mass-analyzer and their integration into the instrument will be presented. Some of the properties of the instrument's essential components will be discussed, along with their mutual interaction and the effect on instrument performance, with an emphasis on the control of interferences.

LASER ABLATION PLASMA SPECTROMETRY TECHNIQUES IN DEPTH
PROFILE ANALYSIS: LIMITATIONS AND POSSIBILITIES

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During the several last years the significance of information on spatial distribution of elements in various materials and structures increased. Substantial development in depth profile analysis was enhanced at the end of the eighties of the last century when the methods underwent considerable improvement in terms of depth resolution and accuracy of quantitative determination.

For coatings and layers of thickness between tens of nm and tens μm , the glow discharge optical emission spectrometry (GD-OES), is currently employed for quantitative depth profiling. Laser ablation (LA) combined with ICP-MS or as an emission source for laser-induced breakdown spectroscopy (LIBS) might be useful tool for the depth profile analysis of coatings and layers with thickness in the range from units to tens of micrometers.

However, a depth resolution and a depth profile shape might be deteriorated due to a too large ablation depth per laser shot, a non-uniform radial energy distribution (Gaussian) in the laser beam, and rugosity at the bottom of the crater. Development of the crater shape during ablation, mixing of eventually molten constituents coming from individual layers or substrate, elemental fractionation due to preferential vaporization as well as transport effects associated with a particle size distribution and, finally, fractionation because of particle size-dependent vaporization in the ICP sources for mass spectrometry/atomic emission spectrometry, and some other processes make the laser ablation-based depth-profiling techniques rather qualitative.

Among important parameters influencing the analytical performance of LA-based techniques belong: laser pulse duration, lasing wavelength, radial distribution of energy across the laser beam, beam focusing, fluence, power density, laser shot repetition rate, sample displacement/single spot ablation, crater aspect ratio, ablation cell/transport tubing volume, carrier gas composition and flow rate in ICP spectrometry together with some other ICP-MS/OES operating parameters, conditions for measuring of time-dependent emission signals in LIBS.

LA-based depth profiles (ICP-MS/OES, LIBS) of temperature-resistant (ZrTiN), low-fusing/boiling (Zn) and glaze (SiO₂-based) coatings will be discussed. The influence of laser wavelength, pulse energy, crater diameter and laser shot repetition rate was studied to improve depth resolution and depth profile shape. Comparison with GD-OES and EPMXA was performed for some cases.

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A NEW FILTRATION DEVICE FOR WATER SUITABLE FOR ULTRA TRACE ELEMENTAL ANALYSIS

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There is no general technology to purify water suitable for trace elemental analysis, therefore complementary purification technologies are combined to produce ppt/ppq grade water from drinking grade water. Most of purification systems are put with a final filter at the use point of water to remove particle and bacteria in water.

In this paper, the efficiency of a new point of use purification device is demonstrated. This new final filter adaptable on the water purification system consists of an ion exchange grafted filtration media and a conventional membrane filter. The efficiency was evaluated by spiking typical cationic contaminants into water purification system. Quality of water produced by the system equipped with this filter was also verified by its blank equivalent concentration of each element on trace analysis by ICP-MS.

Most elements were significantly better removed by this purification device than by conventional filter. Some specific elements, such as zinc and iron, which forms stable chemical species other than ion exchangeable forms remain difficult to remove.

The results demonstrate that this device participates to water purification at the point of use, in addition to its original role for particle retention. The filter acts as a security filter to adsorb accidental ionic load or trace leakage from main purification cartridge due to its capacity saturation.

ARSENOSUGARS AND OTHER ARSENIC COMPOUNDS IN LITTORAL ZONE
ALGAE FROM THE ADRIATIC SEA

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Arsenic occurs in seawater mainly as inorganic arsenic, in the trivalent (As(III)) and pentavalent (As(V)) states, in the low ng g^{-1} range [1]. Marine organisms have the capability to accumulate arsenic originating from the seawater up to some $\mu\text{g g}^{-1}$ concentrations and transform it into less toxic or non-toxic organic compounds [2]. However there are some organic As compounds, especially arsenosugars, whose toxicity is under investigation. Several papers have been dealing with the arsenic speciation in marine organisms. They have all established that arsenobetaine (AsB) is the major arsenic species found in animal tissues while in plants like algae, the most frequently occurring species are arsenosugars [3, 4].

Ten samples of marine algae collected from Adriatic Sea and two commercially available algae were analysed for arsenic compounds by the means of a high performance liquid chromatography (anion and cation exchange) – UV photochemical digestion – hydride generation – atomic fluorescence spectrometry (HPLC-(UV)-HGAFS). The total arsenic content of the alga samples were determined by ICP-MS. Algae contained from 1.43 to 12.06 $\mu\text{g g}^{-1}$ fresh weight of total arsenic. In all algae but two the most abundant arsenic species found were arsenosugars with minor amounts of other arsenic compounds. Two algae investigated contained high amounts of mainly inorganic arsenic.

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AIRBORNE PARTICLES BY ITV-ICP-AES (IN-TORCH VAPORIZATION-
INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY)
AND ITV-GC-MS (ITV-GAS CHROMATOGRAPHY-MASS SPECTROMETRY)

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Analysis of particles with sizes below 10 μm (PM₁₀) and in particular with diameters below 2.5 μm (PM_{2.5}) is receiving increased attention due to potential health effects associated with inhalation of such particles. For example, while the human body has removal mechanisms for inhaled particles with sizes above 10 μm , no mechanism exists for removal of particles with smaller diameters. Therefore once inhaled, PM₁₀ and PM_{2.5} particles remain in the lungs, thus posing potential health problems. For analytical purposes, such particles are collected on filters and particles so collected are analyzed typically using gas chromatography-mass spectrometry (e.g., to determine the composition of organic components) and ICP spectrometry (to determine elemental composition). We developed a portable, battery-operated electrostatic particle sampler (EPS) to collect airborne particles on coiled-filaments of an in-torch vaporization (ITV) sample introduction system. For determination of organics, low volatility organic compounds (e.g., pyrene, phenanthrene) we desorbed into a newly developed ITV-GC interface and were subsequently detected using ITV-GC-MS. To determine elemental composition (without acid digestion) on the same sample using in-torch vaporization sample introduction and ICP-atomic emission spectrometry (ICP-AES). Throughout this work, urban dust standard reference material was used. In this presentation, development and characterization of the battery-operated EPS system, of ITV-ICP-AES and of ITV-GC-MS will be described in detail.

ELEMENTAL ANALYSIS OF MICRO- AND NAN-SIZE SAMPLES BY
RHENIUM COIL-FILAMENT IN-TORCH VAPORIZATION (ITV) SAMPLE
INTRODUCTION AND AN AXIALLY-VIEWED ICP-AES SYSTEM

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When using in-torch vaporization (ITV) as a sample introduction system for inductively coupled spectrometry (ICP), a liquid or solid micro- or nano-size sample is deposited into or onto a probe (e.g., a metal-cup, a coiled-filament) that is secured on a metallic or a ceramic support. The support and the sample-carrying probe are inserted into a small volume vaporization chamber that clips-on a typical ICP torch with a ball-joint. A seal is formed at the bottom of the vaporization chamber, thus ensuring formation of a well-defined central channel in the plasma. The sample-carrying probe is connected to an external power supply using cables running through the support. Low electrical power is applied to the sample-carrying probe to dry a sample, (should it be required) higher power is applied to pyrolyze it and, even higher power to vaporize it (max of ~100 Watts). In many respects, ITV can be thought of as a mini electro-thermal vaporization (ETV) device attached to the base of an ICP torch, but without the transport effects, power requirements and carbide formation problems of ETV [1-7]. To further exploit the improvements in detection limits [5, 6], the Re-cup of the ITV system was replaced by a Re coiled-filament and development, characterization and applications of Re coil-filament ITV with an axially-viewed ICP-AES system will be described in detail. As well as, it will be shown that significant advantages accrue when using Re coiled-filaments as sample carrying probes.

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DEVELOPMENT AND CHARACTERIZATION OF BATTERY-OPERATED
MICRO PLASMA DEVICES (MPDs) BY ATOMIC EMISSION SPECTROMETRY
AND MASS SPECTROMETRY

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Although the inductively coupled plasma (ICP) is a workhorse in elemental analysis, ICPs are bulky and heavy and they consume relatively large amounts of gas (e.g., Ar at 10-20 L/min) and power (1-2 kW). Therefore, they are typically anchored to a lab and tethered to a wall socket. Would it not be ideal if gas- and power-consumption were reduced (without sacrificing power density) so that micro-plasmas could be taken out of the lab and into the field?

Among their many advantages, micro-plasmas offer cost savings due to reduced gas- and power-consumption [1]. Due to their small size, they can be made portable, thus they can be used on-site for (near) real-time measurements in the field. Despite their advantages, researchers in plasma spectrochemistry have only recently begun to look seriously at the effect of scaling laws on plasma miniaturization, on fabrication technology, on power consumption and battery-operation and, overall, on micro-plasma characterization for possible inclusion in either bench top size analytical systems or in portable total analysis micro-instruments.

In my laboratory, we have been developing and characterizing battery-operated (e.g., re-chargeable drill-battery) micro plasma devices (MPDs). For sample introduction, we used a mini in-torch vaporization (mini-ITV) sample introduction system. The mini-ITV is a scaled-down version of the ITV sample introduction system originally developed for elemental analysis from micro- and nano-size samples by ICP spectrometry. In this presentation, development and preliminary characterization of (mini) ITV-MPD using atomic emission spectrometry (AES) and mass spectrometry (MS) will be discussed in detail.

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CHERNOBYL PLUTONIUM AND AMERICIUM IN EASTERN EUROPE:
SOURCE AND TRANSPORT STUDIES BY SECTOR ICPMS
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The 1986 Chernobyl accident released about 10¹⁴ Bq of ²³⁹+²⁴⁰Pu; this material was dispersed regionally in the form of large diameter (> 1 μm) fuel particle aerosols. Pu atom ratios are useful in “fingerprinting” studies, which attempt to distinguish between Chernobyl Pu and other sources such as global fallout. Compared to global fallout, Chernobyl Pu exhibits higher abundances of the heavier isotopes ²⁴⁰Pu, ²⁴¹Pu, and ²⁴²Pu. In addition to resolving Chernobyl Pu from global fallout Pu by analysis of the isotopic composition, the analysis of large numbers of samples will be required to better understand the distribution and behavior of Chernobyl actinides in the environment. It is attractive to use mass spectrometry in these studies; ICPMS is arguably the best-suited for large-scale survey applications.

We use sector ICPMS in three specific studies of Pu sources and distribution in eastern Europe. ²⁴⁰Pu/²³⁹Pu and ²⁴¹Pu/²³⁹Pu atom ratios in soils and peat samples from Poland demonstrate substantial Chernobyl influence in northeast Poland, while Pu from several locations in southern Poland is consistent with global fallout. A second study has determined Pu atom ratios in Black Sea sediments from the Danube Delta. The Danube drains portions of Eastern Europe that received substantial deposition from the Chernobyl accident. ²⁴⁰Pu/²³⁹Pu atom ratios in a sediment core from the Danube Delta indicate global fallout compositions in the 1955-1985 time frame; however, several post-1985 horizons exhibit Chernobyl signatures, with ²⁴⁰Pu/²³⁹Pu ratios exceeding the characteristic global fallout signature of 0.180 ± 0.014. A third study has analyzed a suite of soils from Ukraine and Belarus, in the immediate vicinity of the Chernobyl site. Pu atom ratios of these samples indicate that the Chernobyl releases were of non-uniform isotope composition; a range of 0.27 < ²⁴⁰Pu/²³⁹Pu < 0.47 was determined, with corresponding ranges for ²⁴¹Pu/²³⁹Pu and ²⁴²Pu/²³⁹Pu. We interpret this finding as an indication that individual samples contain different mixtures of isotopically heterogeneous “hot particles”, most likely originating from different portions of the reactor core that had different irradiation histories. Therefore, the Chernobyl accident does not have one specific Pu fingerprint but rather a range of fingerprints.

We have also characterized ²⁴¹Am/²⁴³Am atom ratios in selected Chernobyl-vicinity samples. Samples are fused with potassium pyrosulfate, and Am is isolated using a sequential three-column extraction chromatography procedure (TEVA, UTEVA, TRU in series). ²⁴¹Am/²⁴³Am is determined with a RSD of ~ 5% using medium resolution (R = 3000-4000) to eliminate PbCl⁺ isobars. The ²⁴¹Am/²⁴³Am atom ratios are found to range from 35-45, and these data are used to estimate core inventories and releases of ²⁴³Am.

DETERMINATION OF $^{239+240}\text{Pu}$ ACTIVITIES AND Pu ATOM RATIOS IN
SOILS AND SEDIMENTS USING SECTOR ICPMS AND A RAPID FUSION
TOTAL DISSOLUTION PROCEDURE

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Plutonium (Pu) in the environment is mainly derived from “global fallout” which was rather uniformly deposited worldwide from the stratosphere as a result of atmospheric weapons testing. Global fallout Pu is characterized by $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in the range 0.180 ± 0.014 , and it is generally recognized that this Pu is easily recovered by simple leaching processes with HNO_3 and/or HCl . However, some samples contain “refractory” Pu of non-global fallout origin; refractory Pu consists of insoluble, high-temperature fused Pu oxide particles, or particles produced during surface tests that contain Pu directly incorporated into silica matrices. In North America, the presence of refractory particles has been demonstrated in the vicinity of the Rocky Flats former weapons site (Colorado, USA) and in the vicinity of the Nevada Test Site. In studies of Pu in the environment near these sites, a rapid method is needed for effective total dissolution of refractory Pu-containing samples.

We have developed a procedure for total dissolution of samples up to 10 grams and complete separation and analysis of Pu by sector ICPMS in as little as 4-5 hours. Dried, pulverized sample is spiked with 0.007 Bq ^{242}Pu and fused for 30 minutes with KOH (2.5 times sample mass). Fusions are conducted in inexpensive, disposable borosilicate glass containers; counter to intuition, the containers survive the procedure very well. The sample flux is dissolved in 4 M aqueous HNO_3 ; NaNO_2 is added to adjust Pu to Pu(IV), and Pu is isolated with TEVA resin. A column rinse procedure produces Pu fractions effectively decontaminated of Th, U, and PbCl^+ . The Pu recovery in each sample is measured using a double-spike approach with ^{236}U added at the completion of the column elution sequence. Samples are characterized by mass spectral scans and electrostatic sector scanning peak-jump integrations; ICPMS throughput is 5-7 samples per hour. This procedure is applied to determinations of Pu activities and $^{240}\text{Pu}/^{239}\text{Pu}$ in standard reference materials and environmental samples from the western USA.

NICKEL SPECIES ANALYSIS OF HUMAN COLONIC TISSUE USING LIQUID CHROMATOGRAPHY, GEL-ELECTROPHORESIS AND MASS-SPECTROMETRY

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Cancer of the large intestine is one of the major sites of human malignant disease. Genetic and environmental factors play a major role in the occurrence of each abnormality and in the rate of progression from one step of carcinogenesis to the next. It is known, that Nickel as a cancerogenic compound can have adverse effects e.g. cancer development. The daily uptake of nickel via diet is more than triple of the daily supply and the quantity of nickel absorbed by the gastrointestinal tract depends on the nickel species in the food, the total nickel content in food, and the individual capacity for absorption. The binding partners of nickel in tissues of the gut and colon and the role of nickel in carcinogenesis of colonic cancer are practically unknown.

In previous studies of 11 cytosols of tissues from the human colon, two main nickel species were detected by CE-ICP-MS. Now, our aim is to isolate and to characterize these nickel species, which are probably low molecular weight proteins, by combination of chromatographic, spectrometric and biochemical methods (SEC, ICP-MS, ESI-MS and SDS-PAGE).

Besides the human tissue, a human colonic cell line (HT29/B6) for pre-concentration of the nickel species was used. A cell line was chosen, because it has similar biological properties like the cells in human tissue, and can easily be grown in cultural flasks. Another advantage is the lower matrix of the cells compared with the cytosol of human tissues. The cells were incubated with a nickel standard solution and after incubation the cytosol and the corresponding culture medium (RPMI 1640) were analysed for the desired nickel-species.

To separate the species from the matrix and also for pre-concentration, we focused on size-exclusion chromatography as the first dimension and directly tried to detect the species with RP-HPLC coupled to ESI-MS for determination of the molecular mass and with RP-HPLC coupled to ICP-MS to see, if the species contains nickel. For comparison, this method was applied to the HT29/B6-cytosol and the corresponding culture medium and also to freshly prepared cytosol from human colonic tissue.

of the culture medium and the corresponding HT29/B6 cells by SEC showed that there must be nickel containing species in low molecular mass range, but after pre-concentration we could not detect any protein by organic mass spectrometry.

Size-exclusion chromatography of the cytosol from human colonic tissue also showed, that the nickel-species possess a relatively low molecular mass (about 10 kDa). The SEC-fractions were analysed by ICP-MS and nickel containing fractions were pooled and pre-concentrated by freeze drying. Following analysis with RP-

HPLC coupled to ESI-MS showed that the pooled-fractions contain a protein with a molecular mass of 16 kDa. Under identical chromatographic conditions, but with an element specific detection (ESI-MS), it can also be shown, that this protein also contains nickel.

Additionally, the pre-concentrated nickel-containing fractions were analysed by gel-electrophoresis (SDS-PAGE) to see, if proteins, especially in the lower molecular mass range could be detected.

Another approach to get more information about the nickel-species, is to analyze the crude cytosol by two-dimensional gel-electrophoresis and evaporate protein spots by laser-ablation-ICP-MS to determine the elemental distribution.

After that, nickel containing spots can be cut out of the gel for further analysis (e.g. enzymatic digestion and organic mass spectrometry).

FACTORS TO BE CONSIDERED IN THE PREPARATION OF CERTIFIED
REFERENCE MATERIALS, AND THE REPORTING OF CERTIFIED VALUES,
FOR ICPMS ANALYSIS.

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The detection limits for ICPMS instruments are at part per billion and part per trillion levels. At these extremely low levels, the standards (reference materials) used for the calibration of these instruments have analyte working levels at low ppm and ppb levels. Slight changes in the analyte and trace impurity concentrations at these concentrations can give rise to errors in calibration and therefore errors in the analytical results. Further, reference material stability issues are greatly amplified at these very low levels.

Regardless of the skill of the analyst and the performance of the instrument, the quality of a result can be no better than the quality of the standard used for the analysis. The presentation covers various factors that one must take into consideration in the preparation of the calibration standards, the manufacturing environment, and the statistical analysis of the uncertainty of the certified values.

FRACTIONATION OF PRIMARY AEROSOLS PRODUCED BY NEAR-
INFRARED FEMTOSECOND LASER ABLATION OF SILICATE GLASSES

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The quantification of laser-produced aerosols by inductively-coupled plasma mass spectrometry (ICP-MS) is being considered as one of the most versatile methods for the analysis of solid material due to its conceptual simplicity and outstanding flexibility. During recent years, the methodical progress of LA-ICP-MS has been dominated by the continuous improvement of instrumental performance characteristics such as sensitivity, interference suppression (usage of hexapole-type collision cells), or acquisition speed (TOF-coupling). However, LA-ICP spectrometry is still far from being completely accepted as a quantitative method as a result of the persistent deficiency of adequate reference materials and the resultant, matrix-dependent fractionation effects during analysis [1, 2]. In fact, the examination of these effects represents a crucial issue due to its inherent complexity involving laser-, transport-, and ICP, i.e. plasma-induced phenomena. Among these, the investigations of laser-induced fractionation is of primary interest since it determines both transport- and plasma-induced phenomena. The present contribution reports on laser-induced fractionation of dielectric aerosols produced by near-IR femtosecond LA. According to investigations previously published [3] the aerosols were classified using low-pressure impaction of particles covering a size range from about 10 nm up to 10 μm . After classification the collected material was element-selectively analysed by total reflection X-ray spectrometry (TXRF). In order to specify conditions advantageous for the suppression of laser-induced fractionation, analyses were performed for varying fluences, ranging from threshold-close values of 1 up to 20 J/cm².

It has been found, that for medium fluences above 5 J/cm² the Ca-, Zn-, Cd-, Pb-, and Ba-selective composition of these aerosols corresponds to that of the bulk material even though the size-dependent particle composition strongly departed. Typical deviations were of the order of 5 %. In contrast, fluences below 5 J/cm² usually resulted in stronger differences from the bulk composition indicating intensified fractionation during the ablation process. Our results moreover indicate, that the major part of the aerosol mass is generally located within the mesoscopic particle size range, i.e. from 20 up to 100 nm, independent on the fluence applied. However, the relative percentage of micrometer particles (> 0.5 μm) has been found to slightly decrease for fluences beyond 1 J/cm².

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LC-ICP-MS AND LC-ESI-MS FOR THE CHARACTERIZATION OF
METALLOPROTEINS IN INTERDISCIPLINARY BIOINORGANIC STUDIES

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Since their discovery, metal-binding proteins have been the focus of research in biology and medicine because of their various functions in connection with transport, storage and detoxification of both essential and toxic trace elements in different organisms. They play a crucial role in a number of key metabolic processes. One third of all enzymes are metalloproteins. The metals either fulfill structural functions or are essential for the catalytic process. So far ineffective methods of protein purification and insensitive metal analysis impeded progress in molecular metal protein biology. The presented study is an example for modern bio-metal science as emerging interdisciplinary research. This field uniquely integrates molecular protein biology and analytical sciences with emphasis of identification of metalloproteins as well as their function in biological systems. Our study addresses the complementary use of LC-ICP-MS and LC-ESI-MS for characterization of biotechnologically produced copper proteins. SEC-ICP-MS and IC-ICP-MS (ICP-SFMS, Element1, Thermo Finnigan, DRC II, PerkinElmer SCIEX, Concord, ON, Bremen, Germany; ICP-DRC-MS, ELAN Canada) were successfully employed for accurate quantification of metal to sulphur ratios in the investigated metalloproteins representing the degree of metal integration in the investigated proteins. The molecular weight of the intact metalloproteins could be obtained by ESI-MS (LC/MSD TOF, Agilent Technologies) after careful optimization. The analytical figures of merit of both elemental and molecular detection methods will be presented. Moreover the use of isotopically enriched proteins in tracer studies employing ICP-MS and ESI-MS will be illustrated.

ANALYSIS OF OXIDE LAYERS BY GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY USING AN ARGON HYDROGEN MIXTURE AS PLASMA GAS

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The formation of oxide layers on metallic surfaces in air mainly depends on temperature and time. In some cases, e.g. stainless steels or chromium, oxide layers are important for colour, brilliance and corrosion resistance of the surface. For the analysis of such layers with depth profiling methods, the sputtering rate plays a special role. In most cases the sputtering rate of an oxide layer is very low compared with the underlying metal or alloy. The difference in sputtering rate can lead to some undesirable effects like poor depth resolution due to the preferential sputtering of uncovered metal. If the instrument is opened to air before sample introduction and the sample itself gets no special cleaning treatment before the analysis starts residuals like water can pollute the plasma. Most glow discharge analytical systems do not have very clean sources or pretreatment routines. Consequently results for oxygen concentration are in doubt in many cases of glow discharge measurements, especially when layers in the nanometer scale are concerned.

When oxidised surfaces, namely those of Cr and Cu, are analysed using pure argon, the hydrogen signal varies greatly with time, and the varying amount of hydrogen affects the intensities of other spectral lines. It has been shown that the use of argon hydrogen mixtures in analytical plasmas can give improved results under certain conditions. The use of these mixtures for the analysis of oxidised surfaces, namely those of chromium and copper, is presented here. Both elements are well known for the formation of oxide layers in the nanometer scale. Results derived with pure argon and with argon hydrogen (2% v/v) demonstrate the problems mentioned above. There are some evident advantages with the use of hydrogen containing plasma for this application.

PARALLEL ICP-MS AND EI-MS DETECTION AFTER GC SEPARATION AS
AN UNIQUE TOOL FOR SPECIATION OF ORGANOMETAL(LOID)S IN
BIOLOGICAL SAMPLES

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When facing the task of speciation two main questions have to be answered by the analytical method: Which species are present and how much of it can be detected ? significant attention is often paid to the precise and accurate quantification and assurance of the amount of an analyte in complex samples. This is unquestionably perfectly justified, however it is indispensable to invest similar same effort into identification of unknown species and undoubted verification of target analytes. We present a hyphenated technique which combines the qualitative advantages of highly selective and molecule specific detection by EI-MS with the quantitative benefits in sensitivity and linearity characteristic for ICP-MS techniques. In particular, for the investigation of organometal(loid) compounds, which is restricted by a very limited availability of standards, EI-MS capabilities of providing information about the molecular structure in addition to the sensitive, elementspecific signal of ICP-MS detection is extremely helpful. ICP-MS also allows element specific calibration which is useful if species specific calibration is not realisable due to multitude of species, instability or non-availability of standards.

Combined with the high resolution power and automatisation potential of modern capillary GC the benefits of this technique are demonstrated with several applications in different biological systems.

Protein extracts, headspace gases from microbial cultures as well as human body samples (blood, urine, faeces) were investigated with the main focus on organometal(loid) species of mercury, arsenic and bismuth. Results of gas sampling measurements with and without previous derivatisation are reported. Ethylation is presented as a well suited derivatisation technique for the investigation of methylated bismuth species even in blood and urine.

In conclusion, it can be stated that the introduced technique of parallel EI-MS and ICP-MS detection after cGC provides excellent opportunities for the investigation of biotransformation of organometal(oid) species.

HIGH-PRECISION IN-SITU SULPHUR ISOTOPE MEASUREMENTS BY
LASER ABLATION MC ICP-MS

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In-situ isotopic analysis of sulphur can provide useful information on a number of geological processes, including the formation of economically important sulphide and sulphate ore deposits. Conventional in-situ methods of sulphur isotopic analysis suffer from relatively low spatial resolution and extensive sample handling (low sample throughput). Here we report results of laser ablation multiple-collector (MC) ICP-MS technique for the analysis of sulphur isotopes in sulphide (IAEA-S3), sulphate (SRM-127) and sulphur (Soufre de Lacq SRM) reference materials. We ablated rectangular shaped volumes of material (ca. 300 x 60 x 2 μm) by rastering the UV laser beam (either 266 or 213 nm) on the sample surface in a He atmosphere to generate aerosol that was subsequently analyzed by MC ICP-MS. Two different methods were used to deal with oxygen- and nitrogen-based polyatomic interferences on masses 32, 33 and 34 that are commonly generated in the ICP. Resolving the interferences at high mass resolution ($M/\Delta M=4000$) using the Thermo Finnigan Neptune, and attenuation of interfering molecules in the hexapole collision cell of the GV Isoprobe MC ICP-MS produced results of comparable precision that was typically better than 0.2 permil $\delta^{34}\text{S}$ (2 sigma).

Measurements of $^{37}\text{Cl}/^{35}\text{Cl}$ and $^{30}\text{Si}/^{29}\text{Si}$ isotopic ratios in a standard solution that was analyzed simultaneously with the aerosol from the ablated sample were used to correct the measured sulfur isotopic ratios for instrumental mass bias. However, deviations of several per mil from the true value of sulfur isotopic composition were still observed for the three studied samples. A sample–standard (matrix-matched) bracketing technique can be used to improve the accuracy of mass bias correction to ~ 0.3 permil (2 sigma). Alternatively, a more robust mass bias correction of sulfur isotopic measurements can be achieved by applying both the internal ($^{30}\text{Si}/^{29}\text{Si}$ tracer) and external (matrix-matched standard) corrections. In addition, when Si rather than Cl is used in the tracer, the solution can be introduced to the ICP through a desolvating nebuliser, which reduces the formation of SH^+ which might also interfere with the analyzed isotopes. However, significant variations in accuracy of sulfur isotopic measurements were also found when applying an external correction against samples with different matrices, suggesting that non-matrix matched external correction for instrumental mass bias does not produce accurate results. With further improvements in spatial resolution and analysis at low concentrations the technique is expected to show significant improvements over conventional techniques of sulphur isotopic analysis.

DIRECT INTRODUCTION OF ORGANIC MODIFIERS TO ICPMS:
ENHANCEMENT OF DETECTION LIMIT FOR SELENIUM IN AQUEOUS
SOLUTIONS

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The effect of signal enhancement of elements having ionisation potentials in the range from 9 to 11 eV by carbon-containing compounds is a well-known phenomenon in inductively coupled plasma mass spectrometry [1]. It has traditionally been exploited through the addition of organic solvents to the sample matrix or to the mobile phase to improve sensitivity. In the present work, an organic solvent was not added to the sample matrix, but was directly pumped into the spray chamber through a capillary inserted in an additional hole in the end-cap of the double pass spray chamber. Through this capillary, different aqueous solutions of volatile carbon compounds such as acetone, methanol and acetic acid (supplementary solutions) were introduced using a peristaltic pump. It is presumed that no aerosol is produced from the supplementary solutions and only vapours of organic compounds are swept into the plasma together with the sample aerosol. Among the tested elements (beryllium, arsenic, selenium, rubidium, cadmium, mercury and lead), the highest signal enhancement factors, in the range from 3 to 4, were obtained for arsenic and selenium. The usefulness of this approach was demonstrated through achievement of lower instrument detection limits for selenium at m/z 82 (0.1 ng/mL) compared to the standard configuration. The method was applied for the determination of traces of selenium in natural waters. The described modification of the sample introduction system also has great potential in HPLC-ICPMS analysis, since it eliminates the need to add the organic modifier to the mobile phase, which could change the chromatographic behaviour of the analytes and could contribute to a contamination from the mobile phase.

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EFFECT OF DIFFERENT CHEMICALS ON THE SIGNAL OF DIFFERENT
ELEMENTS USING ICP-MS INSTRUMENT

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In our laboratory for analysis of elements of different samples (plant, soil, food raw material and food, feed, organic fertiliser, irrigation- and soil-water, sewage, sewage sludge) there are a Perkin-Elmer (Aanalyst 300) flame atomic absorption spectrometer (FAAS), a Unicam (939 QZ) graphite furnace atomic absorption spectrometer (GF-AAS), a Perkin-Elmer inductively coupled plasma optical emission spectrometer (ICP-OES) and a Thermo Elemental inductively coupled plasma mass spectrometer (ICP-MS). In the latest time many researchers want to analyse smaller and smaller concentrations of elements. From the above elements the inductively coupled plasma mass spectrometer capables of analysing the smallest concentration of elements. The ICP-MS instrument has Collision Cell Technology (CCT) also. The CCT method has better detection limits with 1-3 magnitudes comparing to the normal ICP-MS analytical method.

Analysing the above types of samples a new interfering effect emerged, namely the effect of various matrixes having different evaporation and nebulization effectiveness, moreover having different quantity of carbon content.

In our research work an X7 type (Thermo Elemental, Winsford, UK) ICP-MS equipment was used to analyse the effects of different chemicals containing various carbon content as matrix.

The effect of different type of chemicals was applied, furthermore the effect of various quantity of carbon content. As the ICP-MS instrument is capable to analyse in the way of multielemental analytical method so 16 various elements applying different isotopes (Cr, Co, Ni, Cu, Zn, Ge, As, Se, Mo, Cd, Sn, Sb, Te, Hg, Pb, Bi) were tested. In our research work we determined the long of time period after analysis of a high effectiveness matrix when the effect is stopped. We experienced that the effect of carbon content is depending on the measured concentration of different elements (Cr, Co, Ni, Cu, Zn, Ge, As, Se, Mo, Cd, Sn, Sb, Te, Hg, Pb, Bi).

Finally we tried to improve or advise a method which can eliminate the effect of the above interference (more or less), so we can decrease the extent of error in the analysis of the above elements (maily selenium and arsenic).

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IDENTIFICATION OF VOLATILE ORGANOTIN COMPOUNDS IN LANDFILL GAS BY GC-ICP-MS

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Volatile organotin compounds in landfill gas are trace compounds within a complex matrix containing CH₄, CO₂ and H₂O as major parts and hydrocarbons, chlorinated hydrocarbons or siloxanes as minor parts [1]. Organotins can be formed in the environment under anaerobic conditions but they were also used as herbicides and PVC-stabilizers. More than 10 different volatile organotin compounds could be found in landfill gas but have not been identified yet [2].

Due to the complexity of the landfill gas and the low concentrations of organotins a powerful detection system is needed. As GC-MS suffers from higher detection limits and problems with this gas matrix, a GC-ICP-MS coupling was used: It combines the good separation capabilities of capillary GC with the low detection limits of ICP-MS. Sampling of landfill gas was carried out by means of Tedlar® bags as they are easy to use and suitable for analysis of volatile organometal(loid)s [3]. By using ICP-MS as detector, no molecular information is gained. Therefore identification of volatile organotins was carried out by comparing retention times of landfill gas samples with gas standards. Organotin standards were produced by Propylation and Ethylation of aqueous solutions of organotin salts followed by pentane extraction. Gaseous standards were made by injection of these pentane extracts into 1L Tedlar® bags filled with Nitrogen. However, retention time shifts between sample and gas standard can occur because of the totally different composition of the gases and their separation behaviour on a GC column. Therefore both gases, standard and sample, were mixed in one bag and unknown peaks could be identified by this standard addition method.

Using this procedure we were able to identify 5 volatile organotin compounds in landfill gas: Tetramethyltin, Ethyltrimethyltin, Diethyldimethyltin, Triethylmethyltin and Tetraethyltin .

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DETERMINATION OF PROTEIN PHOSPHORYLATION DEGREE WITH LC-ICP-MS AND LA-ICP-MS: A COMPARISON

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Due to their outstanding role in cell regulation and signalling, phosphoproteins are in the focus of biomedical and microbiological research. Modified and unmodified forms of the same protein often differ significantly with respect to their function and localisation. Therefore, site and degree of phosphorylation are both of interest in the molecular characterisation of phosphoproteins. Usually protein phosphorylation analysis is focussed on determination of the modified sites and is performed by ESI- or MALDI-MS on the level of proteolytic peptides. However, the results of this approach do not allow reliable extrapolation to the phosphorylation degree of the intact protein, since complete sequence coverage is not guaranteed. Moreover, comparison of intensity ratios is often biased by unequal ionisation efficiencies of phosphopeptides and their unmodified counterparts.

HR-ICP-MS in combination with chromatographic or gel-based electrophoretic separation is an ideal tool to overcome these limitations, because ICP signal intensities are not sequence-dependent. Sulfur is incorporated in essentially all proteins, opening the possibility to use the ^{32}S or the ^{34}S signal as a measure for the protein amount, whereas the phosphoprotein amount is monitored by the ^{31}P signal [1]. In order to calculate the molar phosphorylation degree, the protein amino acid sequence and the respective sensitivities for P- and S-detection with ICP-MS have to be taken into account. The latter vary for different sample introduction systems or different solvents and thus have to be determined for each method individually.

There are two separation principles which are used routinely for protein separation, namely liquid chromatography and gel electrophoresis. Reversed phase capillary LC and size exclusion chromatography can both be coupled on-line to ICP-MS. In case of gel electrophoresis, proteins were separated by 1-dimensional SDS-PAGE, blotted onto a PVDF membrane and the blot was scanned by laser ablation ICP-MS [2].

The aim of this study was to evaluate different ICP-MS-based approaches for determination of the protein phosphorylation degree with respect to their sensitivity and reliability. We will show that correct P/S-ratios can be determined with either of the methods, direct LC-coupling and laser ablation from PVDF-blot. Differences with respect to detection limits, accuracy and purification efficiency will be outlined, and a comparison concerning advantages and limitations of the methods will be presented. In conclusion, the presented combinations of ICP-MS with different microseparation techniques allow an independent and flexible access to the phosphorylation degree of isolated proteins.

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SAMPLING AND DETERMINATION OF CHROMIUM(VI) AS WELL AS OF
OTHER METALS IN AIR SURROUNDING OF A FOUNDRY

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Special aspects of direct emission of a foundry and immission to very closed living areas are studied. Apart of the determination of more ten heavy metals, Cr(VI) speciation was carried out. With respect to toxicity Cr(VI) species are playing an important role. Human studies have clearly established that inhaled Cr(VI) is a human carcinogen, resulting in an increased risk of lung cancer.

Sampling took place on different days during a period of six weeks. The foundry was busy with the activities of welding and founding in two different halls of the foundry. It was guaranteed that normal working activities took place in the foundry during all sampling periods.

From the analytical point of view two approaches were carried out:

For the determination of Cr(VI) sampling took place in special impinger systems by absorbing air particles in a buffer of Na₂CO₃ / NaHCO₃. As analytical challenge an older procedure of selective extraction of Cr(VI) and measurement by graphite furnace atomic absorption spectrometry (GF-AAS) was changed to allow more sensitive determinations of Cr(VI). Wherefore the extraction step was optimised and sensitive measurement by high resolution inductively coupled plasma mass spectrometry (HR-ICPMS) followed. Within this study blanks and recoveries were also controlled.

Several other heavy metals (Al, Ca, Cd, Co, Cr (total), Cu, Fe, Mn, Ni, Pb, Sb, Zn) were sampled on filters. After digestion with aqua regia the elements were measured with quadrupole (Q-) ICPMS.

The obtained analytical data are the basis of an indirect exposure study with respect to people who are living in the next surrounding of the foundry and not with respect to direct exposure study of workers in the foundry

DUTCH STUDY ABOUT “DUPLICATE 24 h - DIET” IN 2004 – ANALYTICAL
STUDY ABOUT METALS IN DAILY FOOD –

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”What is the Dutchman eating? What about metal concentrations in his food?”

In spring 2004, the fifth Dutch study about “duplicate 24 h - diet” was carried out. Around 60 volunteers collected duplicate portions of their food, drinks and drinking water they consumed in a period of 24 h. Participants in this study reflecting the whole “18 to 80 year” old Dutch population. The composition of food and drinks was the quota random check.

Following homogenisation, each duplicate total diet sample was split in several sub-samples. Within this presentation aspects of sample pre-treatment by microwave digestion and the analysis of selected elements are presented. The determined elements are grouped as macro-elements (Na, Ca, Mg, Zn, Fe) and as trace-elements (Mn, Cu, Se, Cr, Pb, As, Cd, Hg). Efficiency processes led to the use of analytical multi-element techniques like inductively coupled plasma mass spectrometry (ICPMS) instead of single elements techniques (e.g. atomic absorption spectrometry / AAS). Nowadays the measurements were performed by sensitive high resolution (HR-) ICPMS. With respect to possible memory-effects only for Hg another technique of atomic fluorescence spectrometry (AFS) was applied.

Various statistical results of the study in spring 2004 are presented. Furthermore interpretations about the results and the trends from nowadays in comparison to former studies (since 1976) are given for several elements.

HUMAN URINARY METABOLITES AFTER INGESTION OF PURE SELENIUM COMPOUNDS

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Selenium is well known for its dual role as toxicant and essential trace element for humans. Since urine is a major excretory route of selenium, urinary selenium metabolites can be used to obtain information about the selenium metabolism in the human body. During the past 35 years there have been several reports of different selenium compounds identified in urine. In 2002 Kobayashi and coworkers¹ succeeded in identifying methyl-2-acetamido-2-deoxy-1-seleno- β -D-galactopyranoside (selenosugar **1**) as a significant urinary metabolite for rats administered selenite. Gammelgaard and coworkers² showed that this selenosugar was also a significant urinary metabolite when humans were administered selenized yeast. Two other selenosugars were subsequently identified by the same research group as trace urinary selenium metabolites in humans.³

The present study reports the urinary excretion of selenium compounds after ingestion of defined quantities (1.0 mg Se) of selenium compounds. Two pure selenium compounds, sodium selenite and L-selenomethionine, and a mixture of DL-selenomethionine were ingested by a male human volunteer in three separate experiments. In all three experiments, selenium was rapidly excreted with maximum concentrations occurring in the first urine sample collected 6 hours after ingestion. Selenium concentrations had essentially returned to baseline levels within 48 hours, by which time about 25 - 40% of the ingested selenium had been excreted in the urine. Selenosugar **1** was the major metabolite in all cases accounting for about 90% (selenite or L-selenomethionine) and 70% (DL-selenomethionine) of the sum of selenium species in the urine sample. Two unknown selenium compounds were also present in the urine samples as minor metabolites. Selenomethionine was present at trace concentrations after ingestion of selenite and L-selenomethionine, but it was a significant species (*ca* 20% of sum of excreted selenium species) after the ingestion of DL-selenomethionine, probably as a consequence of poor human metabolism of the D enantiomer.

These results show that both selenite and L-selenomethionine are quickly and efficiently metabolized to selenosugar **1** in the human body. Presumably, this is a process to quickly remove excess (potentially toxic) selenium.

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NEW INSIGHTS TO PARTICLE FORMATION PROCESSES DURING LASER
ABLATION: VAPOUR CONDENSATION VERSUS DROPLET EJECTION.

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Particle formation processes during laser ablation and the agglomeration state of aerosol particles are of great importance in LA-ICP-MS since large particles cannot be vaporized by the ICP [1]. In literature, two main mechanisms for particle generation are discussed leading to large, spherical particles in the μm range and to condensed particles smaller than 100 nm [2-4]. Furthermore, the ablation pulse length was discussed to significantly influence the particle size distribution in the aerosol [5].

For the present study, aerosol particles were collected on membrane filters and investigated by scanning electron microscopy (SEM). By filtering only few particles, it could be shown that for various matrices, the condensed nano-particles are mainly in a range smaller than 10 nm and that they are transported as agglomerates, which are up to several μm in size. However, the shape of the agglomerates is significantly different for various matrices such as glass, fluorite or brass.

Results presented at the conference will point out the influence of the ablation wavelength (266 nm / 193 nm) and sample absorptivity on the particle formation process. Furthermore, strategies to enhance the fraction of condensed particles, leading to a more complete ionisation of the aerosols in the ICP, will be presented.

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INVESTIGATION OF ANALYTICAL CAPABILITY IMPROVEMENT OF ARGON STABILIZED DC ARC BY CURRENT SQUARE MODULATION

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Important characteristic of argon stabilized d.c. arcs is the radial inhomogeneity of spectral emission. Spectral line intensity maxima of elements with different ionization energies are located at different radial positions from the arc plasma axis. The intensity maxima of the low ionization energy elements are located close to the plasma periphery, while those of the higher ionization energy are located close to the plasma core. It was shown¹ that radial electric field (induced by ambipolar diffusion) hinders the analyte to enter the hotter plasma zone, close to the arc axis. The influence of repulsive electrostatic force on the partially ionized analyte produces partial demixing of initially homogeneous aerosol mixture. Inefficient aerosol sample introduction into the central zone of d.c. arc discharge is the main reason of insufficient analytical benefit from the hottest plasma zone in the analyte excitation process.

Radial electric field decreases with decrease of arc current and with increase of easily ionized element concentration (EIE) in the plasma². For the arc current of 3 amperes and for potassium chloride concentration of 2% in nebulized solution, potential barrier for analyte penetration is significantly decreased, but under these conditions, the temperature of plasma core is rather small, about 3000K. At higher arc current the arc temperature is higher, however the analyte concentration becomes smaller.

The aim of this paper is to overcome demixing effect by combining the high analyte concentration at the arc axis for low current with the high temperature of the arc operating at high current. To achieve this, we tested square wave modulation of the arc current in conjunction with time resolved intensity measurements. Namely, a sudden increase (at microsecond scale) of the arc current results in fast temperature increase and simultaneously in rather slow decrease (at millisecond scale) of analyte concentration due to diffusion. After sudden current jump, in time interval in which analyte concentration decreases to the value that corresponds to higher arc current, emission intensity higher than in stationary state may be expected. Jump from low to high arc current, in the presence of EIE gives larger intensity jump due to increased analyte concentration in the arc column during the low current period.

Current of U-shaped, argon stabilized d.c. arc with aerosol supply was square modulated between 3 and 9 amperes. Modulation frequency of 10 to 50 Hz, with variable ratio of low to high current interval, was applied. Temporal evolutions of analyte spectral emission were obtained by measuring anode current of the photomultiplier tube, which was amplified 50 times with a wide band d.c. amplifier and acquired by a digital storage oscilloscope managed by a PC computer. Measured temporal evolutions of spectral line intensities for elements with low ionization energy confirm assumption that, in comparison to the stationary values, higher intensities may be obtained, especially in the region closer to the arc axis.

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POSSIBILITY OF THE VIRTUAL STANDARDS APPLICATION IN ATOMIC-EMISSION SPECTRAL ANALYSIS

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Atomic-emission spectral analysis is used for checking the chemical composition material in industry at production aircraft, machine-building, railway technology and others. At present on machine-building enterprise in Russia development of the considered methods analysis is executed in the following directions. Using more making receiver spectral radiation, allowing raise validity executed analysis. Use the more stable sources of the reception spectrum, allowing raise the metrological features an analysis. The Development of the processing result measurements methods, capable to perfect such factors, as efficiency and economy.

In work is considered development of the methods of the using virtual standard, as facilities of the measurement, when undertaking analysis material in machine building. The Known approach to making the virtual facilities of the measurement electric parameter by National Instruments Corp. [1]. In Russia known developments making the new class of the facilities of the measurement, which are a virtual standards [2].

Information presentation parameter real standard is understood Under virtual standard. For this is designed physical model, taking into account condition of the undertaking the measurements for standard and under investigation sample [3]. They Are Carried in consideration parameters insulated systems, reflecting change the conditions of the undertaking the measurements. When undertaking analysis material it is enough to define the condition of the undertaking the experiment and use the information presentation standard sample, keeping in memories of controlling computer.

The Results of the work are received on modernized spectrometer with use CCD detector to registrations spectrum from "Slavna" company [4]. The Designed methods of the recognition spectral line analysed element, reducing instrumental error of the radiation intensities measurement.

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DETERMINATION OF Cr(VI) IN COMPOST BY ION CHROMATOGRAPHY-
ICP-MS: TROUBLES AND SOLUTIONS

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Composting is an efficient way of urban solid residues management, which recovers the organic fraction of the waste to produce an useful product. Composts are widely used in agriculture as soil amendments, improving the physical properties of soils and providing plant nutrients. However, composts from urban solid residues can contain high levels of heavy metals, restricting its agricultural uses. In order to guarantee the quality of this end-product, different quality standards have been developed in the European Union, USA, Canada, Australia and New Zealand. These standards pay attention to several physical parameters, the presence of pathogens and the content of nutrients and heavy metals.

Chromium is included in almost all regulations about compost standards, with maximum levels of total chromium ranging from 50 mg kg⁻¹ in Netherlands up to 1000 mg kg⁻¹ in New Zealand. In spite of Cr(VI) compounds are known to be toxic and carcinogenic for a variety of organisms, only Italian and Greek regulations include this chromium species.

In order to know the Cr(VI) content of compost, as well as the fraction of chromium that can be mobilised from compost as Cr(VI) in function of pH, a method based on anion exchange chromatography with ICP-MS detection has been developed. Total Cr(VI) is determined after alkaline extraction of the compost following the EPA3060A method, whereas mobile Cr(VI) is determined after leaching of compost samples at different pH's. Extracts are injected in an IONPAC AS-7 column and eluted with ammonium sulphate. In addition to Cr(VI), chromium species bound to organic matter are also detected.

The high organic content of the samples (30-50%), as well as the carbonate content of the EPA3060A extractant, contributes to the carbon polyatomic interferences on ⁵²Cr and ⁵³Cr. A significant contribution from chlorine polyatomics on ⁵³Cr is also observed. These problems caused by the presence of carbon in inorganic and organic forms and chloride have been circumvented by optimising the chromatographic separation, as well as by mathematical corrections.

Attainable detection limits of the hyphenated method are in the range of 0.5 ng ml⁻¹, although they can be improved by proper selection of chromatographic and ICP-MS data acquisition parameters. A critical evaluation on the selection of such parameters (injection volume, flow rate, dwell time, points per peak) will be presented.

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MODIFIED PRESSED POWDER SAMPLE PREPARATION FOR LASER
ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has become an extremely useful technique for low level analysis of solid samples. One of the main advantages associated with LA-ICP-MS is the simplicity of sample preparation as many samples can be directly ablated or need relatively little preparation. As solid samples have inherent calibration problems associated with matrix matched standards, pressed powders provide the analyst with the ability to add an internal standard or use an isotope dilution method for the quantification of trace elements.

A problem commonly encountered in the direct analysis of solid samples is low ablation efficiency. Meaning larger fragments entering the plasma leading to incomplete ionisation, causing a reduced sensitivity and stability. By the use of pressed powder discs the addition of chromophores can improve the ablation characteristics associated with certain samples.

This work involves a simple sample preparation method concerning pressed powder discs, suitable for analysis by LA-ICP-MS. The influence of varying pressing methods, support materials, chromophores and internal standard addition have been investigated.

IMPROVING THE PERFORMANCE OF ICP-MS FOR DIFFICULT MATRICES

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As ICP-MS is a 'flow into' technique, rather than a 'flow by' technique such as ICP-AES, problems are therefore commonly encountered with environmental and geological samples. High levels of dissolved solids are typically present in such samples, and due to this, a severe effect on the signal may be seen caused by deposition around and within the cone orifices. There are a number of different approaches which can be undertaken to overcome these difficulties. These approaches include altering the sample introduction technique to prepare the sample aerosol in the most efficient form. Optimisation for robust plasma conditions is extremely important to process the samples, and effective design of the cones is essential to promote performance consistency and resistance to blockage. If the sample still causes measurement difficulties after instrumental alterations then the separation of the analyte of interest from the matrix is also a possibility.

A description is given of the study of instrumental and chemical approaches to remove the problems associated with high levels of dissolved solids in liquid digests, such as those encountered when determining gold in alumina/silica matrices.

ELEMENTAL MAPPINGS IN MATERIAL SCIENCES - FROM IMAGES TO
QUANTITATIVE INFORMATION BY LA-ICP-SF-MS

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In order to discuss the significance of trace element heterogeneity for corrosion processes, it is very important to recognize both the topology of their distribution as well as their concentration gradients within a given material. One method of choice to determine the lateral distribution of elements is to perform electron probe micro analysis (EPMA) with a qualitative mapping procedure. However, this technique is often limited to the detection of main elements, because of the low detection potential for trace elements. As a complementary technique, laser ablation inductively coupled sector field plasma mass spectrometry (LA-ICP-SF-MS) offers high spatial resolution as well as quantitative analysis of trace elements in solid samples.

In this study, a magnesium-based alloy sample was analyzed over an area of 350 x 350 μm^2 by LA-ICP-MS with a lateral resolution of 32 μm and limits of detection in the lower mg kg⁻¹ range for Ti, Cr, Mn, Fe, Co, Ni, and Cu. To establish a quantification procedure to generate 2D-concentration profiles was hereby of particular interest. Therefore, a sum normalization calibration procedure was carried out and the results for the main elements Mg, Al, and Zn were compared to EPMA measurements at the same sample area. The agreement for Mg was 2.2 % between the two techniques. The influence of the laser parameters, like repetition rate and laser spot size were studied and the conditions of the ICP-MS were optimized for single spot analysis to achieve high lateral resolution capabilities.

It will be demonstrated that the combination of two surface analytical techniques, EPMA and LA-ICP-MS, can be successfully applied to fully characterize the lateral quantitative distribution of main- and trace elements in the micrometer range of magnesium-based alloy samples. Remaining limitations of both techniques in the practical spatial resolution achievable and the quantification procedure will be given and alternative strategies will be presented.

COUPLING OF LIQUID CHROMATOGRAPHY (LC) TO A 90 DEGREE ION
OPTICS ICP-MS (LC-ICP-MS)

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Toxicity, mobility and bioavailability can vary greatly between various forms of an element and hence merely reporting the total concentrations can often be misleading. Arsenic is one such example, with toxicity and mobility varying between the various forms. Arsenic exists in a variety of forms with the trivalent form (As III) being the most toxic, followed by the pentavalent form (As V). Other common forms of arsenic include monomethyl arsenic (MMA), dimethyl arsenic (DMA) and arsenobetaine (AsB) which have significantly reduced toxicities. Consequently it is necessary to quantify the individual forms of an element for an accurate assessment of their impact.

The coupling of LC to ICP-MS provides the benefits of efficient separation and detection of the various forms.

Results will be presented from the coupling of an LC with an ICP-MS comprising of;

- revolutionary 90-degree reflecting ion optics configuration;
- minimized spatial and energy aberrations ensuring sensitivity is maintained across the mass range;
- a low noise double offset quadrupole mass analyser;

This system will be shown to produce both high sensitivity and selectivity for superior detection of toxic and non-toxic elemental species/compounds.

SPECIATION OF CANCEROSTATIC PLATINUM COMPOUNDS IN HOSPITAL
WASTEWATER FOR DEVELOPMENT OF ELIMINATION PROCEDURES

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Many cytostatic agents used in cancer therapy have potentially cytotoxic, mutagenic and teratogenic properties. One important and widely used group of cytostatic agents are cancerostatic platinum compounds (CPC), such as cisplatin, carboplatin and oxaliplatin. Hospital effluents are regarded as the major source of CPC in the environment, since platinum compounds are generally administered in in-patient treatment wards. With the excretions of patients under medical treatment significant amounts of the drugs are spread into the environment. Although chemical and toxicological properties as well as the antitumor activity of the platinum-based anti-neoplastics are closely linked to their chemical form, the metabolism and occurrence of the substances in urine, wastewater and sewage treatment plants has not been studied in detail yet.

In the present study wastewater from the oncologic ward of the Vienna University Hospital (VUH) was collected over a time period of two month and analysed for cisplatin, carboplatin and oxaliplatin using ICP-MS. As the selective collection and treatment of the highly loaded sewage stream from the oncologic in-patient treatment ward could minimise the CPC concentrations in the environment, a pilot plant membrane bioreactor system was installed at the VUH and operated with sewage from the oncologic ward. Over a time period of one month the influent, effluent and sewage sludge of the pilot plant were analysed for CPC using ICP-MS. This procedure allows a basic assessment of the elimination of CPC from the water phase during biological wastewater treatment. As the chemical form of the CPC plays a decisive role concerning their elimination capacity, the influent and the effluent of the pilot plant were specified by coupling HPLC to ICP-MS.

As it could be observed that the membrane pilot plant did not eliminate the CPC to a satisfying degree, adsorption experiments with activated carbon were conducted and measured using on-line ICP-MS detection.

THE USE OF ICP-HIGH RESOLUTION-MS, AS PART OF A MULTI-TECHNIQUE 'METABOLOMIC' APPROACH, TO INVESTIGATE FOOD PRODUCTION-RELATED PHENOMENA.

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Advances in ICP-MS technology have allowed scientists access to many elements that were traditionally deemed 'out-of-bounds' for conventional quadrupole-MS instrumentation. Whether through the use of collision/reaction cell technology or Sector-Field-MS, many elements (including several physiologically important ones, e.g., P, K, S) have become more readily accessible for measurement by ICP-MS. This development has provided the researcher with an opportunity to delve into areas, such as proteomics and metabolomics, not necessarily associated with the use of this technique. When this capability is combined with other, complimentary, techniques, e.g., nmr, LC-MS, MALDI-TOF-MS and SELDI-TOF-MS, the potential breadth of information that can be achieved is quite breathtaking. This talk will investigate the potential of this 'multi-technique' approach, and present data from a number of successful/not-so-successful examples.

Mad Cow disease has been a very high profile issue within Europe, yet the mechanism of its onset is still not completely understood. Although several 'element-specific' theories (Cu, Mn and Zn interactions) have been expounded, none have led to either a greater understanding of the disease or to the identification of a robust biomarker of its onset. Therefore, in the work presented here, the multi-element capability of ICP-HR-MS has been used, in conjunction with nmr, to verify previous findings and to attempt to identify a suitable biomarker of the onset of the disease. Multivariate data from blood samples of over 350 infected and control animals will be presented, and compared to existing literature-based assumptions.

Multivariate data from 2 other projects will also be presented:

§ Identification and development of a bio-indicator capable of establishing if mozzarella cheese has been fraudulently produced using bovine milk rather than that from buffaloes.

§ An investigation into the possibility of establishing a methodological approach to discern the method of egg production (caged or non-caged) and also to explain the phenomenon of eggshell thinning in non-caged eggs.

EFFECT OF TEMPERATURE AND PRECIPITATION RATE ON THE ISOTOPIC
COMPOSITION OF LITHIUM IN MARINE CARBONATE

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The continental crust represents the main source of Li in the ocean water. It has been demonstrated that significant fractionation towards the heavy Li isotopic composition in the riverine input to the ocean takes place during the rock weathering on the continents (Huh et al. 1998). However, additional fractionation of Li isotopes must take place in the ocean to account for the heavy Li isotopic composition of the sea water. Based on laboratory precipitation of inorganic carbonate (Marriott et al. 2004), it has been proposed that ^6Li is preferentially incorporated in the calcite, shifting the isotopic composition of the sea water towards higher $^7\text{Li}/^6\text{Li}$ values. This observation seems to contradict the observation that carbonate shells of recent planktonic foraminifera have a Li isotopic composition which corresponds to that of the modern sea water (Kosler et al. 2001). Alternatively, vital or temperature effects or variable rate of carbonate precipitation might also affect the isotopic composition of Li in the carbonate and potentially compensate for the isotopic shift observed during the calcite precipitation experiments.

We will report results of MC ICP-MS measurements of Li isotopic composition of carbonate grown at variable temperatures and precipitation rates to evaluate the processes that may lead to the isotopic fractionation of Li in sea water. Ultimately, this will help us to evaluate whether Li isotopic composition in the sea water could be used as a proxy for mechanisms of continental weathering.

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SIMULTANEOUS PHOSPHOR, SULPHUR AND METAL ION SPECIATION IN
PROTEINS USING HPLC / SECTOR FIELD ICP-MS

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Phosphor, sulphur and metal containing biomolecules play an important role in proteomics and biochemistry. Carbon, oxygen and nitrogen based interferences (NO⁺, NOH⁺, COH⁺, H₃CO⁺, O₂⁺) are the principal limitation in phosphorus and sulphur detection by ICP-MS, metal ions suffer Argon and matrix based interferences. Using sector field ICP-MS, phosphorus and sulphur are completely resolved from these interferences even in 100 % acetonitrile by their small difference in mass. Interferences formed by the constituent elements of different mobile phases will always be separated from the phosphorus, sulphur or metal ion analytes. Therefore, gradients consisting of different solvents can be used.

The magnet technology of the Finnigan ELEMENT2 incorporates a high power magnet field regulator enabling rapid mass scanning subsequently allowing simultaneous determination of different elemental species in one chromatogram. In order to show the potential of sector field ICP-MS for the simultaneous speciation of Phosphor, Sulphur and metal ions in biomolecules, mixtures of deoxyribonucleotides (dAMP, dTMP, dGMP, dCMP) and of proteins have been separated by HPLC with simultaneous on-line detection using the sector field ICP-MS Finnigan ELEMENT2.

PLASMA SOURCE TECHNIQUES: FROM SPECIATION ANALYSIS TO METALLOMICS

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The interest in speciation analysis has been shifting from the determination of anthropogenic metal species and products of their environmental degradation to endogenous and biosynthesized metal compounds. The extreme complexity of the biological matrix, the trace concentrations present and the non-availability of calibration standards have been powerful limiting factors in the acquisition of speciation-relevant information in these areas. The lecture discusses the evolution of the analytical techniques based on plasma source detection in chromatography from GC - MIP AES to nanoLC-ICP MS to reflect the changing objectives of speciation analysis [1,2]. The ultimate challenge to speciation analysis is providing information necessary for the understanding of the mechanisms of the response of an organism to a metal stress and of the biosynthesis of a metal binding ligands.

Recent developments in analytical techniques capable of providing information on the identity and quantity of heteroatom-containing biomolecules are discussed. The impressive progress toward lower detection limits in ICP MS, higher resolution in separation techniques, and higher sensitivity in electrospray MS for molecule-specific detection at trace levels in complex matrices allows new frontiers to be crossed. This applies in particular to the identification and/or structural characterization of endogenous species of essential, beneficial and toxic elements and to metabolism studies of metal probes in biology and medicine.

Particular attention is paid to the emerging areas of bioinorganic analysis including: (i) a comprehensive analysis of the entirety of metal and metalloid species within a cell or tissue type (metalloomics), (ii) the study of the part of the metalloome involving the protein ligands (metalloproteomics), and (iii) the use of a heteroelement, naturally present in a protein or introduced in a tag added by means of derivatisation, for the spotting and quantification of proteins (heteroatom-tagged proteomics).

ICP MS, used as detector in chromatography and electrophoresis, and supported by electrospray and MALDI MS, appears as the linchpin analytical technique for these emerging areas. This review focuses on the recent advances in ICP MS in biological speciation analysis including sensitive detection of non-metals, couplings to capillary and nanoflow HPLC and capillary electrophoresis, laser ablation ICP MS detection of proteins in gel electrophoresis, and isotope dilution quantification of biomolecules.

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INVESTIGATION OF VAPORIZATION PROCESSES FOR ELECTROTHERMAL
VAPORIZATION SAMPLE INTRODUCTION IN INDUCTIVELY COUPLED
PLASMA MASS SPECTROMETRY

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Inductively coupled plasma mass spectrometry (ICP-MS) with electrothermal vaporization (ETV) sample introduction was used to study the processes taking place in a graphite furnace normally used for atomic absorption spectrometry. Monitoring of carbon release during the pyrolysis stage provided information on the solid-state reduction processes. It was found that gallium and arsenic oxides practically do not reduce during the pyrolysis stage. According to the data on carbon release, two reduction processes of lead species (at 555-780 °C and 910 - > 1000 °C) take place in the furnace. Two separate peaks of lead (in the end of the pyrolysis stage and at the vaporization stage) were probably formed by unreduced lead oxide and elemental lead, respectively. A pre-reduced palladium modifier suppresses the low-temperature lead losses, whereas the high-temperature lead peak is increased. In the absence of a modifier, a gaussian-shape arsenic signal was formed only if small arsenic masses were introduced into the vaporizer. Increase in the arsenic mass resulted in formation of a pronounced plateau after the peak, in spite of very high vaporization temperature applied (2500 °C). In the presence of pre-reduced palladium modifier, a gaussian-shape arsenic signal was already formed at 1700 °C, with a 4-15-fold increase in sensitivity depending on the analyte mass. The palladium modifier apparently prevents strong interaction of arsenic with graphite. The data obtained prove very high potential of ETV-ICP-MS in detailed investigations of processes occurring in graphite furnaces used in analytical atomic spectroscopy, especially during the pyrolysis stage.

ION PAIRING-REVERSED PHASE CHROMATOGRAPHY COUPLED TO
SECTOR FIELD ICP-MS (IP-RPC-ICP-SFMS) FOR THE DETERMINATION OF
METAL-BOUND PHYTOCHELATINES (ME-PC) IN *SILENE VULGARIS*
EXTRACTS

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Phytochelatins (PCs) are small metal binding peptides characterised -Glu-Cys)_n-Gly for n=2-11. They are enzymatically by the general structure (synthesised in plant cytosol due to the presence of heavy metal ions that induce the reaction (Cd²⁺, Pb²⁺, Zn²⁺...)). Once complexed, the heavy metal ions are stored in the vacuole so that they represent no longer a danger for the plant and the PCs are separated in their constituting amino acids. The formation and the function of PCs and their complexes have been widely studied, but frequently using non-metal specific methods. Up to now many authors have often employed acid mobile phases in the chromatographic separation, even if they cause the dissociation of almost all the Me-PC complexes, and the peptides have been detected via a non-specific detector, other have derivatised the Me-PC complexes and most of them have detected separately and off-line the -SH and the metal content.

In this work we optimised an ion-pairing reversed phase chromatography (IP-RPC) separation on algae extracts containing Cd-PC, employing non acidic buffer solution in order to actually elute the complexes and detect the related Cd and S signal. The high sensitivity of the ICP-MS coupled to the high performance of the developed chromatographic separation allowed us to analyse also complex matrix samples in order to detect the presence of Me-PC complexes, where Men⁺ could be Cd²⁺ as well as other toxic or essential heavy metals.

With this aim, plants of *Silene Vulgaris* were cultivated under stress of high concentrated heavy metal solutions. Stipes, leaves, flowers and roots have been collected from the plants at different times, softly digested and analysed. The complex matrix and the low concentration of the many different trace elements of interest have nevertheless been no obstacle to the on-line detection and identification of the Me-PC complexes. A structural analysis through a soft-ionisation mass spectrometry, such as an ESI-MS, would give in future the confirmation of the peaks identity and probably the indication on how Cd and other heavy metals are actually bounded to the peptide.

FRACTIONATION OF IODINE IN IODINE-ENRICHED ALGAE CHLORELLA
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Iodine as an essential element has a great importance in human and animal health. Concerning animal husbandry, feed fortified by iodine provides adequate supply of this element and influences the health of animals and the quality of production. The bioavailability of iodine depends on the form of iodine. This work deals with determination of iodine forms in iodine-enriched algae *Chlorella*, which is cultivated in Institute of Microbiology (Czech Academy of Science) and consecutively applied in in-vivo experiments at University of Veterinary and Pharmaceutical Sciences. Fractionation protocol including sequential extraction by chloroform, water and sodium dodecylsulphate solution was designed. Inductively coupled plasma optical emission spectrometry was employed for determination of iodine in fractions solubilized with TMAH. Iodides were quantified in aqueous extract using vapour-generation ICP-OES after separation of iodides on anion exchange resin. Fractionation gives information on the content of iodine in non-polar, protein, polar water-soluble and non-soluble organic fractions and iodides. Methodology was applied in analysis of twelve algae samples that were cultivated with different cultivating conditions (hetero- or autotrophic). Results of this research are used in optimization of cultivation conditions to get desired composition of iodine-enriched *Chlorella*.

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VAPOUR GENERATION – INDUCTIVELY COUPLED PLASMA OPTICAL
EMISSION SPECTROMETRY IN DETERMINATION OF FREE AND TOTAL
SULPHUR DIOXIDE IN WINE

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Sulphur dioxide is used as a preservative and stabilizer in wine production preventing must and final product from undesired biochemical processes. Concentration of sulphur dioxide is restricted by national regulations. There are two main forms of sulphur dioxide in wine: free (inorganic forms) and bound (fixed to organic compounds like aldehydes). Iodometric titration method is commonly employed for determination of SO₂ concentration (either by direct titration or using pre-separation by distillation) or other alternative techniques are used. In this work inductively coupled plasma - optical emission spectrometry with vapour generator was applied for determination of free and total SO₂ in wine. Gaseous SO₂ is released from the sample by means of addition of acid and swept into the ICP by argon stream. Intensity of sulphur atomic emission lines is measured in vacuum UV region. For determination of total SO₂ hydrolysis of bound forms by sodium hydroxide precedes. Concentrations of acid for vapour generation and sodium hydroxide for hydrolysis were optimised. Methodology was applied for determination of free and total SO₂ in red and white wine samples and results were compared to those of iodometric titration.

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MECHANISM AND EFFICIENCY OF CHEMICAL VAPOUR GENERATION OF SILVER

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Chemical vapour generation (CVG) of transition and noble metals using the same acid/ BH₄⁻ system as hydride generation is gaining attention as a sample introduction technique for atomic spectroscopy. Successful volatilization of as many as 15 elements other than traditional hydride forming elements was reported; the most frequently studied ones besides Cd are Ag, Au, Cu and Ni. Unfortunately this promising technique still has not reached the phase of maturity. The problems include generation efficiency, signal stability and method robustness.

A mechanistic study on CVG of silver with ICP-OES detection is summarized. It is likely that the reaction does not occur in one step as with classical hydrides, but rather in two steps. The generation efficiency is improved by more than an order of magnitude by presence of surfactants in the solutions; however, the optimum surfactant concentrations are too low to allow for an explanation of the improvement being due to formation of organized media.

Metallic analyte deposits formed on the generator surfaces formed in the course of the CVG process were causing positive sensitivity drifts and long sensitivity stabilization times. A deliberate permanent modification of the surface of a

continuous flow / flow injection systems by reduced noble metals was therefore tested. Single introduction of the modifier to the CVG system is sufficient to achieve permanent stabilization of sensitivity and to avoid long conditioning periods following cleaning. A possible mechanism responsible for improvement is discussed—the modifier catalyzes the reaction of analyte with borane complexes formed in the later

phases of the NaBH₄ decomposition process in the reaction mixture, which is beneficial for metal volatile compound formation and/or its release from solution.

In contrast to classical hydrides, volatile species can be completely trapped on a Teflon filter. Based on the Ag retained on the filters, an overall sampling efficiency higher than 20 % was determined. Additionally, the volatile species can be trapped by simple impact on surface at room temperature. Our data suggest that volatilized analyte is still transferred as part of the condensed phase transported by

gas flow rather than a truly gaseous compound; a hypothesis of the actual volatile species as metal nanoparticles, supported by preliminary electron microscopy experiments, will be discussed.

Nearly forty fold better efficiency of Ag transport to the plasma by CVG was observed compared to use of a cross flow nebulizer.

ANALYSIS OF SIZE DISTRIBUTION OF OXIDES IN STEEL BY OPTICAL EMISSION SPECTROSCOPY

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The particle size distribution and the amount of oxides in steel affect product qualities such as formability, weldability and resistance to fatigue. Conventionally, the optical microscopy method, the electron beam melting method and the laser diffraction method after chemical extraction are used for the measurements of size distribution of oxides. However, a rapid analytical method has been required because measuring with such methods takes a lot of time. Spark-discharge optical emission spectroscopy (OES) is widely used in steel-making analysis because of its high sensitivity and rapidness. And the anomalous emission of the oxide-forming element is observed in OES when the discharge occurs at the oxides. We have developed a new rapid analytical method of oxides in steel by using anomalous emission.

A Shimadzu PDA5017 with a horizontal emission stand was used. The laser diffraction method after dissolving the specimen in acid solution was used as a reference method.

- 1) For each discharge, the anomalous emission was defined when both the value of the intensity ratio of Al to Fe and that of O to Fe were bigger than the median of both of them respectively. One anomalous emission was found to correspond to one particle of oxide when the size of the oxide particle is larger than 1 micron in diameter.
- 2) The size distribution of aluminum oxide particles was calculated by transforming the Al/Fe to the amount of aluminum oxide for each anomalous discharge. The size distribution obtained by the developed method was in good agreement with that obtained by the laser diffraction method for low alloy steels in spite of the difference in sample amount.
- 3) The maximum particle size was estimated by using extreme values statistics. The estimated maximum particle size obtained by the developed method was in good agreement with that obtained by the laser diffraction method.

HELIUM COLLISION MODE – THE ULTIMATE SOLUTION FOR COMPLEX, UNKNOWN SAMPLE MATRICES

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The rapid acceptance of collision and reaction cell technology in conventional quadrupole ICP-MS instrumentation is due to the improvement in the measurement of interfered elements, which previously proved difficult to analyse at the required levels in complex sample matrices.

The elements affected can be divided into 2 groups, those that suffer from plasma-based interferences and those that suffer from matrix-based interferences. This is because plasma-derived interferences are relatively constant and easy to predict, with one, high intensity interferant typically being the main target. Matrix-derived interferences, on the other hand, may be complex (several interfering species occurring at the same analyte mass), unpredictable and can vary by several orders of magnitude between ostensibly similar samples.

While research laboratories may have the opportunity to evaluate each sample type individually, to identify the most critical matrix-based interferences, this approach is not practical in the routine laboratory. Routine labs require a matrix-independent interference removal technique, that can be applied to as many interfered elements as possible, in order to make maximum advantage of the collision/reaction cell.

Operating the cell in collision only mode, using pure He as the collision gas has been found to be a reliable and widely applicable way to remove matrix-based interferences. The use of an inert gas - pure He - means that no new interferences are formed as a result of reaction with sample matrix or analyte, and no matrix-dependant loss of analyte or internal standard (by reaction) can occur. The interference removal efficiency of He collision mode is increased by the use of Kinetic Energy Discrimination (KED), which itself is dependant upon precise ion energy control in the interface. This is achieved by the use of a physical shield to isolate the plasma from the RF field generated by the ICP coil.

We have developed and validated consistent collision/reaction cell conditions that are effective at reducing or eliminating all of the plasma- and matrix-based interferences commonly encountered in a typical range of environmental sample matrices including, but not limited to, surface waters, saline waters, soil digests and synthetic Analytical Quality Control (AQC) samples.

The interference removal capability of these consistent cell conditions will be illustrated using spectral scans (as applied to the screening of unknown samples), quantitative recovery data from synthetic, high matrix samples and a simulated, routine environmental sample batch. In addition, isotope selection, internal standard use and the elimination of interference correction equations will be discussed.

Towards High Sensitivity Measurement of Phosphorylated Proteins – Gel Electrophoresis and Flow Injection–Inductively Coupled Plasma–Mass Spectrometry

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Reversible protein phosphorylation is known to play a major role in most signalling pathways and is regulated by protein kinases and protein phosphatases. Mutation, over-expression or malfunctions of these proteins are thought to underlie many human diseases. Molecular mass spectrometry coupled with separation techniques such as polyacrylamide gel electrophoresis (PAGE) or high pressure liquid chromatography (HPLC) have long been established for determining structural information of phosphorylated proteins. In recent years Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) coupled with Laser Ablation (LA) has been developed as a powerful new tool for studying phosphorylated proteins on electrophoresis gels¹⁻³. However the laser ablation method is not particularly sensitive and direct ablation of gels may be problematic due to the presence of phosphate as trace contaminant.⁴ An alternative strategy, showing promise, is to electroelute separated protein bands into fractions which are then amenable to high sensitivity ICP-MS (also molecular analysis via MALDI and ESI methods). A further feature of this approach is the incorporation of an on-line sample clean up stage based on aluminium microcolumn separation. The presentation will outline progress to date with the new methodology.

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Elemental Mapping of Gunshot Residues via LA-ICP-MS

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In gunshot residue (GRS) analysis ‘identifier’ elements include antimony, barium, lead, aluminium, calcium, copper, iron, magnesium, mercury, tin and zinc. As evident in SEM-EDX studies ^{1,2,3} four kinds of particles are considered to be characteristic of firearm discharge, i.e. (i) Pb-Sb-Ba; (ii) Ba-Ca-Si with traces of S; (iii) Ba-Ca-Si with traces of Pb; and (iv) Sb-Ba. Although SEM-EDX is considered to be the benchmark technique for forensic investigation, LA-ICP-MS is potentially very competitive. First, laser probing utilises light rather than charged particles and can analyse both conducting and non-conducting material; also fingerprinting based on both elemental and isotopic data is afforded. Finally, the LA technique gives high sensitivity with good spatial resolution. In this study, we present preliminary mapping data on GSR samples originating from the UK and China.

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Interrogation of laser capture microdissection tissue and microtomed tissue samples by LA-ICP-MS – a comparative study.

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LA-ICP-MS is under development as an alternative strategy to autoradiography for establishing the spatial distribution of candidate metallo-drugs and innate elements in microtomed sections of model species, a distinct advantage of LA-ICP-MS for this application being its multi-element capability.

Organs conventionally considered elementally homogeneous, such as brain or liver contain different functional tissues, sub-structures and blood vessels that prevent even large diameter laser analysis from providing unquestionable bulk concentrations. 2-Dimensional interrogation has the capacity to elucidate representative levels of elements throughout a sample and identify inhomogeneities, thereby permitting assessment and comparison in different tissues and providing more information regarding the phenomena responsible for signals observed. Resolution can be enhanced by reducing beam diameter thereby permitting investigation of small, complex regions of tissue, or sensitivity improved by increasing beam diameter.¹

Laser capture microdissection (LCM)² is capable of removing and transferring small groups of cells directly from tissue to a suitable mounting for presentation to the LA cell, and reduces the requirement for manual sample manipulation necessary to prepare microtomed tissue for laser ablation. Thousands of microdissections can be transferred to a single “stub”, thereby providing rapid means for interrogating many samples with no interruption to the laser ablation process. The process also provides an interesting alternative to variation of laser beam diameter for high resolution interrogation of tissues.

We present performance data for comparative laser ablation studies of microtomed tissues and equivalent LCM samples, with particular emphasis on spatially resolved measurement of Mg, Fe, Cu, and Zn.

¹ R. Hutchinson, A. Cox, C.W. McLeod, D. Green. **Spatially Resolved Measurements of Microtomed Tissue via LA-ICP-MS.** Presented at 2004 Winter Conference, Fort Lauderdale, FL.

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MULTIELEMENT MAPPING OF MICROTOMED TISSUE VIA LASER ABLATION
ICP-MS

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LA-ICP-MS is under development as an alternative strategy to autoradiography for establishing the spatial distribution of candidate metallodrugs in model species. In essence the approach provides a very competitive route for determining the bulk concentration of drug in target organs. In addition there is an opportunity, through repetitive line rastering, to probe and map structures in terms of chemical composition. A particular challenge is to be able to exploit narrow laser beam diameters ($<30\ \mu\text{m}$) to probe structures at the cellular level. The presentation will review progress in the field with special reference to the measurement and mapping of essential trace elements (Mn, Cu, Zn, Mg and Sr), candidate metallodrugs (La and Sr) and anthropogenic elements (Al and Pb) in soft and hard tissue. A complementary approach based on linking laser capture microdissection to laser ablation will also be elaborated.

CHARACTERISATION OF SELENIUM ENRICHED YEAST AS A CANDIDATE CRM

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The bioaccumulation and metabolism of selenium in yeast allows for bioavailable species that are found to act in cancer prevention and prevent deficiency syndromes. The subsequent use of selenized yeast in food supplements for health purposes has urged the NRC to characterize a selenium-enriched yeast as part of its reference materials program. Extractions specific to amino acid analysis and the proteome as a whole have been employed with liquid chromatography (LC) separation protocols for the characterisation of selenium.

The elevated selenium levels in growth media encourage the non-specific incorporation of selenomethionine into the yeast proteome. The extent of the incorporation of selenomethionine in place of methionine has been investigated by several analytical techniques. Isotope dilution ID is a popular technique for quantification of elemental species (e. g. organotin, organomercury) with on-line gas chromatography (GC) or LC protocols, but its application to selenium quantification is less advanced. Species specific ID LC ICP MS with ^{74}Se -enriched selenomethionine allows for the quantification of selenomethionine by LC ICP MS. In addition, quantification by ID MS with LC ES MS yields data for both methionine (^{13}C -enriched methionine) and selenomethionine (^{13}C -enriched selenomethionine).

The identification of selenomethionine containing proteins in yeast by top-down multidimensional LC is investigated. A shotgun approach of protein identification after tryptic digestion of the yeast proteome was employed. The challenge of identifying proteins from selenopeptides with relatively low molecular ion intensities (due to low selenopeptide abundance in the peptide mixture and selenium isotope distribution) will be discussed.

SPECIATION ANALYSIS OF INORGANIC AND ORGANIC TIN USING
BAKER'S YEAST AND INDUCTIVELY COUPLED PLASMA OPTICAL
EMISSION SPECTROMETRY DETERMINATION

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A method for speciation analysis of inorganic and organic tin by combining inductively coupled plasma optical emission spectrometry (ICP-OES) and solid phase extraction using baker's yeast (*Saccharomyces cerevisiae*) is proposed. The procedure is based on selective retention of tributyltin (TBT) by the yeast at pH = 6 while Sn (II) and Sn (IV) remain in solution. Since only the Sn (IV) and the TBT were retained by the yeast at pH = 2, redox speciation can be also included in the analysis when the concentration of TBT has already been determined. Determination of tin in the solid phase was easily carried out by introducing a slurry of the yeast (0.5 g / 40 ml) directly to the ICP-OES. Several factors affecting the retention of the analytes by the yeast, such as pH, amount of biomass, temperature and time of contact were evaluated. Two mixed solutions of tin (Sn (II) / Sn (IV) and TBT / Sn (IV)) were analyzed using analytical curves plotted with 0-80 mg L⁻¹ of single standard solutions. For the mixed solution containing Sn (IV) and TBT, recoveries of 109 ± 1 % for Sn (IV) and 105 ± 1 % for TBT were obtained. For the other one, recoveries of Sn (II) and Sn (IV) were 104 ± 2 and 98 ± 5 %, respectively. The proposed approach was evaluated for speciation analysis of TBT and Sn(IV) in sea water and redox speciation of tin in river water. Results obtained were in good agreement with expected values.

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THE EFFECT OF AR/H₂ MIXTURES AS PLASMA GAS ON DIRECT CURRENT
AND RADIOFREQUENCY GLOW DISCHARGE - MASS SPECTROMETRY.
ANALYSIS OF CONDUCTING AND INSULATING MATERIALS
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The glow discharge (GD) has evolved within the last decade towards a fast, reliable tool for the analysis of bulk materials, coatings and surfaces. The usual characteristics of a GD plasma are drastically varied by several discharge parameters such as voltage, current, power, plasma gas composition, gas pressure, and so on. In particular, the plasma gas plays an important role, both in the sample sputtering rates and in the excitation/ionization of sample atoms. Unlike most other plasma sources, GDs are easily maintained using a wide variety plasma gases. Although argon is usually used as the plasma gas, various plasma gases and their mixtures have been investigated (1).

Nowadays, GD analytical detection is mostly carried out either by optical emission spectrometry (OES) or mass spectrometry (MS). The use of GDs coupled to MS is increasing because of the recognized advantages in terms of sensitivity, spectral simplicity, isotopic information, etc (2). In particular, the use of time of flight (TOF) mass analysers offers particular interest because of the capability to collect complete mass spectra with the same precision, sensitivity and resolution regardless of the total number of isotopes being measured.

In a previous work it has been carried out a preliminary study about the effect of Ar/H₂ mixtures on direct current (dc) GD-TOFMS while keeping constant the electrical current and voltage (3) and some interesting features were observed. In this communication, it will be presented a thorough and comparative study about the effect of these plasma gas mixtures for dc (two operation methods were investigated: a. fixed pressure and voltage, b. fixed voltage and electrical current) and radiofrequency (working at constant pressure and forward power) glow discharges coupled to TOFMS.

Experiments have been carried out both, for homogenous samples (conductors for dc-GD and both, conductors and insulators for rf-GD) and for layered materials. Results show that the sputtering rates generally decrease by the presence of hydrogen in the plasma gas. However, the ionic intensities of certain elements in homogeneous samples and the relative depth profiling resolution of the layered materials can be improved by using Ar/H₂ plasma gas mixtures.

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ANALYSIS OF ARRAYS OF NI NANOWIRES INTO SELF-ALIGNED TITANIA
NANOTUBES BY RADIOFREQUENCY GLOW DISCHARGE–OPTICAL
EMISSION SPECTROMETRY

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The discovery of the self-organized nanostructures formation is attracting a great interest. The finding and fabrication of self-ordered magnetic nanowires based in Fe, Ni, Co, or its alloys, by using nanoporous membranes formed by silica, alumina or carbon self ordered nanoporous arrays as templates, have revealed a wide variety of fascinating properties. Very much effort has been made up to now, to obtain self-ordered nanostructures of TiO₂ membranes prepared by sol-gel coating, nano-imprint, or electrochemical processes due to the higher corrosion and oxidation resistance, low density, high yield strength at low and high temperatures, and excellent biocompatibility exhibited by this oxide semiconductor. All that becomes it in an outstanding candidate for application in wide scientific and technological areas (1).

Glow discharge (GD) spectrometry is established nowadays as an important analytical technique for the direct analysis of solid samples and a powerful tool for the quality control of many materials. Radiofrequency (rf) GDs coupled to optical emission spectrometry (OES) have proven a great capability for the direct analysis of both, conducting and insulator materials (2).

In the present work, arrays of Ni nanowires electrodeposited into self-aligned and randomly disordered titania nanotube arrays grown by an anodization process are investigated by radiofrequency glow discharge optical emission spectroscopy (a JY 5000 rf instrument was used). The titania nanotubes outer diameter is about 160 nm, wall thickness ranging from 60 to 70 nm and 300 nm in depth. The so-obtained Ni nanowires reach about 100 nm diameter and 240 nm length. As can be seen in this communication, the excellent depth resolution of GD-OES is revealed by the good agreement with the average deposited thickness for the particular deposition conditions.

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REMAINING CHALLENGES IN ICP-AES

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A question is more and more often raised : « is it still possible, necessary or beneficial to perform research in atomic emission spectrometry ? » considering that research may include i) search for new physical/chemical processes that can be used for analytical chemistry ; ii) understanding of the processes : diagnostics, mechanisms, modelization, matrix effects ; iii) development of the method : instrumentation, data processing, optimization, applications ; and iv) method validation : analytical performance, uncertainty, linearity of the calibration graph.

Considering that the analyst is a problem solver and needs accurate and precise results, along with low limits of detection and quantitation, some challenges remain in ICP-AES : i) design of a hf generator that can easily accept significant changes in the load, e.g. wet vs dry aerosol, volatile organic solvents, large amounts of foreign gases, or simply change in the matrix nature or concentration in aqueous solutions, without a change in the plasma characteristics such as temperature, electron number density or spatial distribution ; ii) intelligent software for automatic line selection including several to many lines per element, taking into account matrix spectral interferences and relative concentrations ; iii) design of sample introduction system with a trend to total-consumption devices, producing either smaller droplets or directly vapor or volatile species, along with noise reduction ; iv) optimization of axial viewing to minimize matrix effects and to enhance signal-to-background ratio ; v) decrease in the shot noise by improving photon collection so as to minimize detector integration time and to allow time correlation between signals ; vi) study of non-spectral interferences (matrix effects) : origin, minimization and efficient compensation for improving accuracy when matrix matching is not possible ; vii) improvement in limits of detection to fill the missing gap between current ICP-AES systems and quadrupole-based ICP-MS ; viii) availability of solid-state multichannel detectors with fast readout, improved dynamic range and minimization of the pixelation effect ; ix) improvement in data processing to take full benefit of the increase in available information, which implies an efficient use of chemometrics ; efficient semiquantitative analysis, true self-diagnostics and feedback, optimization of the operating parameters and x) and guidelines for method validation with an emphasis on uncertainty.

Elemental analysis is widely used in routine laboratory and will be used for ever as the determination of elements in various matrices will always be a request. The only change will involve more and more elements with lower and lower concentrations, in more and more complex matrices, with a demand for more information such as speciation (bioavailability and toxicity) and structure. As ICP-AES is still a most appropriate technique for elemental analysis with some unique features, the reply to the question mentioned above is clearly yes.

SPECIATION OF SELENIUM IN YEAST
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Since the discovery in 1957 that selenium is an essential trace element for mammals [1], it has been increasingly implicated in a beneficial role for human health. Selenium is an essential trace element, present in several proteins as selenocysteine (SeCys) and selenium availability is directly linked to the regulation of selenoprotein expression [2]. Due to low levels of selenium available in the average human diet [3], it has become increasingly popular to use supplements. Selenium is most often supplemented in the form of SeMet; the major form found naturally occurring in foods and generally thought of as one of the most bioavailable. Selenium-enriched yeast has become the most popular matrix for food supplements as it contains SeMet as the major species and is economically viable. Inorganic selenium in yeast growth media intrudes the sulfur assimilation pathway, ultimately forming SeMet. The SeMet is then believed to be non-specifically incorporated into the protein in the place of Met [4].

A short review will be presented on recent developments in selenium speciation. Special attention will be given to the identification of Se containing proteins and peptides. The state of the art in small molecular selenium species determination will also be discussed. [5] The challenges related to the development of a new selenized yeast CRM will be discussed.

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ARSENIC SPECIATION IN CUCUMBER PLANTS BY HPLC-ICP-MS

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The arsenic contamination of ground water used for irrigation in the south-eastern part of the Great Plain of Hungary has geological origin. Due to the elevated concentration of arsenic in ground water the terrestrial plants cultivated in this region may be contaminated. Therefore, it is necessary to study the uptake and metabolism processes of the arsenic compounds. Cucumbers were grown in modified Hoagland nutrient solutions contaminated with arsenite or arsenate in concentration of 2000 nmol/dm³. In the xylem sap collected from these plants arsenite, arsenate and dimethylarsinic acid were determined by HPLC-ICP-MS. Independently of the arsenic compound added to the nutrient solution, in all cases arsenite was the dominant arsenic compound in the xylem sap. The redox potential formed in the root zone seems to be responsible for the reduction of arsenate to arsenite in case of plants grown in arsenate containing nutrient solutions. Moreover, as biomethylation is not a common feature of the terrestrial higher plants, the microbiological activity of the root zone may cause it. Therefore, the arsenic speciation of the nutrient solutions is also necessary in order to find a possible answer to the similar results obtained for the saps.

CHARGE AND TRANSPORT PROPERTIES OF PARTICLES DURING LASER ABLATION SAMPLING

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The complexity of the physical and chemical processes related to laser ablation of solid samples has so far prevented a detailed understanding of mechanisms that result in decoupling of particular elements during laser ablation ICPMS analysis. Fractionation may occur at the ablation site, during transport of ablated material to the plasma source of ICPMS, and in the plasma itself (by incomplete volatilization of delivered particles). The size distribution of particles produced during laser ablation is thought to exert a significant control on the nature and size of elemental fractionation. Major factors affecting the size distribution of particles reaching the ICP are the fluence, wavelength and pulse duration of laser radiation; the aspect ratio of laser pit; the composition of the sample carrier gas; and the size-dependent transport efficiency of the ablated particle. Particles with diameters below 0.5 μm are transported with high efficiency to the ICP and are thus most completely atomized and ionized in the plasma. Coarse particles ($>1.0 \mu\text{m}$) may be deposited as a thin deposit (ejecta blanket) on the sample surface around the pit, or most effectively trapped in the sample transport system. It has also been demonstrated that chemical and phase compositions of ablated particles vary with their sizes. An outstanding issue is whether laser ablation of different sample matrices produce particles with different charge size distributions and whether such variations have a significant effect on particle transport properties.

Here we report results of series of experiments where, prior its ionization in the ICP source of the mass spectrometer, the aerosol produced by UV laser ablation of silicate samples has been passed through the charge neutralizer. In the neutralizer particle charge size distributions reach fast equilibrium state characterized by Boltzman charge size distribution. The combination of the neutralizer with particle size selector allows to measure differences in the charge of particles of selected size ranges caused by ablation of samples with various matrices. This study contributes to our better understanding of particle properties and it will help to identify the dominant processes producing elemental fractionation during laser ablation ICP-MS analysis.

SPECIATION OF ALUMINIUM IN TEA INFUSIONS BY THE USE OF SEC AND FPLC
CHROMATOGRAPHY WITH ICP-OES AND ES-MS-MS DETECTION

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Study of the distribution of Al species in tea infusions has been performed by size exclusion (SEC) and anion-exchange FPLC with ICP-OES detection. Six black, two green, one red tea and one oolong tea samples were investigated. The total concentration of Al in tea infusions was determined by ICP-OES and ranged between 0.5 to 4 mg kg⁻¹. pH of samples were between 4.9 and 5.1. 1 mL of sample was injected onto SEC column (Superdex 75). Isocratic elution with TRIS-HCl + 0.15 mol L⁻¹ NaCl (pH 5), flow rate 1 mL min⁻¹ was applied for 40 min. Chromatogram was followed by UV detection at 278 nm and separated Al species determined “of line” by ICP-OES in 0.75 mL fractions. Results indicated that 10 to 35% of total Al in tea infusions was eluted at the retention volume corresponding to molecular mass of 6.5 kDa. However, it should be stressed that the synthetic solution of Al-citrate (pH 5) exhibit the same retention volume, indicated poor selectivity of the column for low molecular mass (LMM) species. The remaining Al was adsorbed on the column resin and did not disturb the following determinations. 1 mL aliquots of the same tea infusions were also injected onto anion-exchange FPLC (Mono Q) column using linear gradient elution 0-100% 4 mol L⁻¹ NH₄NO₃ at flow rate 1 mL min⁻¹ for 10 min. 0.5 mL fractions were collected and Al determined by ICP-OES. It was experimentally found that the same percentage of total Al as in SEC column was eluted at the retention volume 3.5 to 4.5 mL that corresponded to the elution time of negatively charged Al-citrate. The remaining Al was adsorbed on the column resin and did not disturb the following determinations. In order to identify Al binding ligand eluted under the chromatographic peak analyses by ES-MS-MS using Z spray ion source were also applied. It was proven that citrate was LMM organic acid that complex Al. On the basis of this investigation it may be concluded that ionic Al species in tea infusions (10-36% of total Al) corresponded to negatively charged Al-citrate. The remaining species that is adsorbed on SEC or FPLC column is probably Al bound to phenolic groups. The percentage of negatively charged Al-citrate was the highest in Golden Nepal black tea (36%), followed by green teas (about 27%), oolong tea (23%) and other black teas (14 – 22%) and was the lowest in red tea (10%).

The transformation of Al species was also studied when drinking tea with milk or lemon. For this purpose 1 mL of milk (0.5% fat, ultra high temperature) or 1 mL of citric acid (0.22 mol L⁻¹, the average concentration of citric acid in lemon juice) were added to 25 mL of tea infusions. Speciation analysis of tea infusions with addition of milk were performed by SEC-ICP-OES. On the basis of the retention volumes it was experimentally proven that Al-citrate in tea infusion was not transformed, while about 60% of total Al was transferred to HMM-Al species. This Al containing fraction was subjected to SDS page electrophoresis. Results indicated that Al was occluded by milk proteins (molecular mass 30-35 kDa). When citric acid was added to tea infusions speciation analysis were performed by FPLC-ICP-OES – ES-MS-MS. Results indicated that the percentage of negatively charged Al-citrate remained either the same or was in some tea infusions enhanced up to 40% of total Al (in general in black teas). Data of the present investigation indicate that the bioavailability of Al in tea infusions is increased when drinking tea with milk and may also be increased when drinking tea with lemon.

DIRECT INJECTION MULTI-GAS INDUCTIVELY COUPLED PLASMA
SOURCE FOR MS AND AES

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Inductively coupled plasma mass spectrometry (ICP-MS) and ICP atomic emission spectrometry (ICP-AES) using argon ICP as an ionization or an excitation source have been widely utilized for trace elemental analysis. In this study, a new direct injection multi-gas ICP source for MS and AES is developed. With the new ICP source, not only Ar but He, O₂, N₂, CO₂, air... plasmas can be stably generated in atmospheric pressure. Furthermore, aqueous solutions can be directly introduced into the plasma using conventional nebulizers. The torch has smaller area gas inlet to generate an adequate vortex flow at the plasma generating region even when helium gas is used. Helium has about nine times higher kinematic viscosity than other gases so the vortex flow of helium easily turn into the laminar flow. The torch has cooling gas flow around usual ICP torch configuration to avoid torch melting. And it has shorter configuration to use conventional nebulizers as direct injection nebulizer. Reported direct injection nebulizers were high-cost and difficult to handle like direct injection nebulizer (DIN) or direct injection high-efficiency nebulizer (DIHEN).

In our prototype direct injection multi-gas ICP[FACSS??], stable plasmas can be generated under low sample flow rate. And the emission profile of argon is easily turned from doughnut shape into the filament shape. To improve these problems, the new torch has a support gas flow around the nebulized solutions. The support gas reduce diffusion of the injected solutions into the plasma. As a result, stable generating conditions of plasmas with direct sample introduction are extended and the emission intensities from the sample are increased.

In this study, the fundamental characteristics of multi-gas plasmas sustained by the new torch are investigated using spectroscopic method and mass spectrometry. The effect of the RF input power and the flow rate of sample, nebulizer gas, support gas and plasma gas on the emission intensities are measured. The fundamental properties of mass spectrometry also investigated.

INITIAL STUDIES ON VANADIUM METABOLISM IN MAMMALIANS BY
MASS SPECTROMETRIC TECHNIQUES

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Certain vanadium species have showed a variety of insulin-mimetic actions such as the increase of glucose transport and oxidation and the stimulation of glycogen synthesis in the liver both, in-vivo and in-vitro. Short clinical studies of 2-4 weeks duration performed at vanadyl or vanadate doses of 33-50 mg per day showed also improved insulin sensitivity. For these reasons, V compounds have been proposed as potential agents in the Diabetes Mellitus Type 2 treatment, where the level of insulin production is insufficient or the correct assimilation of this insulin is not possible. However, the mechanism of V action remains unclear and a lot of work is still necessary to clarify biochemical forms and physiological functions of this element in higher organisms [1].

When V salts are administered orally, they can bind rapidly to different physiological components on their way from the gastrointestinal tract to the intravascular space (blood). In this sense, the present work describes the initial speciation experiments performed in order to study V metabolism in mammals. For this purpose, serum and urine of exposed rats to a daily dose of 40 mg V(IV) is collected and analysed for one and two weeks respectively. Anion-exchange separation by Fast Protein Liquid Chromatography (FPLC) with ICP-MS (Quadrupole and Collision Cell) detection is used for studying vanadium (V (IV)) association to proteins present in serum. Additionally, MALDI-TOF complementary detection is used to characterize the organic moiety associated to V fractions present in human serum. Similarly, Size Exclusion chromatography in conjunction with ICP-MS and ESI-MS is investigated for fractionation and identification of the V species present in rat urine samples after one and two weeks of exposure.

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INCREASING THE QUALITY OF ENVIRONMENTAL MEASUREMENTS: THE
VIRTUAL INSTITUTE FOR REFERENCE MATERIALS (VIRM ASBL).

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The growing importance of analytical measurements in modern society has rendered the development of measures to improve the quality of analytical results and to guarantee their quality to the end users urgent. In all analyses, the analyst has to demonstrate the quality of his work i.e. that the method does not contain sources of errors, and that it leads to reliable and comparable results.

The two milestones for achieving comparability and reliability of results obtained in any field of measurement is the harmonisation of the procedures used and the availability of proper quality control tools for validation and for monitoring long-term method performance.

Reference materials, both certified and not, are one of the most powerful quality control tools allowing the evaluation of the accuracy and reproducibility, and comparability of the data produced worldwide. The use of Certified Reference Materials (CRMs) is, in fact, the easiest way to demonstrate accuracy and to verify the performance of the laboratory at any desired moment (ISO, 1992; 1997). Quality Control Materials (QCMs), which are reference materials not carrying all necessary information about traceability, are suitable for the evaluation of the long-term reproducibility, establishing quality control charts, and also for the evaluation of the comparability of data produced in various laboratories, in intercomparison exercises.

However, there is still a scarce availability of reference materials on the market and scarce information on what and where these materials are available and how they should be used.

The dissemination of information on availability and proper use of Reference Materials (RM) is still a critical issue.

The European Commission has been funding the Project “Virtual Institute on Reference Materials – VIRM”, that started on 1 January 2003 aiming to build an independent and economically self-sustainable institute. Its central mission is to improve the quality control of products and processes by encouraging, catalyzing and facilitating the increased use of reference materials throughout Europe. A Knowledge Network and a facility to encourage the interaction between all stakeholders in the field of Reference Materials is thus being created. The VI-RM shall become the meeting place for the European reference material community, and the major information pool for dissemination, advice and training on reference materials for producers, distributors, (potential) users, service providers and research organizations.

The services of VIRM Asbl are offered through an advanced website, including above all an extensive RM database and a regular e-Newsletter, and via the Secretariat and the technical HelpDesk that is the only physical structure of VIRM Asbl.

CHEMOMETRIC STUDY OF SURFACE WATERS FROM RÍA DE AROUSA
ESTUARY ACCORDING WITH TRACE METALS CONTENT AFTER SOLID
PHASE EXTRACTION ICPOES DETERMINATION

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Surface seawaters from Ría de Arousa estuary were analysed for trace metals (Al, Cd, Cu, Fe, Mn, Ni, Pb, Sn, V and Zn) by inductively coupled plasma optical emission spectrometry, ICPOES, after C18 chemically bonded silica gel solid phase extraction. Surface seawaters were sampled by triplicate at different points (thirtyone sampling stations) along the Ría de Arousa estuary in March 2002. Before solid phase extraction, metal ions in seawater samples (100 ml) were complexed with 5 10⁻⁴ M 8-hydroxyquinoline at a compromise pH of 8.0 ± 0.1. The seawater sample was then passed through cleaned and conditioned C18 cartridges at a fixed flow rate of 6.0 ml min⁻¹ by using a peristaltic pump. The cartridges were then rinsed with 10 ml of 0.01 M ammonium acetate in order to remove the saline matrix, and the adsorbed metalcomplexes were eluted with 2.5 ml of 2.0 M nitric acid at a flow rate of 4.5 ml min⁻¹. A preconcentration factor of 40 was achieved under these operating conditions. Measurements by ICPOES were made under standard plasma conditions (1300 W and 1.5, 0.5 and 0.8 l min⁻¹ for plasma gas flow, auxiliary gas flow and nebulizer gas flow, respectively) and using a GemCone nebulizer cyclonic spray chamber. All determinations were carried out by using the standard addition technique and the recommended wavelengths emission lines.

Trace metals concentrations in seawater were used as discriminating factors to study possible sources of contamination in Ría de Arousa estuary. Principal component analysis, PCA, and cluster analysis, CA, have been used as unsupervised pattern recognition procedures. The half-range central value transformation was used as data pretreatment to homogenise data. The highest concentrations of Cd, Cr and Cu have been observed near the mouth of the Ulla River and in the innerleft part of the estuary. This suggests riverine freshwater inputs as the main source of these metals and agrees with the water circulation in Ría de Arousa estuary, in which marine currents enter in the estuary from the right mouth and go out by the left mouth. In addition, the input marine water flow is higher than the output flow, with the highest residence time in the innerleft part of the estuary. Therefore, contaminants mainly associated with the Ulla River inputs are moved to the innerleft part of the estuary and they remain in this area for the longest times. Other elements, such as Pb and Sn, are present at high concentrations near Arousa Island and this is mainly associated with sport and fishing activities in this area.

Acknowledgements

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THE DETERMINATION OF FIVE ARSENIC SPECIES IN URINE SAMPLES
FROM OCCUPATIONALLY EXPOSED AND UNEXPOSED PERSONS IN THE
UK BY LC-ICP-MS

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The aim of the study was to establish levels of arsenobetaine, trivalent (As³⁺) and pentavalent (As⁵⁺) inorganic arsenic, monomethylarsonate and dimethylarsinate species in urine from exposed and unexposed persons. The effects of smoking and seafood were also investigated.

Using a LC-ICP-MS method for separating the arsenic species, urine samples from 34 control samples, 50 timber treatment workers and 50 semiconductor workers were analysed. The controls supplied a urine sample having eaten no seafood for 72h and another sample 24h after eating seafood.

Unexposed people show no significant levels of inorganic arsenic species in urine. Eating fish does not significantly elevate the levels of DMA or MMA, but does increase arsenobetaine levels. However, this does not affect the determination of occupational exposure. Inorganic arsenic species were prevalent in the timber treatment workers but not the semiconductor workers. The method is validated by successful participation in the G-EQUAS proficiency testing scheme.

A routine method for speciation of arsenic in urine that is robust and reliable has been developed. The use of this LC-ICP-MS method for arsenic speciation in urine allows better interpretation of both high and low arsenic values obtained and thus better assessment of exposure and any risk to health.

COPPER, CHROMIUM AND ARSENIC LEVELS IN URINE SAMPLES FROM
TIMBER TREATMENT WORKERS

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This study reports a survey of occupational exposure to copper, chromium and arsenic (CCA) based wood preservatives during vacuum pressure timber impregnation. The survey involved biological monitoring based on the analysis of copper, chromium and arsenic in urine samples collected from UK workers. The aim of the study was to determine the extent of systemic exposure to these elements in the UK timber treatment industry.

Urine samples were collected from volunteer workers at six monthly intervals for 2 years. In total 748 urine samples from timber treatment workers were analysed for copper, chromium and arsenic. Arsenic in urine was determined using hydride generation coupled with ICP-MS and copper in urine was determined using direct nebulisation ICP-MS. The ICP-MS in both cases was a Perkin Elmer 6100. All chromium in urine was determined using a Perkin Elmer 5100 GF-AAS. Samples from a control population (n=247) were also analysed for copper, chromium and arsenic. Certified reference material (Bio-Rad) was analysed in every analytical run after every ten urine samples for all of the elements and analysis. In addition HSL successfully participates in the TEQAS proficiency testing scheme (University of Surrey, Guildford, UK).

The main findings show that workers exposed to CCA wood preservatives have concentrations of inorganic arsenic and chromium in urine that are significantly higher than those from non-occupationally exposed people but below biological monitoring guidance values. The effects of consumption of seafood on urinary arsenic were not significant using the hydride generation method for inorganic arsenic.

There was a significant increase in the urinary concentration of chromium in workers over the 4 sample collection rounds indicating increasing exposure to chromium during the 2 years of the study. This unexpected finding may be worth further investigation.

Overall, the study demonstrated the utility of biological monitoring for assessment of occupational exposure to copper, chromium and arsenic.

MEASUREMENT OF CELLULAR ASSOCIATION OF NICKEL AND
CHROMIUM IN KERATINOCYTES USING ICP-MS
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Chromium and nickel are elements that are well known causes of contact dermatitis. An investigation was carried out to look at the effect both nickel and chromium on skin cells called keratinocytes. Using isolated human keratinocytes as an in vitro human skin model the effects of nickel and chromium upon both primary and passaged keratinocytes was investigated.

The cells were grown from skin removed during routine operations at a local hospital. Once confluent, a range of concentrations of nickel and chromium (0-10 000 μMol) were added to the cells for 24h. Metal association with keratinocytes was determined by direct nebulisation ICP-MS following washing of the cells and an acid digest. In order to reduce the chloride content of the cells and subsequent interferences the cells were washed in a chloride free buffer to remove the non-associated excess nickel and chromium from the cells. Cell viability measurements, respiratory activity and the release of inflammatory mediators (IL-1a and IL-8) produced by keratinocytes when exposed to nickel and chromium were also measured.

The main findings from this project were that human keratinocytes respond very differently to chromium and nickel in terms of metal uptake, respiratory activity, viability and cytokine reduction. Chromium is much more cytotoxic to both primary and passaged keratinocytes than nickel (by approximately 10 fold). Chromium is highly cytotoxic to keratinocytes and therefore may react directly with the epidermis, promoting local damage and inflammation. As keratinocytes constitutively produce IL-1a intracellularly, the dose dependant increase in IL-1a release observed with chromium may be due to the damaging effect of the metal upon keratinocyte viability.

Nickel is considerably less cytotoxic than chromium and may not directly interfere with keratinocytes. This can be hypothesised as there was no dose-dependent increase in IL-1a after incubation with various concentrations of nickel. As nickel is known to promote sensitisation, nickel haptens may pass through the skin without causing an irritant reaction.

There was also considerable inter-individual variation in keratinocyte responses to chromium and nickel in terms of respiratory activity, viability, metal uptake and cytokine release.

SELENIUM AND MERCURY SPECIATION IN PLANTS BY HYPHENATED TECHNIQUES

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Selenium is an essential micronutrient and functions through selenoproteins in humans and other mammals. In land plants the question of selenium essentiality is still of great interest. Mercury is also a metal of environmental concern due to its high toxicity to humans and mammals. Mercury accumulation in plants occurs from the uptake from soil or the atmosphere. A selenium protective effect against mercury toxicity was reported in mammal bloodstream by forming complexes containing the co-administered two elements. Also the mercury-selenium species was found to bind selenoprotein P, the major plasma protein.[1] The literature lacks of information regarding the mutual interaction of selenium and mercury in plant.

This contribution will present research on the investigations of selenium and mercury species in selenium and mercury-enriched wild-type *Brassica juncea* plant. Three compartments of the plant system are examined (1) the root exudates, (2) the head-space and (3) the plant tissues to detect any selenium-mercury-containing species.

For selenium and mercury-containing species in the root exudates solution, ion-pairing reversed phase chromatography was coupled to ICP-MS was used. Multiple selenium and mercury species were detected and one mercury peak was observed at the same elution time as selenocystine. Head-space solid phase micro extraction gas chromatography coupled to ICP-MS allowed the simultaneous detection of dimethylselenide and a mercury species. Because of the low levels detected, our attempts for the identification of the mercury volatiles by GC-MS was not successful. For plant tissues, roots, stems and leaves were individually treated and screened for selenium-mercury-containing species. The sample preparation consisted of a sequential extraction of water-soluble species, water-soluble proteins and SDS-soluble proteins. Size exclusion chromatography coupled to ICP MS allowed fractionating the selenium and mercury species. Only low molecular weight selenium species were released from the plant tissues by means of aqueous extraction; no signal could be detected in the mercury channel. The selenium-mercury-containing species were mainly found in the protein precipitate of the plant roots in the high molecular weight fraction (> 70 kDa). The later was collected and its behavior was further investigated under proteolytic degradation. (protease and trypsin). Protease was found to be inefficient, whereas the chromatogram of the tryptic digest shows low molecular weight selenium and mercury-containing fractions. This suggests a possible presence of selenium-mercury protein complexes in the plant roots.

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COMPARING A SELENIUM ACCUMULATOR PLANT (*Brassica juncea*) TO A
NON-ACCUMULATOR PLANT (*Helianthus annuus*) TO
INVESTIGATE SELENIUM-CONTAINING PROTEINS

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Selenoproteins, proteins containing selenocysteine (SeCys), the 21st essential human amino acid, have been identified in diverse organisms including bacteria and mammals. However, their existence in the land plant kingdom is still under study and evokes a great interest. This presentation will focus on the investigation of high-molecular weight selenium fractions in a selenium-enriched accumulator species (*Brassica juncea*) and a selenium-enriched non-accumulator sunflower species (*Helianthus annuus*).

Water-soluble protein extracted from the leaves and the roots are first screened by size exclusion chromatography coupled to inductively coupled plasma mass spectrometry and selenium specific detection is achieved by monitoring characteristic isotopes. The root extracts of the *Brassica juncea* plants display mainly low-molecular weight selenium-containing species, whereas the major selenium found in sunflower roots is in the higher-molecular weight protein fraction. Furthermore, it was estimated that the selenium-containing protein concentration is ca. 20 times higher in the *H. annuus* extract than in the *B. juncea* extracts. Selenium-containing protein fractions were collected and subjected to 1-D gel electrophoresis in non-denaturing conditions for further separation. Distinguishable protein bands were digested with trypsin and analyzed by liquid chromatography coupled to electrospray mass spectrometry in an effort to find peptide fragments of reasonable size. Also the selenium content in each tryptic digest was determined by means of flow injection ICP MS.

Additionally, protein extracts were digested enzymatically with Proteinase K. Proteolytic digests were analyzed by reversed phase HPLC-ICP MS to investigate the seleno amino acid and peptide content. Results show that selenocysteine is found in greater amounts than selenomethionine in the proteolytic digests of the accumulator plant, while selenomethionine is observed to be the primary constituent of the proteins of the non-accumulator plant. One selenium-containing peptide was also observed at higher levels in the root digests than in the leaf digests. Also the accumulator *B. juncea* gave higher amount of this peptide than the non-accumulator *H. annuus*.

DESIGN AND DEVELOPMENT OF ELECTRODEPOSITION TECHNIQUE FOR
SEPARATION AND PRECONCENTRATION OF Co, Ni, Au, Pt, In, Pt IN
ENVIRONMENTAL SAMPLES PRIOR TO FAAS AND
ICP-AES MEASUREMENTS

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Recognition and determination of ultra-trace elements especially heavy metals in chemical, biological, environmental and mineral samples are very important task because of their impact on animals and human health.

AAS and ICP-AES have shown a high ability for measurement of most trace elements. However, sometimes the very low concentration of the elements in environmental samples are below the detection limit of these techniques. Moreover, the complex matrices of the sample may cause serious interference in these measurements. Therefore, the technique of electrodeposition coupled with FAAS (ED-FAAS) has been used for separation and preconcentration of extremely low concentration of traces of Co, Re, Ni, Au, Pt and In from the complex matrices of real samples. The goal is electrodeposition of ultratraces analyte onto the Pd-coated renewable substrate at optimised conditions of voltage and time of deposition and pH of electrolyte prior to measurement with the above techniques.

The characteristic masses and detection limits in the determination of these elements are superior to those of obtained from conventional measurements. The detection limits for the interested elements have been improved with precision of the determinations in the range of 1-3 %RSD. The characteristic concentrations for Co, Ni, Au, In, Pt and Re are 1.72, 2.67, 2.98, 9.6, 27.8 and 663 ng/ml respectively in the specified %RSD using the ED-FAAS hyphenated technique.

The developed technique has been applied to the environmental and geological samples for determination of the traces elements content and results are compared to those of conventional measurements with FAAS and ICP-AES techniques.

DETERMINATION OF TRACE METALS IN COAL BY INDUCTIVELY
COUPLED PLASMA SPECTROMETRY WITH MICROWAVE-ASSISTED
DIGESTION NOT USING A 'TROUBLE MAKER'; HYDROFLUORIC ACID
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Coal contains many kinds of trace metals and some of the metals are toxic. Since it is possible to expose environment through the fly-ash and the ash generated in combustion furnace and secondarily used as a reclaimed material. For evaluation of the environmental risk, it is important to determine the trace metals in coal. In the case of inductively coupled plasma (ICP) spectrometry, the dissolution of the coal sample is required prior to the ICP measurements.

Microwave-assisted digestion with mineral acids can accelerate the dissolution of coals, and, as a result, the digestion time shortened to only 1-2 hours. Since coal contains not only large amounts of organic matrices, but also inorganic ones, this digestion was conventionally performed using several varieties of acids, such as nitric, hydrochloric, and hydrofluoric acids. In the resultant solution, however, the unreacted hydrofluoric acid remains and seriously damage to ICP instruments, especially, its glassware, e.g., nebulizer and spray chamber. In order to prevent the damage, the glassware must be exchanged to non-glassware when the dissolved solution is directly analyzed or the residual hydrofluoric acid must be removed. However, the latter operation frequently causes loss of volatile elements. Additionally, both post-digestion operations are unbeneficial to shorten sample pretreatment time and to obtain accurate analytical results.

In this study, we developed a new digestion method without a 'trouble maker'; hydrofluoric acid. The digestion condition was optimized, and, as a result, the optimized digestion requires no hydrofluoric acid and the ICP spectrometry combined with the digestion technique achieved determination of trace elements in coals. In this presentation, we will discuss the figures of merit and demerit of the developed method.

ROUTINE BIOMEDICAL AND PETROCHEMICAL APPLICATIONS FOR
HPLC-ICP-MS & GC-ICP-MS

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Total element concentrations are readily determined in sample matrices using the rapid, sensitive and multi-element technique of ICP-MS. However, it is increasingly recognized that stand-alone total element data is insufficient for elucidation of an elements intrinsic chemical behavior and potential for toxicity to biota. An elegant analytical approach to enable highly selective on-line elemental speciation analysis can be achieved readily by coupling chromatographic techniques such as HPLC and GC with sensitive element specific ICP-MS detection. These hyphenated techniques can offer unprecedented levels of sensitivity and the potential for determinations of inorganic, organo-metallic and bio-molecules in liquid samples, often with minimal requirements for sample preparation.

This presentation highlights the increasing interest and requirement for speciation methodologies in the commercial laboratory environment and describes emerging applications for elemental speciation analyses in the Biomedical and Petrochemical market sectors. Topics to be covered will include routine HPLC-ICP-MS analyses of As species in human urine samples for occupational exposure monitoring and GC-ICP-MS analysis of Hg species in selected petrochemical samples.

COMPLEMENTARY HPLC-ICP-MS AND ESI-Q-TOF FOR THE ELUCIDATION OF As AND Cd METABOLITES PRODUCED IN EXPOSED PLANT TISSUES

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Mining, industry and agriculture lead to accelerated release of metals into ecosystems, causing serious environmental problems and posing a threat to human health. Therefore, phytoremediation, i. e., bioremediation with plants of polluted sites has received much attention over the last few years due to its relatively low cost of performance and environmental compatibility. The bio-induction of a class of oligopeptides, known as phytochelatins (PCs) is the principal mechanism developed by certain plants to cope with the stress of some metals (Cd, Cu, Pb) and metalloids (As). PCs are peptides synthesized from glutathione (GSH) in the presence of some heavy metals during a reaction catalysed by the enzyme PC-synthase. PCs consist of just three amino acids: g-glutamic acid (E), cysteine (C) and glycine (G) having the general formula: (EC)_nG where n = 2-11. Owing to the high cysteine content, PCs bind metal ions, forming intracellular metal complexes thereby reducing the intracellular free metal ion concentration and thus, their toxicity [1].

However, most known hyperaccumulators tend to grow slowly and produce relatively low biomass. Due to these limitations, the use of genetic engineering to enhance plants' phytoremediation potential for metal/metalloids have been studied. In this regard, the present study deals with the study of the complexes formed in wild type and genetically modified *Brassica juncea* (Indian mustard) when exposed to Cd and As as toxics. Genetic modification by over-expressing the enzymes ECS (g-glutamylcysteine synthetase) and GS (g-glutamyl linkage between glutamic acid and cysteine) have been assayed. These two enzymes are responsible for GSH formation from glutamic acid, cysteine and glycine and had been overexpressed for possible increasing of Cd and As accumulation. Isolation of As and Cd-PC complexes from macromolecular proteins is performed by Size Exclusion Chromatography (SEC) and monitored by ICP-MS from the plant extracts. Further purification of such compounds by Reversed Phase-HPLC allows the adequate purity of the species to be analyzed by organic MS. In this regard, ESI-Q-TOF will be used to elucidate the structures of the species synthesized by wild type and genetically modified *Brassica juncea* tissues when exposed to As and Cd [2].

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RICHARD PAYLING MEMORIAL LECTURE :
EMISSION YIELDS IN RF GLOW DISCHARGE

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Glow Discharge Optical Emission Spectroscopy can be split in three separate processes: Sputtering, Excitation/Emission and Detection. Over the last decade Dr Richard Payling has made significant scientific, technical and educational contributions to all three aspects of GDOES. His contributions to the concept of emission yield, however, may well be the most interesting, on occasions controversial. The presentation will give a critical review of his work on emission yields in GDOES, show some aspects of the link between personality and scientific progress and finally new results obtained with pulsed rf-GDOES will be presented.

STRATEGIES FOR RAPID, ROUTINE BIOMEDICAL ANALYSIS USING ICP-MS

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Elemental analysis in biomedical samples is generally achieved using flame atomic absorption spectroscopy (FAAS) and graphite furnace atomic absorption spectroscopy (GFAAS). Flame AAS is fast, simple to use and economical, but although effective for performing assays such as Na and K in serum and urine, lacks the detection limit capability needed for other routine measurements, such as the determination of Pb and Cd in whole blood. Consequently, these more challenging assays have led to the adoption of the more sensitive GFAAS for trace elemental biomedical analysis for the past few decades. ICP-MS has to date had relatively little impact on the biomedical community. Despite its low detection limit capabilities and wide elemental range, ICP-MS has been regarded as expensive, difficult to use and prone to interferences, by many biomedical users. However, advances in ICP-MS technology during the past few years have reduced the problem of interferences (through the development of collision cell technology), simplified the instrumentation and reduced the purchase costs. As a result, biomedical analysts are becoming more interested in ICP-MS. This paper will demonstrate and discuss the performance of ICP-MS in comparison to GFAAS, for routine trace element assays in biomedical samples.

THE USE OF SPECTRUM, A STELLAR SYNTHESIS CODE,
FOR LABORATORY CARBON PLASMAS ELICITED BY A ND: YAG LASER

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A modification to the SPECTRUM code elaborated at ASU was used to attempt simulations of spontaneous emission spectra from laser induced graphite (carbon) plasmas in the near UV/visible spectral range (350-650 nm). Several models have been developed to describe the spectral and chemical behavior of such plasmas at conditions near laboratory electron and ion temperatures and number densities. Although such models cannot correspond closely to shortlived plasmas they are expected to give a rough approximation to time averaged emission spectra and allow a glimpse to the chemistry of such plasmas using simple thermodynamical approximations at local thermal equilibrium (LTE) conditions. Details of results shall be presented.

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ORGANOTIN SPECIATION USING FAST FLOW GLOW DISCHARGE MASS SPECTROMETRY

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Organotin compounds are widely used as biocides, agrochemical products, PVC stabilisers, wood preservatives and catalysts. These numerous applications represent a significant source of contamination in marine, freshwater and terrestrial ecosystems, with detrimental effects from a few ng Sn l⁻¹. This has necessitated the development of sensitive and selective analytical procedures for the monitoring of tin pollution.

5W) fast flow glow discharge (FFGD) ion source, coupled to gas chromatography, has been used for the analysis of tetraalkyltin compounds (R₄Sn and R₃SnPr where R=Me, Et, Bu). This source differs to other GC-GD techniques in that the sample is introduced into a flowing afterglow and not the active discharge region. A rapid flow of Ar gas carried the analyte towards the sampling cone, reducing diffusional losses to the internal surfaces of the source and source fouling. Following optimisation of the cell pressure, Ar gas flow rate and discharge power, detection limits were <1 pg (as tin).

The sampling cone could be biased negatively with respect to the anode (0-60V). This was found to have significant effects on the relative ion intensities and analytical sensitivity. The increased analyte fragmentation observed at higher applied voltages has been attributed to a low energy CID process close to the cone surface and involving excited state precursors. At low cone voltages (<10V) and a low source pressure sufficient structural information was obtained to identify the analyte from the resultant mass spectrum at the 5-500 pg level (depending on the compound). Comparisons with other techniques will be discussed.

COMPARISON OF DIGESTION TECHNIQUES FOR DETERMINATION OF
IODINE IN MILK BY VAPOUR-GENERATION INDUCTIVELY COUPLED
PLASMA - OPTICAL EMISSION SPECTROMETRY

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Quantification of natural contents of iodine in milk requires sensitive methods. Limit of detection of Inductively coupled plasma – optical emission spectrometry with conventional nebulization is not sufficient and mainly spectral interferences disable determination of iodine. Generation of volatile vapour of iodine to the ICP enhances sensitivity and overcome spectral interference of phosphorus. In our work two different types of decomposition techniques were investigated with consequential generation of iodine to the plasma for determination of iodine in milk. Alkaline ashing with calcium nitrate / potassium hydroxide can be followed directly by VG-ICP-OES from water leachate of ash however carbonates in ash cause spectral interference (CO molecular emission band in spectra). These were eliminated in the sample by acidification and evaporation of volatile carbon dioxide in the presence of reducing agent (sulphite). Using this procedure the spectral interference was completely removed. Low-temperature ashing in oxygen plasma was another investigated method, which is very comfortable because no additional chemicals are necessary. Generation of iodine vapour was established with oxidation mixture of sulfuric acid and hydrogen peroxide in vapour generator with gas-phase separator. Sensitivity of the system is sufficient for quantification of natural contents of iodine in milk samples. Recovery of digestion methods was verified using ICP-MS method with conventional nebulization.

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IDENTIFICATION OF CARBON-BASED SPECTRAL INTERFERENCES ON
PROMINENT EMISSION LINES IN VACUUM ULTRAVIOLET REGION

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There are several important and unique analytical lines in region below 200 nm in inductively coupled plasma optical emission spectrometry. Carbon-based spectral interferences in this part of spectra can be observed in case of analysis of samples rich in carbon. These interferences are not sufficiently described and/or identified in many cases. In this work spectral interferences were observed with high-resolution monochromator in analysis of different samples with high carbon content and were identified experimentally. Structured background in the vicinity of analytical lines (I 178.280 nm, S 180.731 nm, I 183.038 nm, Sn 189.991 nm and As 197.262 nm) complicates determination of low concentrations of mentioned elements. The shape of interferences corresponds to the structure of molecular emission bands. The behaviour of interfering peaks was investigated with different conditions (forwarded power, gas flow rates, composition of gaseous mixture) and compared to that of well-known emission bands of carbon-containing molecules. Experiments resulted in identification of interferences as a structure of CO emission band.

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COMBINATION OF HPLC-ES-MS/MS AND HPLC-ICP-MS FOR THE IDENTIFICATION AND QUANTIFICATION OF MORE THAN 20 ORGANOARSENIC SPECIES IN STANDARD SOLUTIONS AND EXTRACTS OF MARINE REFERENCE MATERIALS

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The accurate characterisation of organoarsenic species is of utmost importance for understanding arsenic metabolism in marine organisms and for the reliable estimation of the toxicological relevance of arsenic species in seafood.

Up to now, several methods have been developed for the determination of arsenic species on the basis of HPLC-ICP-MS. In contrast, there are much less applications of HPLC-ES-MS and moreover these have mainly focused on the identification, but not on the quantification of arsenic species.

Additionally, a literature survey has resulted in a list of more than 30 arsenic species which have been detected in samples of marine organisms. However, the currently available methods usually include less than 10 known arsenic compounds. The potential of HPLC-ICP-MS is limited by the chromatographic resolution of the individual species, while the much higher selectivity of ES-MS/MS allows for the individual determination even of coeluting arsenic species.

In the present study a HPLC-ES-MS/MS method was developed for the characterization of a large number of organoarsenic species. A combination of cation- and anion-exchange liquid chromatography was applied. ES-MS/MS measurements were performed in the selected reaction monitoring mode (SRM) in order to achieve enhanced selectivity and sensitivity. Collision induced dissociation curves were recorded for 28 arsenic species to optimize the SRM conditions.

For the quantification stock solutions of 21 arsenic species were prepared. The purity of these solutions was checked with HPLC-ES-SRM-MS and additionally with HPLC-ICP-MS as an independent method. ICP-MS was also necessary to determine the total As-concentration in the stock solutions relative to an arsenic single element standard.

Linear calibration curves with low residual standard deviation were obtained for most of the compounds; detection limits estimated from the linear regression are in the sub to low ng/ml-range.

The results obtained for arsenic speciation in extracts of four marine reference materials will be presented to demonstrate the capability and the limitations of the new method in the presence of real sample matrices.

Acknowledgement

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CHEMICAL ANALYSIS OF ARCHAEOLOGICAL POTTERY: PREPARATION OF THE LABORATORY STANDARD

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Archaeological investigations have become more dependent on appropriate chemical analysis of excavated artifacts. Numerous modern analytical techniques exist for this purpose, with each technique becoming increasingly efficient regarding sensitivity and selectivity. Moreover, these techniques are non-destructive and permit the simultaneous determination of a large number of macro and micro components. Results obtained using these methods should fulfill at least two major requirements, i.e. they should be as accurate as possible and they should be traceable in the long-term. Method accuracy can be achieved by using a reference material. Long-term reproducibility with comparability of results using different analytical methods obtained initially in different laboratories, can only be assured through the analysis of a (certified) reference material with a chemical composition closely resembling that of the analyzed archaeological artifacts, as possible.

With the close cooperation of the Dolenjska museum from Novo mesto, Slovenia, a systematic chemical analysis of excavated pottery (early Iron Age, 8-4 century B.C.) was initiated. To improve the inter-comparison of the obtained results, a laboratory reference material was prepared in such a way that approx 3 kg of pieces of archaeological pottery found in different graves (of different historic periods, the pieces were classified as waste after the restoration process was completed) was collected. The pieces were thoroughly cleaned with water, dried and ground in a tungsten carbide-based grinding mill. After grinding, the samples were collected in a plastic container, where they were thoroughly homogenized by shaking (1 day). The homogenized sample was split into four fractions, equipped and was appropriately labeled and sealed. One fraction was used for systematic analysis using ICP-OES, ICP-MS and LA-ICP-MS systems.

When ICP-OES or ICP-MS were used, the first step in the analysis was sample decomposition by fuming with HF or by fusion decomposition with LiBO_2 . When the LA-ICP-MS system was used, the sample was pressed into the pellet form prior to the LA sampling procedure. Matrix components, as well as trace components, were determined by all three analytical systems. Quantification was done on the basis of simultaneous analysis of certified reference materials (SRM 99a SODIUM FELDSPAR for ICP-OES and ICP-MS and NIST 612 for LA-ICP-MS).

ANALYSIS OF POWDERED TUNGSTEN CARBIDE BY LASER INDUCED BREAKDOWN SPECTROMETRY

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Laser Induced Breakdown Spectroscopy (LIBS) is frequently applied in the analysis of resistant materials, such as carbides, nitrides and refractory oxides. LIBS makes it possible to avoid complicated and time-consuming dissolution procedures. Ceramic materials can be presented for analysis either as compact solid or powders. While compact samples are analysed directly, powders are pressed to pellets.

The potential of the LIBS as suitable method for direct analysis of WC/Co powdered precursor of sintered hardmetals was studied. The samples were presented as pressed pellets prepared by mixing with powdered silver binder.

The experimental setup consisted of the Nd:YAG laser operated at fundamental wavelength (1064 nm) and fourth harmonic frequency (266 nm). Emission of breakdown plasma was collected by a fiber optic system. The monochromator TRIAX 320 with gated photomultiplier was used as detection system and signal was recorded by the digital storage oscilloscope. The possibility of determination Nb, Ta, Ti and Co in tungsten carbide powdered materials by LIBS was investigated.

The results obtained by LIBS were compared with results obtained by laser ablation – inductively coupled plasma atomic emission spectrometry (LA-ICP-AES) and solution analysis using ICP-AES.

The authors wish to express their thanks to the Grant Agency of the Czech Republic for the support of this research within the grant: 203/02/P097 The study of interaction of laser radiation with solid materials by plasma spectrometry methods.

SPECIATION OF EUROPIUM AND GADOLINIUM COMPLEXES WITH
HUMIC ACID BY CE-ICP-MS

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Capillary electrophoresis (CE, Beckman Coulter P/ACE MDQ), with its unique separation performance, was coupled to Inductively Coupled Plasma Mass Spectrometry (ICP-MS, VG Elemental PlasmaQuad 3) to gain also a high sensitivity for the determination of the rare earth elements europium and gadolinium and their complexation with humic acid (purified Aldrich humic acid). A fused-silica capillary was flexibly fitted into a MicroMist 50 μ l nebulizer with a Cinnabar cyclonic spray chamber. The chamber was chilled to a temperature of 4 °C for best sensitivity. 200 ppb of caesium were added to the CE separation buffer to observe the capillary flow. A make-up fluid including 4 ppb Ho as an internal standard was joined with the flow from the capillary within the interface to obtain a fluid throughput high enough to maintain a continuous nebulization. Very low detection limits were achieved, 100 ppt for ^{153}Eu and 125 ppt for ^{158}Gd . With this optimized CE-ICP-MS coupling-system it was possible to quantify metal concentrations from the detection limit up to approximately 1 ppm at a linear scale. This setup was used to separate metal / humic acid-species in a 100 mM acetic acid / 10 mM acetate buffer system. With humic acid as complexing ligand, free metal species could be separated from the metal-humate-complexes on a time resolved scale. The ratios of free metal ions and metal-humate-complexes are changing with different experimental conditions like pH values or metal concentrations.

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“SOLUTIONS” FOR CALIBRATING LASER ABLATION-ICP-MS

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Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a technique used for the elemental analysis of a wide range of sample types, whether they are solid, liquid or gaseous in their composition. The long recognised potential of the ICP, enabling the direct sampling of solid materials. In this coupling, a high-power, highly focused laser beam is used to vaporise and sputter material from a sample surface before transportation to the ICP.

Quantification of elements in solid samples using this procedure presents many problems. Ablation characteristics vary greatly between samples of even slightly differing composition, meaning that external calibration requires the use of highly homogenous, matrix matched calibration materials, which are often not readily available for the majority of sample types. LA-ICP-MS has been referred to in the past as barely more than semi-quantitative in nature.

This work provides a comparison between various calibration techniques, employing aqueous standards. Such techniques are used to eliminate the dependency of accurate and reliable quantification of analytes, within a solid sample, on the availability of highly matrix matched, homogenous reference materials.

DETERMINATION OF TOTAL MERCURY AND MONOMETHYLMERCURY
IN BIOLOGICAL TISSUE USING DIFFERENT ANALYTICAL TECHNIQUES:
RESULTS FROM THE MERCYMS INTERLABORATORY COMPARATIVE
STUDY

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In studies investigating the fate of mercury in the natural environment is of essential importance to obtain reliable and precise data, which can be achieved by implementing adequate QA/QC protocols. Therefore, in the initial phase of the EU project »MERCYMS - An Integrated Approach to Assess the Mercury Cycling in the Mediterranean Basin«, an interlaboratory testing program was conducted to assure the validity and comparability of results among the research teams. In this work, the results from the interlaboratory study carried out between the Jožef Stefan Institute (JSI), Ljubljana, Slovenia and the Laboratoire de Chimie Analytique Bio-Inorganique et Environnement (LCABIE), Pau, France are presented. Independent analytical techniques used by two different laboratories for determination of total mercury (Hg-T), and monomethylmercury mercury (MeHg) in biological samples (zooplankton, oyster tissue, sea urchin, mussel tissue, golden grey mullet, anchovy) from the Mediterranean Sea and Atlantic Ocean were compared.

Alkaline dissolution/ aqueous phase ethylation/isothermal techniques by GC/CV AFS detection was used to determine the MeHg and inorganic (IHg) mercury in the selected biological samples at JSI. Mercury speciation (MeHg, IHg) in biological tissues at LCABIE was determined by microwave extraction, ethylation, isotope dilution and CGC ICPMS detection. Moreover, total mercury analyses at LCABIE were performed using a total microwave extraction and ICP MS by external calibration (EE), standard addition (SA) and isotope dilution (ID). The isotope dilution method was found to be the most suitable method for total mercury analysis in the investigated biological samples. The results of speciation analyses indicate that methods used in both laboratories (LCABIE and IJS) are comparable for determination of IHg and MeHg in biological samples using isotope dilution at LCABIE and simultaneous determination of inorganic Hg and MeHg at JSI.

MEASURED PERFORMANCE OF SPETEC LAMINAR FLOW-BOX SYSTEMS

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The SPETEC company is producing a Laminar Flow-Box (LFB) basic system which is available in different sizes. It contains a pre-filter, a ventilator maintaining a constant laminar flow of clean air (0.25 - 0.45 m/s) filtered by a high performance filter (H 14) which offers a particle collection efficiency of 99.995%. That means, the filter system is able to screen out nearly all particles with diameters $\geq 0.5 \mu\text{m}$ or at least 99.95% of all particles measuring diameters of about $0.3 \mu\text{m}$. The isolation factor (number of particles in the surrounding area versus number of particles inside the box) was measured to be about 1 million.

The storage of very pure solutions and the bottle opening can take place in a clean room atmosphere as well as the different steps of sample preparation by using such a LFB. It is also available for heating processes whereby the fume is sucked off by an exhausting device. A telescopic tube can be directed in front of the source to remove the heat and to keep the laminar flow stable.

In the meantime, a shower version of the basic system was constructed to create a local particle-free area there where the sample has to be handled, e.g. in front of the nebulizer input of ICP-AES or ICP-MS instruments. In principle, it can be used to cover any kind of analytical instrument or operation area. The work in a clean-room area is resulting in much lower background values measured in the case of spectrochemical methods, for example. In our opinion, it is necessary to measure the actual number of particles in laboratories and inside the LFB system to show the performance of a laminar flow of clean air. A particle measuring system based on laser diffraction (Fig.) was used here. Some results will be given in the poster, e.g. the time needed to remove 1 million of surrounding particles by the laminar flow inside the box is measured to be 10 seconds only.

Now, we are able to offer our help: Do you want to know how many particles are in your working area? Give us a call and we'll measure it for you.



Met One, Modell 227B

ANALYSIS OF STABLE ISOTOPES AND LONG-LIVED RADIOACTIVE ISOTOPES IN CONCRETE SAMPLES FROM A NUCLEAR REACTOR

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Introduction

In the decommissioning of nuclear facilities, the inventory of radioactive elements in the various materials needs to be assessed for the evaluation of the classification of the nuclear waste as well as the storage facilities needed for the nuclear waste. A part from the reactor cores, the main radioactivity in the reactor comes from the graphite and the construction materials.

An important tool in the assessment of the radioactivity in the construction materials is a modelling analysis of the activity. To do this kind of modelling it is important to know the integrated neutron flux that the material has experienced during the operation of the reactor, the stable isotopes concentrations as well as the identification of all mechanisms for the production of the radioactive isotopes. This work is concerned with the chemical analysis of the stable isotopes and long-lived radioactive isotopes in concrete samples.

Present work

In the present work an accurate chemical analysis of Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U in concrete samples from the Danish Nuclear Reactor-2 has been developed.

For the analysis of the stable isotopes and long-lived radioisotopes in concrete samples it is of primary concern to develop a suitable digestion method. Microwave assisted digestion methods are compared to normal hot plate digestion. The effects of addition of HF to the digestion of concrete has been examined and it has been found that high concentrations of HF leads to unstable solutions, but HF is needed to do an accurate analysis of several elements, especially Mo and Nb but also Ba, Li and Th show increased recoveries when HF is added.

With a suitable digestion method as well as careful selection of analytical conditions it is possible to analyse for Ba, Ca, Co, Eu, Fe, Li, Mo, Nb, Ni, Sm, Th and U with ICP-OES (Varian Vista Pro Axial, Varian Inc., Mulgrave, Australia) and HR-ICP-MS (Plasmatrix 2, Micromass Ltd, Manchester, England) with good accuracy. The developed method is checked against two certified cement reference materials (X0202 and X0203, Breitlander GMBH, Hamm, Germany) and good recoveries for all the above-mentioned elements are observed.

RELATIVE QUANTITATION OF PEPTIDES BY DIFFERENTIAL ISOTOPIC
TAGGING USING ISOTOPE DILUTION MASS SPECTROMETRY.

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High accuracy and reliable quantitative data in proteomics is essential for the comparison of protein/peptide expression in a variety of normal, developmental, and disease states. The current status of peptide analysis in proteomics relies on either derivatisation of the peptides using isotopic tags or the metabolic labelling of amino acids followed by the relative quantitation using organic mass spectrometry such as the isotope coded affinity tag (ICAT) strategy or ¹⁵N labelling of amino acids. Quantitation using these strategies relies on comparison of peak areas and relative intensities of isotopic labelled peptide pairs.

In the present study we have developed a differential isotopic-labelling technique that uses isotope dilution mass spectrometry to accurately quantitate changes in peptide levels. The strategy utilises the separation and detection of hyphenated HPLC-ICP-MS. Samples are derivatised separately using the bifunctional chelating agent cyclic diethylenetriaminepentaacetic anhydride (cDTPA) which specifically binds to N-terminal amine groups of peptides. The samples are then spiked with natural or enriched isotopes of a metal that chelates with cDTPA to form a complex that can be analysed using element specific detection. The samples are then recombined and analysed via HPLC-ICP-MS.

In this poster results are presented detailing the use of enriched Eu isotopes to chelate to bradykinin and other peptides, and the use of isotope ratio analysis to determine the relative concentrations of the peptide in normal and diseased states

THE REMOVAL OF MATRIX INTERFERENCE FROM PLANT MATERIAL
AND FISH TISSUE (RETICULATED & PRICKLY SCULPIN) BY
OCTOPOLE REACTION SYSTEM ICP-MS
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Environmental baseline studies continue to demand improvements in instrumentation and laboratory procedures for the environmental laboratory. Laboratories require high performance instrumentation capable of meeting ever-more-demanding EPA regulations and data quality objectives. Accurate trace metal analysis of surface water, groundwater, marine water, sediments, vegetation and fish tissue is vital for the evaluation of naturally occurring background and contamination levels. More than ever, competitive economic pressures prohibit laboratories from investing in highly-selective analytical methods and extraction techniques, such as atomic fluorescence and hydride generation for achieving required reporting levels for multiple metals. Today's environmental laboratory requires an efficient instrument flexible enough to handle the ever-changing matrices and capable of sub parts-per-billion detection limits.

The presentation will focus on the method development and tuning optimization for matrix elimination of biological tissue and plant material by Octopole Reaction System ICP-MS. Method performance is measured by instrument detection limit, recovery of certified reference materials, data quality objectives and comparison with data from non reaction system ICP-MS, hydride generation-ICP-MS, ICP-OES and GFAA.

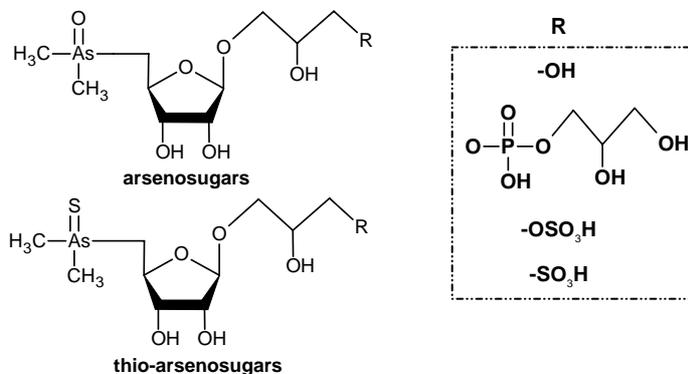
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY DETECTION FOR THE DETERMINATION OF NOVEL THIO ARSENOSUGARS

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Arsenic is an element that is ubiquitous in the environment. Natural metabolic processes in the biosphere result in the existence of a large number of inorganic and organic arsenic compounds. The arsenic species found primarily in marine algae are the arsenosugars. The toxicity of these species has not been fully evaluated yet, but is likely to be complex because they are biotransformed in humans to several arsenic containing metabolites that have not been characterized sufficiently up to now. Recently, the thio-analogues of two arsenosugars (dimethylarsine sulfide sugars) were detected in mollusk extracts.^{1,2}

In the present study a method for the determination of the thio-analogues of all four common arsenosugars was developed using High Performance Liquid Chromatography with on-line Inductively Coupled Plasma Mass Spectrometry detection. Due to the absence of standard compounds of the thio arsenosugars an algal (kelp) extract, which contains the four common arsenosugars, was treated



with H₂S at room temperature to prepare a mixed sample of these new species.

Initially, a PRP-X100 anion exchange column was used for the separation of the thio arsenosugars. This type of column has been used in the majority of arsenic speciation studies. However, it was observed that due to strong interaction of the thio-sugars with this column, very long retention times and extremely broad peaks were observed. In addition, prolonged elution of the thio arsenosugars may result in their on-column transformation to the common arsenosugars.

To overcome this problem, an ion-pairing method was developed using a C18 reversed-phase narrow-bore HPLC column in combination with a cationic ion-pair reagent. This type of chromatography has been used previously for the rapid separation of the four commonly encountered arsenosugar species.³ The influence of various mobile phase compositions (pH, ion-pairing reagent concentration and methanol content) on the separation efficiency was studied. With this method much lower retention times were obtained for all four thio arsenosugars in the modified kelp extracts.

In addition to method optimization, results obtained from the application of the methodology for the analysis of marine extracts will be presented.

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NOVEL ARRANGEMENT FOR ON-LINE ISOTOPE DILUTION IN LASER
ABLATION ICP-MS VIA MICROFLOW NEBULIZATION

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Laser ablation ICP-MS (inductively coupled plasma mass spectrometry) is becoming one of the most important analytical technique for fast multielemental analysis of solid samples. Quantification of analytical results requires matrix-matched standards, which in some cases (e.g. high purity metals, proteins separated by 2 D gel electrophoresis) are difficult to obtain or prepare. In order to overcome this problem solution-based calibration has been successfully applied in laser ablation ICP-MS [1]. But during the measurement of the standard solutions matrix matching is necessary and can be performed by either laser ablation of a high-purity blank target [2] or using the standard addition mode in solution-based calibration [3]. Both methods of matrix matching are not applicable in case of samples where no blank material exist and the sample amount available (only a few mg) is not enough for the number of measurements required in case of standard addition mode. In order to overcome this problem a new strategy of solution-based calibration by performing on-line isotope dilution analysis (IDA) in LA-ICP-MS was developed [4]. New applications of on-line isotope dilution in laser ablation ICP-MS using a novel arrangement with a microflow nebulizer directly coupled to the laser ablation chamber (mono gas sample introduction) will be presented in this work.

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DIRECT SOLID ANALYSIS OF GLASSES BY RADIOFREQUENCY GLOW
DISCHARGE TIME OF FLIGHT MASS SPECTROMETRY

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Developments in the field of materials science have led to special emphasis on the search of new, or improved, techniques for direct analysis of solids with good sensitivity and high depth resolution, to be used in the characterisation of new materials and in quality control. As it is well known, the direct current (dc) or radiofrequency (rf) powered glow discharges (GDs) coupled to optical emission or mass spectrometry (MS) are nowadays established techniques for the direct analysis of solids (in particular, for conducting materials). However, a lot of work remains to be done in the area of the quantification of nonconductors by rf-GD techniques.

Dielectric materials are known to have capacitive effects related to their size (thickness and surface) that influence the amount of effective power that is transmitted through the sample to produce the glow discharge. In this sense, the higher the thickness of the glasses, the higher the power losses and these power losses affect the atomisation and ionisation/excitation processes [1].

In this work, the suitability of a rf-GD coupled to a time-of-flight mass spectrometer (TOFMS), developed in our research group, is examined for the direct solid analysis of thick glasses (3-6 mm) [2]. Calibration curves of homogeneous glasses will be evaluated taken into account the thickness of the sample as well as the presence of some elements like oxygen that are known to quench the Ar metastable atoms (responsible of the Penning ionisation) and, so, decreasing the analyte ion signals. On the other hand, the possibility of detecting the complete mass spectrum with high spectral acquisition velocity (20 kHz) using the TOF mass spectrometer offers a great advantage to analyse any unknown glass (homogeneous or coated). Therefore, the possibility of analysing very thin layers on thick glasses (qualitative depth profiles) using rf-GD-TOFMS is also investigated in detail.

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RELATIVE SPUTTERING RATES AND EMISSION YIELDS FOR GD:
A THEORETICAL POINT OF VIEW

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Glow discharges have been studied in detail for a wide range of applications, and a good understand has been developed for glow discharges in simple configurations. It is know, for example, that the scaling parameters for a glow discharge in a parallel plane electrode geometry are V , the discharge voltage, j/p^2 , the current density normalized to the square of the gas pressure, and pd , the product of the gas pressure and the anode cathode separation. These scaling parameters are valid when nonlinear effects such as gas heating, stepwise ionisation,.. are negligible.

Glow discharge systems used for GDS are of course more complicated because the geometry is two-dimensional and nonlinear effect do start to play a role. This talk will discuss scaling parameters for relative sputtering rates and emission yields in GDS. Results from glow discharge theory and from numerical simulations will be used as the basis for this discussion.

ANALYTICAL APPROACH FOR RESOLVING OF
MASS INTERFERENCES IN GDMS
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Improving of quantification analysis by GDMS is connected strongly with developing of different methods for resolving of mass interferences. In this work a new analytical approach is described and discussed. Typically the intensity of ion currents registered by mass analyzer for a mass number x is a sum of all current intensities of mono- and polycharge atomic and molecular ions that have mass to charge ratio of x . In common case it is difficult task to extract wanted current fraction which corresponds to analyzed element. However, based on analytical conditions and some basic information about sample composition allows to simplify the equation by leaving only the most important terms, which include the following: ion currents of isotopes for elements with mass number x , currents of molecular ions from isotopes of matrix elements as well as of working gas isotopes and currents of these elements forming n -charge atomic and molecular ions having mass nx . In order to solve problem for j unknown terms the $(j - 1)$ expressions have to be written for other mass numbers. Every expression must contain at least one ion current term of any isotope of those elements, which are presented in the original expression. If these expressions contain terms with k new elements k more expressions are needed. Assuming that for any element the ratio of ion currents of different isotopes is the same as the ratio of isotopic abundance the system of $(j + k)$ equations with $(j + k)$ unknown terms can be received. This system can be solved relatively sought ion fraction.

Analytical expression allowing to extract contribution of the analyte ion current from the integral ion current are presented for the cases of: Nb in Cr, Rh in Cu and Ti in Mo when Ar is used as working gas. Results of the calculations are in a good agreement with experimental results of ICP method. It is shown that for case of Ti in Mo the contribution of TiH^+ ion current must be taken into account to obtain correct result.

DIRECT DETERMINATION OF MERCURY AT THE SUB-PG/G LEVEL IN
POLAR SNOW AND ICE BY ICP-SFMS

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An analytical method for the direct determination of mercury (Hg) in Polar snow and ice cores and surface snow based on Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) has been developed. Various Hg isotopes such as ^{199}Hg , ^{200}Hg , ^{201}Hg and ^{202}Hg appear to be free of polyatomic interferences in such matrices and allow the measurements to be done in Low Resolution Mode leading to high sensitivity. Ultra low concentration Hg standards (from 1.5 to 20 pg g⁻¹) were used for the calibration of the Thermo Finnigan Mat Element2, and a detection limit as low as 0.18 pg g⁻¹ was achieved using ^{202}Hg . Ultra clean procedures used from field sampling to final laboratory analysis show no significant blank contributions and appear suitable for the reliable determination of Hg at ultra low concentrations. Precision of the Hg measurements was estimated to be 15% in terms of Relative Standard Deviation on five replicates and accuracy was checked with an analytical reference material (102% recovery). Hg concentrations in surface snow samples from the Northern Hemisphere collected in the Canadian Arctic and in Svalbard (Norway) show high variability (1.2 to 32.0 pg g⁻¹). For Antarctica, Hg was determined in different ice core sections from Dome C spanning the last 18,000 years BP (range from 0.7 to 3.2 pg g⁻¹) and in snow samples from Coats Land covering the last 150 years (range from 0.2 to 16.1 pg g⁻¹).

PROTEOMICS WITH SEC-ICP-MS: INCREASING THE CHROMATOGRAPHIC
RESOLUTION BY SIGNAL POST-PROCESSING

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Due to its outstanding detection limits and versatility the hyphenation of inductively coupled plasma mass spectrometry (ICP-MS) and size exclusion chromatography (SEC) is widely used in proteomics for the speciation of metallo- and metalloid proteins [1]. However the separation power of SEC with regard to protein mixtures has some principal limitations, overcoming of which may be not possible even after any hardware modification or extensive optimization of experimental conditions. Applying alternative separation techniques like SDS-PAGE with XRF or laser ablation ICP-MS detection will provide with better separation power. However, due to the protein denaturation associated with trace element washout and/or insufficient detection limits, this technique is unsuitable for investigation of non-covalent bound elements. Thus the improvement of the chromatographic resolution of SEC separation is very attractive for proteomics.

An approach to increase the chromatographic resolution by mathematical signal post-processing was reported [2, 3]. However, the application of the proposed approach to SEC data of protein mixtures requires the information about the evolution of the chromatographic peak form depending predominantly on molecular weight. A number of single-protein standards was used in the present investigation to reveal the parameters of chromatographic peaks within the weight range of 5-70 kDa. The results obtained after the deconvolution of the signal for protein mixture showed significant improvement of the chromatographic resolution and thus the applicability of the approach [3] to the SEC-ICP-MS data. A comparison of achieved resolutions of chromatographic and SDS-PAGE separations as well as the optimization of the deconvolution procedure will be discussed.

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DEVELOPPEMENT OF A ROUTINE TO ANALYZE IMPURITIES IN
ALKALINE MATERIALS

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The determination of the impurities Na, K, Ca, Al, Si, S and Fe in alkaline materials has been made by ICP/AES. The quantity of the impurities vary between 10 and 500 mg/L. The aim of this work is to present the routine which was developed to quantify with accuracy the impurities. Moreover, it is known that the elements Na, K and Ca are difficult to analyze in alkaline matrix.

To avoid the matrix effect, we have used standard addition and the alkaline matrix was recreated by using alkaline salts when we prepared standard solutions.

This study compares the results obtained with different salts and the optimization of the different operating conditions.

IMPROVEMENT OF THE ABUNDANCE SENSITIVITY OF A DOUBLE-FOCUSING SECTOR-FIELD ICP-MS TO MEASURE LOW $^{236}\text{U}/^{238}\text{U}$ ISOTOPIC RATIOS

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Sector-field ICP-MS are now a major source of isotopic ratio data, notably for environmental monitoring, nuclear Safeguards verification and nuclear forensic studies, which require precise isotopic analysis of uranium. For this, it has been demonstrated [1] that measurement of $^{236}\text{U}/^{238}\text{U}$ is often of particular interest in addition to ratios with natural isotopes, because ^{236}U is produced in nuclear reactors (mainly $^{235}\text{U}(n, \gamma)^{236}\text{U}$). The resulting isotopic ratio in nuclear spent fuel can exceed 10^{-3} depending on the reactor type and fuel history, whereas the natural $^{236}\text{U}/^{238}\text{U}$ isotopic ratio is expected to be about 10^{-14} [2]. Then, ^{236}U is a very useful "fingerprint" of uranium originating from a nuclear reactor. Moreover, the $^{236}\text{U}/^{238}\text{U}$ indicator is much more sensitive for irradiated uranium than the deviation of $^{235}\text{U}/^{238}\text{U}$ from the natural value. Besides, the spent uranium from nuclear reactors may have $^{235}\text{U}/^{238}\text{U}$ isotopic ratio close to that of the natural value (7.25×10^{-3}).

However, there are several factors affecting the detection capability and accuracy of $^{236}\text{U}/^{238}\text{U}$ isotopic ratio in ICP-MS. Instrumental background and uranium hydride formation $^{235}\text{UH}^+$ have to be subtracted to the signal at mass 236. Moreover, in all sector-field mass spectrometers there is a small contribution to peak intensity from adjacent peaks. This contribution is called abundance sensitivity. This mostly results from ions losing energy by collisions with residual gas molecules in the analyser after passing through the magnetic sector and, thus, in theory, mainly on the low - mass side of a peak [3]. This phenomenon also exists with TIMS but as its magnitude is a function of analyser vacuum, it may be significantly worse in sector-field ICP-MS than TIMS, because the ICP ion source is at atmospheric pressure.

As a matter of fact, abundance sensitivity is relatively high with sector-field ICP-MS, typically a few ppm at two mass units from the high intensity peak on the low-mass side. In the laboratory, we used a sector-field ICP-MS "Axiom" (VG Elemental, Winsford, Cheshire, UK) whose abundance sensitivity at 236 atomic mass units due to the ^{238}U peak is typically 4 to 8 ppm. This relatively high abundance sensitivity seriously hinders measurements of $^{236}\text{U}/^{238}\text{U}$ isotopic ratios below a few ppm. In this paper, we describe various attempts aimed at decreasing the contribution of the ^{238}U peak on adjacent masses. At first, we report impact of instrumental parameters including resolution power. As vacuum level plays a crucial role in improving abundance sensitivity, we replaced the original turbo - molecular pump of the analyser by another one with a higher pumping capacity ($555 \text{ m}^3\cdot\text{h}^{-1}$ instead of $250 \text{ m}^3\cdot\text{h}^{-1}$), in order to improve the vacuum in the analyser. We give results of this instrumental modification and discuss how it compares with double and triple sectors TIMS measurements.

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QUANTIFICATION OF A SELENIUM-CONTAINING PROTEIN IN YEAST
EXTRACT VIA AN ACCURATE DETERMINATION OF A TRYPTIC PEPTIDE
BY SPECIES-SPECIFIC ISOTOPE DILUTION CAPILLARY HPLC - ICP MS

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Speciated isotope dilution analysis (IDA) has become an increasingly popular method to improve the precision and accuracy of speciation measurements in complex biological and environmental matrices. To date, it has been used in the field of elemental speciation for the quantification of inorganic species and small organometallic.

Extending applications of the speciated IDA to large biomolecules is a challenging task requiring the availability of isotopically labeled compounds and the development of efficient separation techniques coupled with isotope specific detection by mass spectrometry.

A method based on the species-specific isotope dilution analysis was developed for the accurate determination of an Asp-Tyr-SeMet-Gly-Ala-Ala-Lys peptide directly in a tryptic digest of an aqueous extract of selenized yeast. For this purpose a ^{77}Se labeled peptide to be used as a standard had been purified by 2D liquid chromatography from yeast grown on $^{77}\text{SeO}_3$ -rich culture and quantified by reversed isotope dilution analysis. The sample mixed with the ^{77}Se -labeled peptide spike was analyzed by capillary HPLC - ICP collision cell MS. The isotopic labeling allowed the unequivocal identification of the peptide among all the Se species detected. It compensates for retention time shift and possible peak distortion due to the injection of a complex salt-rich matrix onto a capillary column. The isotope ratio of selenium ($^{77}\text{Se}/^{80}\text{Se}$) was measured in the peak corresponding to the peptide of interest enabling its accurate quantification by isotope dilution. The determined concentration of the peptide, which was quantitatively formed from a selenized 12 kDa heat-shock protein, made the quantification of the latter possible by cHPLC - ICP MS directly in a yeast extract, without any additional purification.

The method developed indicates the feasibility of a generic approach based on HPLC-ICP MS to use an isotopically labeled peptide for the unequivocal identification and accurate quantification of a protein based on the IDA principle. The advantage over the procedures reported in the literature is the use of elemental MS detection which improves the specificity, sensitivity and the quality of the isotope ratio measurements over that obtained with electrospray or MALDI MS. Isotopically labeled peptides can be isolated or synthesized easier than the isotopically labeled proteins and hence, they offer a potential to become convenient spikes in isotope dilution analysis for quantitative selenoproteomics or hetero-atom tagged proteomics in general.

LEAD SPECIATION IN ARABIDOPSIS THALIANA BY HYPHENATED TECHNIQUES

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The contamination of soils with heavy metals is caused by mining and combustion of fossil fuel, usage of fertilizers and pesticides as well as sewage sludge. Heavy metals, in contrast to organic pollutants, cannot be chemically degraded or biodegraded by microorganisms. Their content steadily increases in soil causing their accumulation in plants and animals and significant deleterious consequences for the environment and human health.

Lead, a cumulative poison, released from various industries viz., food canning, paper and pulp, paints, pigments and solid dumps, contribute significantly towards Pb pollution of both lentic and lotic water bodies. According to an estimate 10,500 tones of Pb is released every year globally in fresh water ecosystems through various point and non-point pollution sources. Lead has been found to be accumulated by large number of aquatic plants. Substantial accumulation and high tolerance of lead has been reported in *Sesbania drummondii*, *Marchantia polymorpha*, *Agrostis tenuis* and *Arabidopsis thaliana* showing great potential of plants in phytoremediation.

Phytoremediation may offer a viable solution for the environmental restoration. There were developed many methods based on the use of plant species naturally capable to hyperaccumulate and to clean toxic metals up from contaminated soil or water. The robust development of the plant biotechnology provides an opportunity to employ transgenic plants with increased metal binding capacity. Examination of the mechanism of accumulation of toxic metals indicated the expression of phytochelatins and metallothioneins induced mostly by cadmium and rarely by lead. The monitoring of the metal content in plants is widely used for the estimation of the level of contamination, transport paths and metal accumulation systems - still being not recognized.

The strategy to identify lead accumulation mechanism and transport paths in *Arabidopsis* has been developed using selective and sensitive hyphenated techniques. Speciation of the metal was investigated in cell by SEC – ICP MS in order to uncover the accumulation process. Small inorganic acids, peptides and proteins complexes with lead were extracted from plant and were identified by RPLC – ES MS. Identified phytochelatins were found to be responsible for metal accumulation, its cytosol and membrane transport. The potential of the lead speciation indicates that obtained results could be reliable source of knowledge to confirm the information coming from the well known genomic sequence of *Arabidopsis*.

IDENTIFICATION AND CONTROL OF METAL POLLUTANT SPIKES IN
WASTE TO ENERGY PLANTS - A NOVEL APPLICATION FOR ICP-OES

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Identification and Control of Metal Pollutant Spikes in Waste to Energy Plants – A Novel Application for ICP-OES.

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As a result of the strategic approach of our energy from waste research programme, metal emissions from gas-solid bed combustion has been identified as a key area requiring further study. Our previous work has shown that the formation and destruction of transient channels within the burning bed dominate the combustion process. These sudden changes will result in the release of fly ash, and other gaseous pollutants into the flue gas. It is assumed that heavy metal release will accompany these events, and will be strongly affected by temperature, chemical environment in the bed, and metal content and distribution in the waste.

A specially constructed mobile laboratory, containing a specially configured ICP-OES has been used to obtain exclusive information on the concentration and variation of metallic pollutants in un-cleaned process gas. This unique “continuous emissions monitoring laboratory”, deigned around the Spectro Ciros-CCD ICP-OES, and equipped with a 40 m heated sampling line, was used to simultaneously monitor the concentrations of over 30 elements, including As, Ca, Cd, Hg, K, Na, Pb, Sn, V, Zn, with detection limits as low as 0.0004mg m⁻³, and a time resolution of one minute or less. This demonstrates a novel and successful application of ICP-OES. Previously, various groups have tried to use plasma techniques to monitor metal concentrations in gas streams, with limited success, frequently encountering problems with reliability, interferences, accuracy, or sensitivity. The authors believe that they are the first group to publish semi-quantitative data on metal concentrations in crude process gas, before any clean-up process. This highly contaminated medium presented significant analytical challenges, but the initial results are very encouraging, and very significant to the field of combustion research.

We have conducted considerable experimental investigation at a waste to energy plant in the UK, which handles 20 tonnes of waste per hour on two lines, with Martin reverse-acting reciprocating grates and a steam-raising energy recovery system. Flue gas cleaning comprises of hydrated lime and activated carbon injection followed by bag filters. Our previous work has examined metal concentrations in emitted flue gas, showing them to be very low; certainly below regulatory limits, and without significant variation. New measurements, reported here, made prior to gas cleanup have revealed high in-process concentrations of many of metals, including Na, Pb,

and Zn. These show significant temporal variation, which can be linked to process conditions, such as bed temperature and waste feed. Concentrations of certain key pollutants, such as Cd and Hg, are seen to be generally very low, but with occasional peaks, which are attributed to individual sources of these metals in the waste.

The data obtained from this research is fundamental in understanding the temporal fluctuations in metal emissions from the incineration system. Where occasional high-concentration spikes dominate the release of a metal, this provides strong evidence that better segregation of certain key items from the waste stream could help to considerably reduce the level of key toxic metals in process residues. Careful control of plant conditions could also have a significant impact on the volatilisation of other metals. This paper presents the results obtained from this unique and significant research, which demonstrates the successful novel application of ICP-OES in the most demanding of analytical situations.

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SIMULTANEOUS DETERMINATION OF TRIMETHYLEAD,
MONOMETHYLMERCURY AND BUTYLTINS BY SPECIES-SPECIFIC
ISOTOPE DILUTION GC-ICP-MS IN BIOLOGICAL SAMPLES

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Alkyl compounds of lead, mercury and tin play an important role in biological and environmental samples because they are highly toxic and can be both, of anthropogenic and biogenic origin. Methylated metal compounds are preferably produced in the marine environment by algae and bacteria. These elemental species are expected to be accumulated in marine animals and can therefore also reach the food chain of man, which makes their accurate determination of special importance for seafood quality assurance.

The use of certified reference materials (CRMs) is a usual way to validate procedures for speciation analysis. Unfortunately, there are only a few CRMs available for individual species and matrices and no reference material is available for simultaneous determinations of trimethyllead, methylmercury and butyltins. An alternative approach is the species-specific isotope dilution mass spectrometric analysis (IDMS) with its high accuracy and precision as well as the ability to control possible species transformations during sample preparation. A sensitive species-specific GC-ICP-IDMS multi-species method was therefore developed for the simultaneous determination of trimethyllead, methylmercury and butyltins in biological samples.

Isotopically enriched methylmercury and butyltin spikes are now commercially available. The synthesis of a trimethyllead spike was carried out by the reaction of lead halide with methyllithium and subsequent formation of trimethyllead iodide. The isotopic composition of the spike solution was determined by GC-ICP-MS after derivatisation with tetraethylborate and its concentration was obtained by reverse isotope dilution analysis. Optimised conditions for sensitive and simultaneous determinations of the corresponding lead, mercury and tin species were developed. Several reference materials (CRM 605, CRM 463, CRM 477) were used for the validation of the developed method. Other reference materials, not certified for the organo metal species investigated, as well as seafood samples purchased from a supermarket were also analysed. In these samples the fraction of methylated mercury was always much higher than the fraction of trimethyllead.

This work was carried out in the frame of the Interdisciplinary Research Training Group Program (DFG-Graduiertenkolleg 826) on Trace analysis of elemental species: Development of methods and applications.

PULSED HOLLOW CATHODE AS ION SOURCE FOR SOLID STATE
SAMPLES - TOFMS ANALYSIS

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Pulsed glow discharge (GD) is an effective tool for analysis of solid samples. Usually a Grimm type discharge is used. Analytical system based on GD with Grimm discharge and TOFMS is characterized with detection limits (DL) in range 1 – 10 ppm. However levels of DL for effective using of this technique for such an important area as analysis of high purity metals and semiconductors must be lower (in ppb range). Sensitivity of GD-TOFMS technique can be increased by using a pulsed hollow cathode discharge. This work is devoted to the source and MS interface optimization.

Ion source includes cathode made of Cu or Nb with Cu disk placed on cathode bottom. Ions from cathode extracted through sampler and skimmer orifices to Faraday detector. A mixture of Ar and He gases was used in the discharge cell with pumping rate of 8-300 ml/min. The mixture was introduced into the cathode through stainless steel capillary. In copper cathode capillary was introduced in centre of cathode bottom. Four narrow orifice placed near cathode wall were used in case of Nb cathode with Cu disk.

A value of copper ions flux as a function of pulse frequency, pulse duration, pulse voltage, gases pressure and flow rates, dc voltage of cathode and also of sampler and skimmer geometry was determined.

Experimental data will be discussed in the presentation. These data allow optimizing parameters of discharge cell and TOFMS interface. Under optimal conditions copper ion current on Faraday detector reached 0.004 mA. On the basis of this signal a DL range was estimated to be 5 –50 ppb. Potential applications of investigated GD ion source in commercial GD-TOFMS analyzer will be discussed in the presentation.

HETEROELEMENT SPECIFIC DETECTION OF BIO-MOLECULES USING ICP-MS

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Speciation analysis still represents a growing and innovative application field of ICP based elemental mass spectrometry.

Since the beginning heavy metal or metalloid containing compounds such as organometallic substances, Metalloproteins, Selenoproteins or Arsenosugars were in the focus of interest due to the fact that they all contain an element tag, more or less easily detectable by ICP-MS, which enables their highly selective and sensitive determination.¹

The complementary application of molecule specific detection techniques for a final characterisation of bio-molecules, which have been selected via their metal or metalloid tag, has been demonstrated in various recent studies.

However the successful application of the described approach on bio-molecules is strongly dependent on the presence of a metal or metalloid tag inside the molecule of interest and therefore limited on selected substances.

Recent developments including more stable high-resolution instrumentation, introduction of collision-/reaction cell technology, new and in particular commercially available interfaces and new hyphenation approaches drastically extended the potential of ICP-MS from a metal or metalloid specific detector to an element specific detector, featuring an outstanding sensitivity and specificity for elements.

Therefore the utilisation of heteroelement tags which are often naturally present in various substances, for a selective detection and pre-selection of bio-molecules or environmentally relevant compounds for further experiments, drastically increase the application fields for ICP-MS.²

In combination with already established methodologies such as MALDI TOF-MS or ESI-MS/MS, ICP-MS represents a powerful complementary technique with great potentials especially in life science or environmental related topics such as protein phosphorylation studies or monitoring of hazardous substances in different compartments of the anthropogenic environment.

This contribution will discuss current strength, limitations and recent instrumental development of ICP-MS based heteroelement specific detection and their application on either environmental and life science related topics.

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AN ORIGINAL GLOW DISCHARGE HIGH RESOLUTION MASS SPECTROMETER TO ANALYSE ULTRA PURE CONDUCTING AND NO CONDUCTING SOLID MATERIALS

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Elemental analysis of inorganic solids is a continuous challenge for modern analytical chemistry due to the increasing demands in different areas of material science and quality control for industrial products such as pure metals manufacturers, semiconductor industry, alloy manufacturers and nuclear industry. Particularly great efforts are devoted to the analytical characterization of ceramic materials, while simultaneously the traditional and advanced analysis of metals also remains of actual interest. In the latter, matrix separation and preconcentration techniques are applied more and more often for the determination of selected.

Up to day, ICP operation in both atomic emission spectrometry (AES) and also MS are generally preferred. Nevertheless, dissolution of the sample including a digestion step has the risk of introducing contaminations and is time-consuming procedure. It is the general trend for future development to realize lower detection limits for some elements, to reduce time for sample preparation.

Therefore the development of new techniques for the direct analysis of solids is a permanent challenge. The development of ion generation techniques, besides ICP, glow discharge (GD) has also gained considerable attention for the analytical task of elemental analysis by mass spectrometry. The technique is particularly attractive due to its extremely low detection limits, but suffers from long analysis time and many interference problems. The advantages, especially with GD-MS, are freedom from chemical blanks and minimal sample preparation for the direct analysis of solids [1].

GDMS looks particularly favourable whenever metal samples have to be analysed with very low detection limits. It is meanwhile an accepted experience that GDMS with high resolution has to be applied for analysis in the sub ppb region of materials with a purity level of 6N or even more [2]. GD-HRMS is particularly attractive due to its extremely low detection limits, but suffers from long analysis time and many interference problems. A new generation of GD-HRMS (GD90) has been recently developed by Mass Spectrometry International Ltd. (Manchester, U.K.) and some original design was done to improve the analytical performance. A new ion optic and a fast laminated magnet were employed to decrease the analysis time and the limit of detection and increase the signal noise ratio. Owing to these new specifications, the production of stable ion beam in full transmission is possible at 1000 mass resolution, a very low detection limit down to 0.01ng.g⁻¹ for high purity metals is routinely realized at 4000 mass resolution. Then, a similar sensitivity of common GD-HRMS at 4000 mass resolution is obtained with GD90 at 10,000 mass resolution.

For this type of ultra-trace analysis of pure solid materials with low detection limits, GD90 as a multielement technique (79% elemental coverage) is without competition.

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NEW INTERFACE DESIGN FOR COUPLING CAPILLARY-LC AND
COLLISION-CELL ICP-MS AND ITS COMPLEMENTARY APPLICATION FOR
THE DETECTION OF PHOSPHORYLATED PROTEINS

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The reversible phosphorylation of proteins at the amino acid residues serine, threonine and tyrosine represents a omnipresent and important dynamic process in living systems, that affects the structure of proteins, their catalytic activity during physiological processes, protein-protein interaction or the regulation of gene expression and protein synthesis.

Due to their good compatibility with the optimal solvent flow rates of electrospray ionisation ($1 \mu\text{L min}^{-1}$) and their superior chromatographic properties in comparison with “large bore” chromatography, namely a higher separation efficiency, better peak sensitivity and reduced adsorption and sample dilution effects, low flow separation techniques like capillary LC or nano-LC hyphenated to ESI-MS have become the standard technique for a wide range of biochemical applications for instance peptide mapping, protein sequencing or the determination of posttranslational modified proteins.

Modified and large peptides often cause problems in ESI-MS/MS experiments due to the compound dependency of the electrospray ionisation process.

Therefore the high selectivity of ICP-MS for elements, which is nearly compound-independent especially under low flow conditions, makes it an alternative for the rapid pre-screening of tryptic digest for phosphorylated peptides before their final characterisation via ESI-MS/MS or ESI-TOF-MS.

Handling the low solvent flow rates of capillary LC (normally around $4 \mu\text{L min}^{-1}$) and controlling the background on the mass of phosphorus represents the most critical part in coupling capillary-LC and ICP-MS for phosphorylation mapping.

This contribution focused on the new development of an interface for the direct hyphenation of capillary-LC and a quadrupole based collision cell ICP-MS (CC-ICP-MS) and its application on the determination of phosphorylated tryptic peptides via their “phosphorus tag”. This devise combines highest sensitivities with a low dead volume design and it allows the utilisation of highly organic gradient conditions without any detrimental effects on the plasma or the longterm stability of the setup. ESI-MS/MS is used as a complementary detection technique to further characterise the nominated, potentially phosphorylated peptides, detected via CC-ICP-MS.

BIOMONITORING OF HEAVY METAL INTOXICATION AND MOBILIZATION IN HUMAN HAIR BY LA-ICP-MS

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The present study aims at the determination and medical assessment of the intoxication and mobilization of heavy metals in the human body.

Besides blood, plasma and urine, hair is another bio-indicator and gives information on the long term storage of heavy metals. Hair has been used as early as 1929 to assess human systemic levels of elements. [1] and hair is widely accepted for assessing toxic element exposures. While urine or blood tends to show current or recent body status, hair represents a longer time scale.[2] The IAEA has observed a correlation between Hg concentrations in hair and kidney cortex.[3]

Methods using conventional sampling strategies (i.e. cutting hair segments before digestion) are limited in lateral resolution and are therefore not capable to deliver continuous data on the time dependent course of metal administration and its consequent deposition in hair samples. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) offers excellent lateral resolution in combination with ultimate sensitivity and spectral resolution. The method has already been applied to obtain a signal versus time profile of Tl in a thumbnail by our research group. [4] The final signal is normalized to the ³²S signal as internal standard. Since S is known to show a spectral overlap with the O-O – signal, analysis is performed by using the DRC capabilities of the Perkin Elmer ELAN DRC plus ICP-MS. The method was optimized in order to achieve best results for simultaneous sulphur and metal analysis. In addition, we discuss the quantification procedure in order to obtain final data on the elemental concentration.

In order to obtain accurate data, we investigated pre-cleaning procedures, which are a crucial point since hair is known to accumulate and release heavy metals in wet conditions.

Finally, a time resolved variation of the elemental concentration was recorded as well as the concentration gradient over the cross section of a hair with respect to the hair structure. The time resolved relative variation is a direct bio-indicator of a change of elemental contaminants in the human body.

The method was applied to monitor the Hg intoxication as well as the Hg mobilization in amalgam fillings. The latter Hg mobilization was monitored in human urine in parallel in a series of amalgam patients.

Moreover, we monitored the Pt uptake of a cancer patient in order to follow the Pt concentration in the human body which is directly reflected in the hair. The forensic record was in excellent agreement with our results with respect to time and the dose of given Pt compounds during the cancer treatment.

The method was finally applied to a single hair strain of Ludwig van Beethoven, which was put at our disposal by a well known collector in order to investigate the theory of Pb poisoning. The findings were in good agreement with a possible medical record.

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GEL-ELECTROPHORESIS-ICP-OES HYPHENATED SYSTEM FOR
SEPARATION OF CHROMIUM(III)-COMPLEXES

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Bioavailability of chromium(III)-compounds strongly related to the chemical form of the element. The difference in the toxicity of Cr(III) and Cr(VI) compounds is a widely studied problem, for the separation and measurement of Cr(III) and Cr(VI) compounds from soil and groundwater samples numerous method was developed. Surprisingly there is only a very few method for the separation of Cr(III)-complexes. We had to develop method for measurement of Cr(III) complexes for food supplements and plants. Gel electrophoresis is a powerful technique for the separation of macromolecules such DNA and proteins. Its on line coupling to the atomic emission spectrometers has not been solved earlier. Recently the laser ablation-ICP-MS coupled system was applied for the testing of metalloproteins which were separated on a PAGE horizontal gel.

A new interface was developed in our laboratory for the hyphenation of gel-electrophoresis cell and ICP-OES spectrometer. It was applied for removing and on-line introducing of the solution from the end of gel filled tube to the ICP-OES. The method is suitable for the separation of Cr(III)-complexes such $\text{Cr}[\text{Cl}(\text{H}_2\text{O})_5]^{2+}$, $\text{Cr}[\text{Cl}_2(\text{H}_2\text{O})_4]^+$, Cr-picolinate, $\text{Cr}[\text{EDTA}]^-$, etc.

A 0,5 cm diameter vertical glass tube was filled with PAGE gel in a 2 cm thick layer. The samples (freshly prepared Cr(III) complex standard solutions, or extract of a food supplement pill) were mixed with glycerol with 1 to 5 ratio and 50 or 100 μL sample was injected to the top of gel. 0,001 M nitric acid solutions were applied as electrolyte solution on the upper and lower buffer. 20-50 V electric voltage was applied for the separation and the current was 30 mA. The separated ions went through the gel and entered the lower solution. The special interface introduced every ions came from the columns to a thin plastic tube. The peristaltic pump continuously removed the ions from the tube therefore every ion which come out from the gel was transported to the ICP-OES.

The method directly separates the positively and negatively charged ions because of the different migration direction of anions and cations in the electric field. The first effect what can be used in the separation is the different migration rate in the electric field of ions, e.g. the $\text{Cr}[(\text{H}_2\text{O})_6]^{3+}$, $\text{Cr}[\text{Cl}(\text{H}_2\text{O})_5]^{2+}$ and $\text{Cr}[\text{Cl}_2(\text{H}_2\text{O})_4]^+$ are differently charged ions so they could be separated by the system. The gel electrophoresis itself can separate the ions according they size therefore the Cr-picolinate complex can be separated from the chlorides as well.

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DESCRIPTION OF NONINSTRUMENTAL ERRORS IN ANALYSIS

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The problems of the intellectual analytical measurements demand the development of the theory of used methods and the general theory in analysis. The improvement of the analytical instrument is based on the study of the individual theory of this method. For intellectual analytica it is important to use the common basis of the all methods of analysis. The fluctuation approach allows proposing the universal theoretical ground for any analytical method (IUPAC ICAS 2001, Tokyo, Japan). This theory connects the standard deviation of any analytical measurements with the sensitivity of the equipment and the element concentration. The five levels of the relations between these values may be examined in power 0, $\frac{1}{2}$, 1, $\frac{3}{2}$ and 2 (Analyst. 1984. v. 109. p.305-307). This theory has the good agreement for the instrumental random errors of the analytical methods. It is very interesting to observe the connection of this theory with the noninstrumental errors in analytical chemistry including the blank fluctuations, the matrix interferences, the errors of the analyst and other moments.

The blank fluctuations are connected with the constant and changeable unpredicted factors of the analysis. The constant part of the blank including the concentration of the determined element in solutions and preparations may be calculated theoretically like the additive random error in analysis that connects with the element concentration in power 0. On other hand the changeable unpredicted blank value of the analysis cannot be calculated theoretically. This error depends on the element concentration in the power $\frac{1}{2}$. It value have to be estimated experimentally directly before the measurements of the analyzed samples. The analogous relations may be expected for the random errors of the analyst. The special study is necessary for the characterization of the influence of the matrix interferences. The constant value of the all these errors has to take into account by the specific methods of the measuring of the blank and matrix interferences.

The greatest importance of the all these noninstrumental factors of the analysis obtains for the determination of the micro concentration of the elements. The minimization of all noninstrumental factors allows using for the calculation of the analytical errors the linear approximation in the linear range of the measurements:

$s = s_{bl} + ASc$ (1), where s is the absolute standard deviation; s_{bl} is the blank fluctuations; A is the instability coefficient of the apparatus; S is the instrumental sensitivity and c is the element concentration. The great value of the noninstrumental factors shows the prevalence of the shot type of the random errors. In this case we can receive the following relation: $s = s_{bl}c^{1/2} + ASc$ (2).

Thus it is difficult to describe full theoretically the all noninstrumental errors. The experimental data have to be attracted in this case. The use of the database of the analysis of the all-identical samples with the combination of the universal theory of the analysis and the theory of the method given allows receiving the most complete and precise results of the analysis for the intellectual analytica. The intellectual analytica cannot be cleanly theoretical. It has to combine the achievements in the theory of the analysis with the preceding experience of the analytical determinations.

INTELLECTUAL PLASMA SPECTROCHEMISTRY

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The progress in analytical, computers and electronics makes actual the realization of the intellectual analytical systems. The maximum effect may be received for the multi element analysis of any objects because in this case the reciprocal interactions between all components of the sample it is possible to take into account most complete. The using of database of the analysis of the identical samples is here also extremely useful. The multi element analysis may be carried out widely in atomic emission and mass spectrometry. It is interesting to use the multi element analysis for the intellectual atomic absorption spectrometry and atomic fluorescence spectrometry. The use of the results of the multi element analysis by the different plasma spectrochemistry methods allows eliminating maximally the matrix interferences and the reciprocal element influences because the character of these influences is different for the each analytical method.

We propose the design of the atomizer that allows solving the problem of the multi element analysis by the different plasma spectrochemistry methods – atomic emission spectrometry, atomic absorption spectrometry, atomic fluorescence spectrometry, and mass spectrometry (Prudnikov E.D., Shapkina Y.S. Patent of Russia n. 2018806. Pub. 30.08.94. Inventions. 1994. n. 16, p. 115). The design of this atomizer is distinguished by the following peculiarities. The measurements are produced in axial flame or plasma that are formed by the introduction of the gases on the both hands of the quartz tube with the inner diameter from 10 up to 20 mm. The exit of the gases is makes by the offset in the center of this tube.

The proposed design of the atomizer gives the possibilities to realize the following advantages. It is possible the measurements in the low temperature and high temperature foolproof flames, by the method of the cold vapour and the hydride methods, in the combined flame-plasma sources of the atomization with the combination of the flame and the arc or high frequency discharge, and also for ICP discharge in argon plasma. The all these measurements may be realize without the replacement of the atomizer. The atomic emission and absorption spectrochemical measurements it is better to carry out in the tube volume with the use the polychromator for the multi element analysis. The selection of the ions for mass spectrometry and the element fluorescence may be realized from the drain of the atomizer. The measurements in the parallel pencil of the rays from the hallow cathode lamps on the volume of the atomizer tube allows using the optimum design of the multi element determinations by the atomic absorption spectrometry. In this case the most compact disposition of all hallow cathode lamps with the correction lamp is realized.

The advantages of this atomizer allows receiving the most effective, complete and full intellectual analysis of any sample by atomic emission, absorption, fluorescence and mass spectrometry, using the different methods of the samples introduction, taking into account the possible reciprocal interferences of all components of the analyzed sample, and passing the intellectual process of the element determination with use the database of all analytical measurements.

DETERMINATION OF SULFUR IN DIESEL FUEL BY ISOTOPE DILUTION
ICP-MS: CONTRIBUTION TO THE KEY-COMPARISON 35 AND PILOT
STUDY 26.1 OF THE COMITÉ CONSULTATIF POUR LA QUANTITÉ DE
MATIÈRE

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Sulfur, present in transport fuels as an impurity, is a significant source of atmospheric pollution with negative impact on human health and on the ecosystem. Recently, regulations were revised throughout industrialized countries and, for instance, the new EC Directive 2003/17 requires a value of 10 mg kg⁻¹ on the European community market by no later than 1 January 2009. As a consequence, internationally recognized diesel reference materials with certified values (CRMs) on appropriate sulfur contents must become available to the petroleum industry and to the laboratories of the regulatory bodies controlling the quality of the fuel on the market. Such CRMs, with small uncertainty statements, are in preparation worldwide and two of them were used as test materials for the Key-Comparison 35 and the Pilot Study 26.1 of the Comité Consultatif pour la Quantité de Matière. These exercises were launched to test the capabilities of the National Metrology Institutes to determine the sulfur content and isotopic composition in diesel and kerosene fuels containing ~ 40 and ~10 mg/kg of S, respectively. Measuring sulfur at such low levels in fuel samples is challenging, and relevant analytical chemistry information is very limited.

We present the contribution of the EC-Institute for Reference Materials and Measurements to CCQM K-35 and CCQM P-26.1. For this purpose, we developed some analytical procedures based on isotope dilution inductively coupled plasma mass spectrometry (ICP-MS), applied as primary method of measurement. After blending and acid digestion (two methods were compared), the samples were additionally treated to reach optimum conditions for the mass spectrometry measurements. The single-detector sector-field ICP-MS employed was operated (4 000) to resolve the sulfur isotopes from m at medium mass resolution ($m/$ the interfering polyatomic ions). Although most of the sample preparation was carried out under clean room conditions, significant contamination effects were observed, most likely due to dissolution of SO₂ present in the ambient atmosphere of the laboratory. However, this detrimental effect could be corrected for. Sulfur content was determined with expanded uncertainty 0.84 % and 4.1 % ($k = 2$; evaluated according to the ISO/GUM guidelines) for the ~ 40 and ~ 10 mg kg⁻¹ of S in fuel, respectively. The excellent agreement between our results and those obtained by three other national metrology organizations (less than 2.3 % difference from the mean value and within the uncertainty range) further validated the analytical procedures we developed.

LOW UNCERTAINTY FE ISOTOPE RATIO MEASUREMENTS IN SEAWATER
SAMPLES BY ICP-MS AT MEDIUM MASS RESOLUTION

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Inductively coupled plasma mass spectrometry (ICP-MS) with variable mass resolution capabilities opened large perspectives for Fe isotopic measurements. The ability to resolve argon-oxygen based isobaric interferences on iron isotopes, and also high sensitivity and low instrumental noise characteristics made possible the determination of Fe isotope ratios in a wide range of sample matrices. Quantification of the iron content in seawater by isotope dilution (ID) – ICP-MS is particularly challenging due to a combination of mostly two problems, the ultra-low natural Fe contents and the presence of high amount of salts. Matrix separation by means of Mg(OH)₂ co-precipitation is not 100% efficient and results into samples containing a remaining 1 g kg⁻¹ inorganic salts matrix, which in turn can lead to various analytical artefacts and biases when they are not recognised and/or corrected for.

Our presentation will introduce our experimental results concerning the best way of correcting for mass discrimination effects Fe isotope ratio measurements in that kind of complex matrix samples. We observed that matrix and concentration matching conditions for the isotopic reference material used for calibration purposes could change the end result by up to 4 % as compared to more ordinary approaches. Furthermore, we observed severe instabilities during ICP-MS single measurement scans, under the form of ultra fast ‘spike’ signals, which could undoubtedly be related to the presence of high amounts of salts in the samples. It turned out that failing to recognise the presence of such instabilities could lead to an additional shift of nearly 2% of the end result. An off-line method was designed to purge the generated data from any outlier related to this phenomenon. We also took into account the constraint posed by the instrument software for isotope ratio measurements at medium mass resolution as described by Tressl et al. elsewhere.

With these modifications, the stability of the repeatability over 150 minutes improved by a factor of ~1.5, the reproducibility of the ratios improved by more than a factor of 2 and the average ratio changed by ~ 3% (and by up to 9% in the worst case). Consequently, these improvements led to a non negligible ~ 4% change of the final IDMS result on the Fe content at ~ 30 pg g⁻¹ level and to a decrease of the combined uncertainty statement on this value by a factor 2.

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METHYLMERCURY IN TUNA: DEMONSTRATING MEASUREMENT
CAPABILITIES AND EVALUATING COMPARABILITY OF RESULTS
WORLDWIDE FROM THE CCQM P-39 COMPARISON

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Regulatory authorities are required to measure Hg in a variety of biological, industrial and food samples for reasons of public health (cf. regulation EC 466/2001 "setting maximum levels for contaminants in foodstuffs"). In addition, many foodstuffs, particularly fish, contain the majority of the Hg as methylmercury, noted MeHg, and the specific measurement of MeHg is of interest to regulatory organisations, as this species has a mammalian LD50 1000 times lower than elemental Hg. The 2003 recommendation from JECFA, the Joint FAO/WHO (Food and Agriculture Organisation of the United Nations and World Health Organisation) Expert Committee on Food Additives, is that the provisionally tolerable human consumption of MeHg is limited to 1.6 µg per kg body mass, per week, a recommendation a fish consumer could easily exceed.

There is thus an increasing need for reliability and comparability of methylmercury measurement results obtained at different places and different times. Demonstrating such measurement capabilities at the highest metrological level was the object of the CIPM – Comité Consultatif pour la Quantité de Matière (CCQM) Pilot Study 39, which involved six Metrology Institutes (NMIs), representing 4 Member States of the Metre Convention and 2 international organisations, and 8 expert laboratories selected from outside CIPM. The study was organised by the Institute for Reference Materials and Measurements (IRMM), from the European Commission – Joint Research Centre.

We hereby present the main results of this study. The participants were free to apply the measurement strategy of their choice. Beside the test material itself, a bottle of the BCR-464 tuna Certified Reference Material (CRM) and an ampoule of the IRMM-670 material (now ERM-AE670), a species specific ^{202}Hg enriched MeHg isotopic CRM, were distributed to all. Four, including 1 NMI, relied on external calibration or the method of standard additions, whereas the other 10 implemented an isotope dilution mass spectrometry (IDMS) approach and choose to use the IRMM-670 for their measurements. Twelve of the results are regrouped within a range of less than $0.3 \cdot 10^{-5} \text{ mol} \cdot \text{Kg}^{-1}$, they nearly all (1 exception) overlap with each other within stated uncertainties and the relative standard deviation on the average value ($n = 12$) of this sub-group is 3.6%. Comparatively, the other 2 results lay respectively at approximately 20% above and 40% below and their associated uncertainty appears to have been underestimated. In the light of this comparisons' results, these two laboratories were able to identify specific problems (particularly in the MeHg extraction stage) of their analytical protocols. Once these problems were eliminated, the results of their second set of measurement lay well within the spread of the initial sub-group of twelve. Overall, the agreement between these results, obtained from the application of a wide range of analytical strategies, is remarkable.

SI-TRACEABILITY AND UNCERTAINTY ESTIMATION AS TOOLS TOWARDS VALIDATION OF SPECIATION MEASUREMENTS

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Speciation measurements present additional challenges over total element measurements. For example, the analyte's chemical form must remain preserved during sample preparation so that it can be measured specifically, at the same time as it must be efficiently separated from the sample matrix. Analytical instrumentation was developed to provide information about analyte species with ever-improving reliability and repeatability, though often at the cost of increased complexity. Despite improvements in methodology and instrumentation, comparability of measurement results obtained for different analytical methods or from different laboratories continues to highlight unanticipated problems with measurement processes, producing results that do not concur.

Speciation analysis is acknowledged to have an ever-increasing relevance in environmental studies, for risk assessment and eventually, for legislation. As such, there is a concomitant need for reliability and comparability of speciation measurement results, obtained at different places and at different times. To assist in the comparability and accuracy of speciation measurement results, the concepts of traceability (to a stated system of reference) and combined uncertainty budgeting can be applied.

The ISO guide "General requirements for the competence of testing and calibration laboratories", ISO/IEC17025, chapter 5.4.5, recommends a number of practices for method validation:

- Calibration using reference materials
- Comparison of results achieved with other methods
- Participation in laboratory inter-comparison schemes
- Systematic assessment of factors influencing the result
- Estimation of the combined uncertainty of measurement

In addition, the requirement exists that laboratories (5.6.2.2) produce measurements that are traceable to a common system of measurement (for example, the SI).

Traceability can be visualised as a chain, or a combination of chains, of between a measurement result and a reference (for example, the kilogram) where each link in the chain is a mathematical expression representing our best understanding of a measurement process. If laboratories' results do not overlap within stated uncertainties, a breakage in the chain leading to a reported result has occurred because the mathematical comparisons do not cover the reality. An example could be the use of external calibration in calculations, without accounting for incomplete analyte

extraction from the matrix. To achieve traceability, each part of the measurement process must be understood, within a declared level of uncertainty. Common items of concern, which directly influence the accuracy of the measurement process, include the chemistry, stability and recovery of analyte species.

With each link of the traceability chain, uncertainties associated to each calculation parameter can be introduced to calculate the combined uncertainty of the measurement. The uncertainty budget demonstrates the level of certainty that exists in the result. Estimating a complete budget can also help method optimisation and in the diagnosis of erroneous results, or those showing high deviation, by highlighting components contributing significant uncertainty to the result provided that each parameter affecting the result is included in the uncertainty budget, and carries an appropriate uncertainty.

This presentation deals with how a comparable species measurement can be made in practice, through an ISO17025 validated method. It will show how better understanding of the measurement process improves reliability and comparability of the result. This will be demonstrated with methods developed at IRMM for the contribution to laboratory inter-comparison, CCQM pilot study 39, on methylmercury measurement in tuna.

CERTIFICATION MEASUREMENT OF THE CADMIUM, MERCURY AND
LEAD MASS FRACTIONS IN SEWAGE SLUDGE USING ISOTOPE DILUTION
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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In environmental monitoring programmes in many countries, the elemental composition of sewage sludge is an important aspect. As sewage sludge can be recycled (road building material), legislation sets minimum requirements with respect to the maximum allowable concentration levels of minor and trace elements (EC directive 86/278/EEC). Sewage sludge was selected as inter laboratory comparison test material for the round 21 of the International Measurement Evaluation Programme (IMEP-21), organised by IRMM, as well as for the CIPM Comité Consultatif pour la Quantité de Matière (CCQM) pilot study P-70 and key comparison K-44.

Our presentation will describe the development of measurement methods for the metrological certification of Cd, Hg and Pb in sewage sludge. The analytical procedures were based on Isotope Dilution Inductively Coupled Plasma-Mass Spectrometry applied as a primary method of measurement.

Sewage sludge material requires a complex digestion procedure by which components such as silicates should be brought into solution. Therefore four procedures based on microwave assisted digestion were investigated and compared. Due to the need to minimize the procedural blank as much as possible, all sample preparation steps were performed in a clean room environment.

The estimation of the total uncertainty associated to each measurement result is a fundamental tool to ensure reliability of this result. Preliminary simulations using as target a relative expanded uncertainty of no more than 2 % ($k = 2$) helped designing and optimising the measurement procedure.

Uncertainty calculation was performed according ISO guidelines. In retrospect, the major uncertainty contributions turned out to be essentially the corrections for moisture content, for homogeneity of the sample, for isobaric interference as well as for procedural blank.

Reference values, traceable to the SI, with total uncertainties of 1.5 - 2% relative expanded uncertainty ($k=2$) were obtained for all investigated elements.

INTERFACING NEEDS AMONG ANALYTICAL CHEMISTRY AND POLICY IN
THE CONTEXT OF THE WATER FRAMEWORK DIRECTIVE
IMPLEMENTATION
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On-going discussions among the scientific and policy-making communities have highlighted the key importance of interfacing science and policy in an efficient and practical way. Regarding analytical chemistry in general, this integration has a direct implication on the way analytical progress is feeding the environmental policy development with respect to compliance-related monitoring programmes. This progress has to respond to specific and timely policy requirements to be of direct value to the policy-making process. This means that analytical chemistry research and development activities (aiming to support environmental policies) should take into account the policy-making agenda and their specific needs to possibly adapt the objectives and scope of their related work programmes. The present situation shows, however, that this interrelationship is not as efficient as it could be, owing to a lack of internal co-ordination and planning.

An example of attempts to improve the science-policy interface is linked to the implementation of the EU Water Framework Directive (2000/60/EC). This legislation has been elaborated as a result of more than 12 years of consultations among EU Member States and stakeholders (including the scientific community) and it is conceived as an integrated water management framework. The overriding objective of the policy is the achievement of “good status” of all waters by the end of 2015, which is closely related to strategies to protect waters against pollution. The directive implementation follows a stepwise approach with milestones such as e.g. analysis of pressures and impacts (2004), monitoring design (2006), river basin management plan (2009) and programme of measures (2012), which are all directly or indirectly concerned with analytical works, in particular concerning the evaluation of the water chemical status. Expert working groups are discussing how to best integrate analytical knowledge into this policy process to help Member States to better design and later operate their monitoring programme. In parallel, an interfacing mechanism is being developed to make sure that successful methods will be easily made known to WFD implementers.

This presentation will recall the main features of the Water Framework Directive and discuss the issue of research integration into the policy-making process, focusing on issues directly or indirectly linked to analytical chemistry research and development.

APPLICATION OF HPLC-ICPMS TO METABOLIC STUDIES OF AN
ARSENOSUGAR IN HUMANS
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Arsenic is present in many sea foods as naturally-occurring organoarsenic compounds, and the toxicology of many of these compounds is largely unknown. This is of particular relevance to arsenosugars, commonly found in algae and in animals feeding on algae such as mussels and oysters. In an earlier study¹ the urinary arsenic metabolites were investigated by HPLC-ICPMS after a subject ingested a small (safe) quantity of a pure arsenosugar (glyceryl-arsenoriboside). Dimethylarsinate (DMA) with smaller quantities of Dimethylarsinoyl ethanol (DMAE) and trimethylarsine oxide in addition to nine unidentified arsenicals were reported.

We report here results from a follow-up experiment carried out to identify these unknown arsenical metabolites. In addition to the previously found DMA and DMAE, four new metabolites were identified: Dimethylarsinothioyl ethanol, Dimethylarsinoyl acetate (DMAA), and the analogous thio derivatives of the starting glyceryl-arsenoriboside and DMAA. Identifications were based on HPLC-ICPMS and HPLC-Electrospray MS analyses including co-chromatography with synthesised standards with different chromatographic systems, as well as monitoring of chemical reactions with H₂O₂ and H₂S. The importance of arsenic-selective detection and quantification of arsenic species in such metabolic studies will be discussed.

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DEVELOPMENT OF A HIGH-THROUGHPUT METHOD FOR LEAD
SPECIATION IN NATURAL SOIL AND GROUNDWATER SAMPLES BY GC-
ICP-MS

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Organolead speciation continues to be an important research topic in environmental studies because the different species exhibit different toxicity, stability and mobility in the natural environment. Some of the organic lead species are so unstable that calibration standards are not available and method validation is often difficult due to a lack of suitable certified reference materials. In our study, the original lead species was tetraethyllead and it was important to understand how this species was being degraded in the soil and water samples taken from the study site. A method was developed with high sample throughput in mind, because one of the main objectives was the application of the technique as a rapid monitoring and assessment tool. Our team developed a method using the propylation approach described by Crnoja et.al³ and the extraction was further optimized by experimentation with different solvents, pH values and by varying the length of time for the extraction and propylation of the lead salts. Natural groundwater and soil samples were used to develop this method and recoveries were assessed by spiking with calibration standards. The origin of some of the breakdown products observed in the samples were traced by comparison of the isotope ratios for m/z 206, 207 and 208 in the different species and samples. An Agilent GC5890n attached to an Agilent 7500c ICP-MS by a heated transfer line was used for these experiments and the total Pb content was measured by ICP-MS after acid digestion. In the absence of SRM's for many of the lead compounds, it is impossible to do a mass balance on all of the species. Our poster will highlight our work to date.

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TRACING THE FOOD CHAIN: TRACE ELEMENTS IN ANIMAL FEEDS
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Trace elements are typically added to animal feeds for disease prevention and enhanced feed efficiency. However, increased concentrations in animal waste increases soil loading of these elements, when used for land application. Equilibration of potentially conflicting requirements requires controlled and known trace element additions. Results of analyses of bovine and poultry feeds, using the GV Instruments Platform XS quadrupole ICPMS, are presented and discussed with reference to existing and proposed regulations.

INORGANICS IN ORGANICS:
TRACE ELEMENTS IN ORGANIC DAIRY PRODUCE
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Commercial organic farming is compromised by economics. Thus, the Soil Association permits the use of 17 compound fertilizers, seven trace elements, two soil inoculants, six sulphur fungicides, eight copper-based fungicides and eight insecticides. In this investigation, organic and traditionally-produced milks are compared. Trace element contents are determined using the GV Instruments Platform XS quadrupole ICPMS, results presented and discussed with reference to existing and proposed guidelines and regulations.

ROUTINE WATER ANALYSIS, ROUTINELY
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Protocols for the determination of water quality typically demand the analysis of in excess of 20 trace metals. While ICPMS is routinely employed for such analyses, analytical methods increasingly depend on exacting reaction chemistry or instrument optimisation on a per element basis, to meet the demands of the regulations. This increase in complexity delegates increased responsibility to the user and/or instrumentation, increasing the potential for error. Re-stabilization of the instrument following re-tuning during analysis necessarily compromises duty cycle and thus sample throughput. Uniquely, the GV Instruments Platform XS quadrupole ICPMS is operated under a single set of analytical conditions, even for multi-element analysis. Results of long-term analyses of water standards and samples, using the GV Instruments Platform XS quadrupole ICPMS, are presented and discussed.

FROM RSD TO RSE: QUADRUPOLES NEAR THE LIMIT

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The determination of precise isotopic ratios and abundances by quadrupole ICPMS requires the minimization of instrumental and analytical limitations, including noise during sample introduction, plasma flicker, sequential scanning, instabilities in the ion optics, instabilities in the detection system, spectral interferences and counting statistics. Methods of performance enhancement and optimization are detailed and applied to uranium, using the GV Instruments Platform XS quadrupole ICPMS. The use of standards for the automatic correction of mass fractionation is described and the results presented. Comparison is made with theoretical limits of precision.

DETERMINATION OF IODINE-129 IN MILK BY ICP-MS: PROBLEMS AND SOLUTIONS

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The determination of low levels of iodine-129 in milk sample digests by ICP-MS is hampered by interference from xenon present in the argon plasma. Using a quadrupole MS equipped with a hexapole collision cell, a collision gas mixture of helium and oxygen successfully removes this interference, via a thermodynamically favoured charge transfer mechanism. However, at the same time a different interferent is introduced, as the signal at m/z 129 is increased by the oxidation of Mo to MoO₂ via a fast, two stage reaction. As Mo is present at relatively high levels in milk (typically 0.3 ppm in milk powder), this constitutes a major problem in the determination of iodine-129 at sub-ppb levels in milk samples.

The approaches we have taken to tackle this interference - and lower detection limits to appropriate levels - will be addressed in the presentation, detailing novel digestion, preconcentration, and separation techniques. These utilise careful control of iodine redox chemistry to prepare suitable solutions for the determination of iodine-127 and iodine-129 (down to sub-ppb levels in the original milk samples), whilst facilitating the simultaneous determination of other elements if desired.

SOLID SAMPLING-ELECTROTHERMAL VAPORIZATION-INDUCTIVELY
COUPLED PLASMA MASS SPECTROMETRY FOR THE DIRECT
DETERMINATION OF TRACES OF IODINE

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In this work, the possibilities of electrothermal vaporization-inductively coupled plasma mass spectrometry for the direct determination of I at the ppm and sub-ppm level in solid samples have been critically evaluated, the goal always being to develop simple and fast procedures, with straightforward calibration.

The importance of the use of pre-reduced Pd in the analysis of biological material was demonstrated. For solutions, the use of this chemical modifier results in a better stabilization of the analyte (up to 700°C), compared with other chemical forms of Pd, and increases the sensitivity by a factor of approximately 4. This performance was also maintained for solid samples, enabling complete removal of the organic matrices without analyte losses. Moreover, for those samples for which some matrix effects were still observed (milk powder materials), the use of the Pd signal as internal standard permitted correction for these effects, allowing accurate results to be obtained. A detection limit of 8 ng g⁻¹ and a sample throughput of 20-25 minutes per determination were estimated for these biological materials.

The potential of the technique for inorganic samples was also evaluated by testing its performance with a soil material (NIST SRM 2709). For this kind of sample, an alternative approach was developed. By taking advantage of the volatility of the analyte in the absence of any modifier and of the refractory nature of most matrix components, it was possible to selectively vaporize I at 1500°C with minimal matrix co-vaporization, ensuring the absence of significant matrix effects. A higher sample throughput of 10 minutes per determination (due to the faster temperature program) and a higher detection limit (30 ng g⁻¹, due to the absence of Pd) were calculated for this kind of material.

In all cases, external calibration with aqueous standards was possible and RSD values were in the vicinity of 10%. It is clear that the technique evaluated presents many advantages for the fast and accurate determination of this complex element at low levels in solid samples, avoiding tedious digestion procedures and minimizing the often reported risk of I losses due to the formation of volatile compounds.

IN VIVO STUDIES OF THE DISTRIBUTION AND DEGRADATION OF
BUTYLTIN COMPOUNDS USING A “TRIPLE SPIKE” ISOTOPE DILUTION
GC-ICP-MS APPROACH

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In the last years, numerous studies related to the development of reliable procedures for the determination of butyltin compounds in different matrices (such as sediments, water samples and biota) and the monitoring of these species in many environmental compartments have been worldwide reported. However, in spite of the evidence that such sources expose humans to butyltin compounds, few studies have been published so far on the analysis of these species in human tissue and even fewer on the actual risk of exposure faced by humans. The toxicities of organotin compounds increase with the progressive introduction of organic groups at the tin atom (TBT>DBT>MBT). The danger posed by these species to humans will depend therefore not only on their solubilisation but also on the possibility that they may degrade during human digestion, absorption and metabolic pathway.

The advantages of species-specific isotope dilution analysis for the quantitative speciation of tin have been fully exploited by using a triple spike methodology previously developed in our laboratory. This approach is able to correct for nine different interconversion reactions and compute not only the three corrected concentrations of the butyltin species sought but also six degradation factors regardless of the extent of the three tin butylation and the three debutylation reactions. The combination of this methodology with in vivo studies with rats exposed to butyltin compounds will be employed to investigate the absorption, degradation and distribution of butyltin species in mammals aimed at predicting the final fate of these species in humans.

Method Validation for Speciation Analysis

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Analytical method validation may be seen as the “business card” of a newly developed or routinely used analytical method [1]. It provides the analytical figures of merit of an analytical method, as well as it demonstrates its temporal stability or influence by external factors. The importance of proper analytical method validation has been recognised in both industrial and research laboratories, and consequently, a number of guides on this topic have appeared [2,3]. While they all cover the general aspects of analytical method validation, none of them takes particular account of the increased difficulty and the particularities of speciation analysis which are due to the partial unavailability of standards and (certified) reference materials, the often observed limited stability of elemental species (with the consequent danger of species interconversion), and the empirical optimisation of analytical methods.

We attempt therefore to point out and to discuss in this presentation the particular requirements for analytical method validation for elemental species. These are greatly supported by the (slowly) increasing number of (certified) reference materials and proficiency testing schemes in this field, and by the increased use of isotopic labelling / isotope dilution techniques which only eventually become available in this area. However, it is believed by the authors that, in the long run, the availability of certified reference materials, of proficiency testing schemes and of isotopically labelled standard compounds will have a great impact for method validation in elemental speciation and all areas in which these techniques are applied [4].

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A NEW GLOW DISCHARGE SECTOR FIELD MASS SPECTROMETER FOR
THE ANALYSIS OF HIGH PURITY METALS

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Glow discharge mass spectrometry is established as the high-end tool for the solid analysis of high purity metals. However, there are several drawbacks of the technique mainly due the sector field analyzer currently used for this technology. Older generations of sector field analyzer suffer mainly from slow scan-speed, weak mass stability and complex GD sources which results in very low sample throughput and difficult operation. The presentation will introduce a new GD-MS instrument using a high throughput Glow Discharge source combined with a modern sector field mass spectrometer (Finnigan ELEMENT2). Combination of magnetic and electric scan techniques deliver duty cycles up to > 99% and mass stability could be proved with < 25 ppm for > 1 week. The combination of a “fast flow” GD source for efficient sputtering with the high scan speed of the sector field analyzer offers the ability for depth profiling from nm to mm dimensions.

The presentation will describe the technical concept of the new spectrometer and demonstrate its abilities on different applications.

ANALYSIS OF Pt, Pd AND Rh IN BIOLOGICAL SAMPLES VIA MATRIX
SEPARATION AND ON-LINE PRECONCENTRATION COUPLED
TO ICP-SFMS

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Today it is obvious that automotive catalytic converters have become the main source of environmental platinum group element (PGE) pollution leading to enhanced levels of the elements platinum, palladium and rhodium in all environmental compartments. In recent studies urban aerosol, road dust, soil and surface waters have been reported to contain elevated concentrations of PGE.

The accurate determination of Pt, Pd and Rh in environmental and biological samples is known to be very sophisticated, as it is hampered by the combined factors of low concentrations and numerous spectral interferences by high abundant elements like Rb, Sr, Cu, Zn, Cd of Hf. Various methods for sample preparation, matrix separation and/or pre-concentration have been developed in the last decades, whereas fire assay and ion chromatography techniques are the most commonly used. However, these techniques are often time consuming and do not completely solve the problems of interferences, especially in low concentration ranges.

In the present work, matrix separation and on-line pre-concentration of platinum group elements was performed. It was found that a matrix separation step prior to the enrichment procedure is a prerequisite for accurate PGE analysis. Selective enrichment was carried out via retention on functionalized silica gels. Elution of PGE was achieved using complexing agents, organic solvents or inorganic acids. Quantification was done by isotope dilution mass spectrometry in the case of Pt and Pd. The concentration of Rh was assessed by external calibration. The highly sensitive method was applied to different biological and environmental samples, well known for their complex matrices. BCR-723 (road dust) served as reference material.

EVALUATION OF STRONTIUM ISOTOPE ABUNDANCE RATIOS AND STRONTIUM AMOUNT CONTENT BY MC-ICP-MS IN CIDERS FOR FOOD AUTHENTICATION
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Food authenticity is receiving an increasing interest since the knowledge of provenance of some foods and beverages is regarded as an additional warranty of their quality. Moreover, with the increasing mobility and low transport costs of goods in our society, there is some risk of frauds and mislabelling in products with a certified brand of origin and an efficient way to prove frauds is providing results from suitable analytical methods.

The strontium isotope abundance ratios have been widely studied for environmental tracing as well as for geochronological applications. Furthermore, values of Sr isotope abundance ratios were demonstrated not to change significantly during biological processes and Sr in plants reflects the environment of growth: bedrock and soil water [1].

Thus, the $^{87}\text{Sr}/^{86}\text{Sr}$ abundance ratio has been studied as a parameter to discriminate between wines of different origin if high precision measurements are performed, with a stated minimum measurement precision of at least 0.01% [2]. Such a precision can be achieved with a MC-ICP-MS, which offers a way to establish high precision isotope abundance ratios as long as the influencing parameters are understood and under control.

For the precise determination of Sr isotope abundance ratios, a separation of Rb from Sr is necessary prior to mass spectrometric analysis. This matrix separation is an adequate method for eliminating possible bias effect due to isobaric and molecular interferences such as $^{87}\text{Rb}^+$, $^{44}\text{Ca}^{40}\text{Ar}^+$ and $^{48}\text{Ca}^{40}\text{Ar}^+$ and it has been developed using Sr and Pb selective ion-exchange resins [3], after microwave digestion of the cider samples. Moreover, the separation efficiency was evaluated and possible mass dependent isotopic fractionations on the resin were investigated by using a certified isotopic reference material.

Strontium isotope abundance ratios of cider samples were determined using a standard-sample-standard bracketing method using the isotopic reference material NIST SRM 987. This external correction was compared with the internal correction using the $^{88}\text{Sr}/^{86}\text{Sr}$ ratio, assuming that the value is invariant in nature. The combined measurement uncertainty of the isotopic abundance ratio was evaluated.

Additionally, the measurement of the amount content of strontium and rubidium in cider by isotope dilution mass spectrometry (IDMS) was considered as a discriminating parameter, therefore the results obtained by both methods for the ciders originating from different regions will be discussed.

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A MULTIDIMENSIONAL HYPHENATION APPROACH FOR STUDYING
SPECIATION OF SELENOPROTEINS IN SELENIUM ENRICHED YEAST AND
SUN FLOWER ROOTS

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Speciation of selenium in terms of selenopeptides and selenoproteins in selenium enriched yeast and sunflower roots will be addressed. Interests in selenium speciation in selenoproteins stem from their role in defense mechanism in various diseases caused by oxidative attacks. In this study, a multidimensional hyphenation approach has been employed as an analytical tool. In the multidimensional hyphenation approach, several orthogonal chromatographic separation techniques are used in hyphenation with mass spectrometric detection. Initial screening of the seleno-species in the separated fractions by inductively coupled plasma mass spectrometry (ICPMS) offers an excellent synergistic effect to the structural characterization by molecular mass spectrometry. It saves the laborious task of going after each of the separated components amidst the myriad of peaks separated by chromatographic separation for selenium species. More over, very low detection capability and excellent sensitivity of ICPMS enable to identify selenium species unidentifiable by the molecular mass spectrometric detection systems.

MAYOR AND TRACE ELEMENTS ANALYSIS IN MILK FORMULAE BY ICP-OES USING MICROWAVE DIGESTION

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Milk formulaes are a daily intake, specially for children. In Mexico there is no specific Official Norm for the milk formulaes analysis. That was our reason to use a reference material to select the analytes.

The objective of the present work is to develop the appropriate method to quantify As, Ca, Cd, Fe, K, Mg, Na y Pb in milk formulaes in order to characterize them and to verify if the trace elements concentrations are not in a toxic level.

The ICP-OES technique, using axial and radial vision, provides the advantage to quantify the mayor and the trace elements simultaneously. The method development includes the optimization of the operation parameters for the ICP-OES as well for the microwave sample digestion.

As a quality control for the analytical results, the Reference Material DMR-277a of the “Centro Nacional de Metrología”, CENAM was used.

The reference material was spiked for As, Cd and Pb analysis (due to the fact than the low concentration were not detected reliably) and good recoveries were obtained: As 94%, Cd 86% and Pb 82% .

All the mentioned elements were simultaneously quantified using only a digestion method and the recovery related to the reference material were: Ca 100.7%, Fe 92.7%, K 100.2%, Mg 100.1% and Na 95.9%

According to the selected wavelengths no spectral interferences were present. The linear range and the recovery percentage is good enough for the mayor elements quantification and the detection limits obtained for: As 0.002 µg/g, Cd 0.004 µg/g and Pb 0.001 µg/g are low enough to analyze the spiked samples.

Five milk formulaes were analysed. As, Cd and Pb were not detectable and the concentration ranges for the other elements were as follows: Ca 5248-9271 µg/g, Fe 1.2-100.5 µg/g, K 7623.5-14315.0 µg/g, Mg 502.5-880.6 µg/g and Na 2386-5370 µg/g.

As conclusion we can be sure that the developed methodology allows to prepare the milk formulae sample with a single digestion and a single determination with the ICP-OES, obtaining reliable concentrations of the mayor and trace elements in a short period of time.

DISTRIBUTION ELEMENTAL PATTERNS AND PROTEIN
CHARACTERIZATION IN HUMAN AND FORMULA MILK WHEY AT
DIFFERENT LACTATION STAGES OF THE NEWBORN

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Human milk (or formula milk) is the sole diet during the first months of a baby's life. Human milk contains components necessary for a nutritionally and healthy diet by the newborn, especially for providing essential trace elements as well as relevant proteins and enzymes. Trace elements and organic compounds chemically interact quickly or are already linked together when being secreted by the mammary gland. It is known that total elemental composition and their distribution of maternal milk changes with postpartum time (1) from colostrum milk (day 1-3) to mature milk (day 14-28). Also, milk composition also changes depending on mother's pregnancy period (28-40 gestational weeks).

On the other hand today it is accepted that the bioavailability of trace elements from a given food depends on their chemical form. In human milk, trace elements normally exist in a form (species) which can easily be absorbed by the newborn infant (2,3). Therefore, only the knowledge on species present in milk will give adequate information on their metabolism and so on the nutritional value of the food.

Thus, the aim of this work was the development of a chromatographic method by coupling size exclusion chromatography (SEC) with ICP-(ORC)MS detection to study the binding patterns of essential and toxic trace elements (Fe, Cu, Zn, Se, Mn, Co, Cr, Br, I, P, S, Al, Cd and Pb) in human milk whey at four different lactation stages (colostrum, 4th, 14th and 28th day after delivery). The different elemental distributions along the lactation period are discussed and compared with those obtained for infant formulas commonly used to feed babies. Besides, our first attempts to identify and characterise, by using molecular techniques (MALDI-TOF, ESI-MS), some metal-biomolecules species present in milk whey will be presented

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SERUM TRANSFERRIN: AN INTRIGUING TRANSPORT PROTEIN FOR METALS

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Serum transferrin (Tf) is a primary member of the family of transferrins. It is a monomeric glycoprotein of 80 kD synthesized in the liver and found in human blood with a normal concentration of around 2,5 grams per liter.

Transferrins play a central role in the iron metabolism and transport of vertebrates and some invertebrates. Also, they may bind and transport many other cations at different oxidation states.

In the recent past we studied extensively the characteristics of Al-Tf human sera complexes (1) and we confirmed by HPLC-ICP-MS that Al-Tf and Fe(III)-Tf sera complexes at physiological levels are very similar in nature, as shown by Maitani's group in Al enriched human sera (2).

On the other hand, it is known that abnormal Tf isoforms, commonly referred to as carbohydrate-deficient-transferrins (CDTs), are excellent biochemical markers for congenital disorders of glycosylation and also for chronic alcohol consumption. As such CDTs are still able to bind one or two Fe(III) atoms per molecule we have investigated the usefulness of typical iron speciation strategies to develop a method of enough resolution and sensitivity for the determination of individual Tf glycoforms (CDTs).

Several hybrid methods have been optimised for this purpose: capillary electrophoresis (CE) and high performance liquid chromatography (HPLC) have been tested for the separation, while ICP-MS (with octapole reaction system) and UV-VIS molecular absorption have been assayed for on-line detection.

A detection limit of 4 nanograms per gram of iron associated to CDTs was obtained by HPLC-ICP-(ORS)MS which allowed the straightforward detection of S2, S3, S4 and S6 Tf glycoforms in healthy human serum after adequate iron saturation.

Finally, in an attempt to shed some light on the transport in the body of Vanadium compounds (used as insulin mimetic drugs) we will describe the use of Fast Protein Liquid Chromatography separation coupled to ICP-MS detectors to investigate V(III) and V(IV) associations to human serum Tf. The observed V-Tf distribution profile turned out to be very similar to those of Fe (III) and Al (III) associations.

Also, intact serum protein analysis by MALDI-TOF and VIS-UV absorption have confirmed that Tf is really the protein associated to the main Vanadium peaks observed in the HPLC-ICP-MS profiles.

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DETERMINATION OF SULPHUR COMPOUNDS IN LIQUID FUELS
BY GC-ICP-MS

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A significant source of atmospheric pollution is the emission of sulphur from the combustion of fuels. Sulphur is responsible for the acid rain, which increases the acidity of soils, damages plant and animal life, accelerates the corrosion of buildings, etc. Sulphur pollution also poses a risk to human health, as long-term exposure can lead to respiratory and cardiovascular illness. Currently, European Community directives concerning about the sulphur content of liquid fuels reflect the increasing concern about the effect of sulphur on the environment. In this vein, there will be a 10-fold decrease in permissible sulphur contents in petrol and 40-fold decrease in diesel fuel over the 12 year period 1993-2005.

There is a great variety of sulphur compound present in fuel which contribution to atmospheric pollution depends on their chemical nature and reactivity. Therefore, sulphur speciation provides important information and is an invaluable tool for environmental risk assessment. The combination of capillary gas chromatography (GC) and inductively coupled plasma mass, spectrometry (ICP-MS) has become an ideal methodology for speciation in complex samples such as fuel hydrocarbon matrices, as it combines the high resolving power of GC with the sensitivity and specificity of detection provided by ICP-MS. Nevertheless, due to the high background produce by $^{16}\text{O}^{16}\text{O}^+$ and $^{16}\text{O}^{18}\text{O}^+$ over ^{32}S and ^{34}S respectively, an ICP-MS equipped with a collision/reaction cell has to be used to overcome these spectral interferences.

In this work, an analytical methodology for the speciation of sulphur compounds present in fuel was developed. Collision/reaction cell parameters were optimised taking into account the natural sulphur isotope ratios ($^{32}\text{S}/^{34}\text{S}$) and maximising the signal to noise ratio of the species measured. Different sulphur compounds were studied and a methodology for the compound independent calibration of sulphur in fuel was developed.

SIMULTANEOUS DETERMINATION OF THE METALS POTENTIALLY
RELEASED FROM METALLIC PROSTHESIS IN BIOLOGICAL FLUIDS BY
HR-ICP-MS

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The failure rate of prosthesis and dental implants has decreased due to the improvements in orthopaedics techniques. Therefore, many people will be able to wear these metallic artefacts for longer periods. However, there are only a few long-term studies about the consequences of these devices on patient health. The main conclusion which can be extracted from those studies is an eventually metallic particle release. Although the extent and implications of this phenomenon are not well established, these solid particles are related with tumours, skin hypersensitivity, prosthesis loosening and other pathologies. These particles can be accumulated in the surrounding tissues of the prosthesis, transported to further organs by blood or excreted via urine. Due to the transport function of blood and urine, both biological fluids were studied as indicators of the possible release of metallic particles.

Most surgical prosthesis are made of different metal alloys, mainly based on Ti, V, Cr, Co, Ni and Mo. A reliable quantification of these metals in biological fluids represents a difficult task due to the low concentrations of these elements in biological fluids (only a few $\mu\text{g/L}$), the low volume usually available (i.e. in blood) and the presence of spectral interferences in the mass range under study. To overcome these difficulties a High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS) working at medium resolving power ($R=3000$) was applied after the development of a suitable and validated analytical methodology.

Patients were classified according to their type of prosthesis in three groups (two sorts of knee prosthesis and another of hip prosthesis). Urine and whole blood were collected into each group of patients implanted 1-2 years ago and from those implanted for more than 5 years. Concentration levels of Ti, V, Cr, Co, Ni and Mo in whole blood and urine of implanted patients were studied in order to find a correlation between the concentration of the metallic particles released and the time of exposure from the metallic artefact.

DETERMINATION OF HEXAVALENT CHROMIUM IN CEMENT BY THE USE OF
HPLC-ICP-MS, FPLC-ETAAS, SPECTROPHOTOMETRY AND SELECTIVE
EXTRACTION TECHNIQUES

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EU legislation recently issued the legislative document(1) prescribing the maximal allowed soluble Cr(VI) content in cement to be below 2 mg kg⁻¹. Since cement samples in general contain higher concentrations of Cr(VI) it is necessary to reduce the content of hexavalent Cr. The recommended analytical technique for the determination of Cr(VI) in cement is spectrophotometry(1). In order to fulfill the requirements of the new EU legislation, reliable analytical techniques should be applied. The aim of the present study was to compare the data of various analytical techniques and to estimate their abilities for the determination of Cr(VI) in cement. For this purpose seven cement samples containing high and low Cr(VI) concentrations have been analysed by the use of HPLC-ICP-MS, FPLC-ETAAS, 1,5 diphenylcarbazide spectrophotometry and selective extraction of Cr(VI)-HCl complex into methyl isobutyl ketone (MIBK). Cement extracts were prepared in duplicate from 10.0 g of sample that was mixed with 40 mL of water, shaken (300 rpm) for 15 min and filtered through 0.45 micrometer filter(1). Aliquots of samples were used for the speciation analysis. The accuracies of the analytical procedures were checked by the spiking of extracting solutions. HPLC-ICP-MS analyses were performed using Dionex IonPac CG5A-CS5A columns connected on line to Elan 6000 ICP-MS. Cr(VI) was eluted with 0.35 mol L⁻¹ nitric acid with a flow rate 1 mL min⁻¹. The chromatographic run was completed in 3 min. FPLC-ETAAS procedure was carried out on an anion-exchange FPLC column Pharmacia applying linear gradient elution from 0-100% of 0.5 mol L⁻¹ NaCl for 15 min at a flow rate of 1.0 mL min⁻¹. The separated Cr species were determined "off line" by ETAAS in 0.5 mL fractions. Spectrophotometric Cr(VI) determinations were performed after addition of 1 mL of 1,5-diphenylcarbazide (dissolved in acetone) and 1 cm³ of phosphoric acid to cement extract and measurement of the absorbance at 540 nm after 15 min. Selective MIBK extraction procedure based on formation of Cr(VI) complex with HCl at 40°C followed by extraction into MIBK and determination of Cr(VI) in organic phase by FAAS. Data indicated good agreement of results between all techniques the differences did not exceed 10%. With exception of selective extraction procedure all techniques applied are accurate (recoveries of spiked samples lied between 95 – 105%) and of adequate sensitivity. MIBK extraction procedure exhibited limitations in cement samples that were treated with reducing agents due to the gel formation in the organic phase. Because of that reason MIBK extraction procedure may not be recommended for the analysis of cement samples. Due to its accuracy, high sensitivity and the highest speed of the analysis HPLC-ICP-MS procedure could be recommended as a technique of choice. However, FPLC-ETAAS and 1,5 diphenylcarbazide spectrophotometry may also be applied as a reliable techniques for the determination of Cr(VI) in cement samples and cement samples treated with reducing agents.

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1 Industrial regulations for hazardous materials, TRGS 613, issue October 2002

ARSENIC SPECIES IN FRESHWATER ORGANISMS FROM THE RIVER DANUBE

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Arsenic bioaccumulates in many marine organisms resulting in higher levels of this element in crustaceans, bivalves and fish than in most other foods. The number of arsenic speciation studies has been quite large during the last decades, since the toxicity of arsenic highly depends on the chemical form in which it is present. It is well known that marine fish contain high concentrations of arsenobetaine (AB), a non toxic species, and that arsenic in marine algae is present mainly as arsenosugars. In Hungary and many other countries, however, the most commonly consumed fish are freshwater species, but there are surprisingly few data on arsenicals in freshwater organisms.

The aim of our work was to determine the total arsenic concentrations and the arsenic species in a range of organisms from a freshwater ecosystem. The samples, including water, plants, algae, mussels, and fish were collected in Hungary from the river Danube during July 2004. All biological samples were freeze-dried and ground to a powder. For total arsenic determinations in the biological samples microwave-assisted digestion with HNO₃ was performed.

Arsenic concentrations in water were 1.1-1.9 µg As L⁻¹. The highest arsenic concentrations were found in mussels (9.4-11.6 mg As kg⁻¹ dry mass), algae (4.9-9.4 mg kg⁻¹) and plants (1.2-6.9 mg kg⁻¹), whereas the fish samples contained much lower concentrations (0.24-1.2 mg As kg⁻¹ dry mass).

Water extraction was used as the sample preparation method, and the identification and quantification of arsenic species was carried out by HPLC-ICPMS employing anion- and cation-exchange chromatography. Arsenosugars were found as the main arsenic compounds in our freshwater green algae. The dominant arsenic species in the plants, however, were inorganic arsenicals. In the case of sponge and sedge (a type of grass) the tetramethylarsonium cation (TETRA) was detected as a minor arsenic compound. In the fish extracts inorganic arsenic and arsenosugars, including a recently reported thio-arsenosugar, were identified, and AB was found only in traces. The mussels contained mainly arsenosugars, and two thio-arsenosugars were also present. In all cases a significant (20 % of total As) unknown peak was detected in the mussel extracts.

DOWNSCALING SAMPLE INTRODUCTION TECHNIQUES FOR
INTERFACING NANO-VOLUME FLOW INJECTION AND CAPILLARY
LIQUID SEPARATION TO ICP-MS

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A recent trend towards miniaturization in several scientific disciplines has also reached analytical chemistry and spurred the development on micro- or nanoliter sample volume analysis and miniaturized liquid separation techniques [1]. Microanalytical techniques coupled with increasingly sensitive ICP-MS offer new tools for trace element determination and elemental speciation analysis when only an amount of few milligrams of a rare, toxic or radioactive sample is available. This is of particular interest in bioanalytical chemistry, where the amount of sample material from a biological tissue or a body fluid is limited. Recent progress in the development of total consumption micronebulizers for ICP-MS allows the complete introduction of nanoliter sample volumes into the ICP-MS. Moreover this technique enables the interfacing of capillary separation techniques to ICP-MS. The advantages to carrying out liquid separations in capillaries with inner diameters of less than 300 μm are obvious: high separation efficiency is combined with low solvent consumption and small sample volumes while the hyphenation to ICP-MS offers high sensitive element-specific detection.

This contribution discusses the current development status of nano-volume sample introduction into ICP-MS based on the combination of a total consumption micronebulizer with a single-pass low volume spray chamber allowing the complete transport (no drain) of flow rates of 0.5 – 7 $\mu\text{L min}^{-1}$. Approaches for interfacing nano-volume flow injection as well as capillary and nano liquid separation techniques with ICP-MS will be presented. Applications on flow injection of 50 nL radionuclides samples show the highest absolute detection limit ever reported for uranium and plutonium on the attogram level. The interface developed for capillary/nano reversed phase HPLC allows sensitive element-specific (ICP-MS) detection in organic-rich mobile phases and be operated without draining, cooling, makeup liquid, or addition of oxygen to the plasma. The analytical performance including detection limits, precision and peak shape will be demonstrated for selenopeptide separation from only 10 nL sample volume. Approaches for quantitative analysis will be discussed.

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ADAPTION OF THE SHIP-OES-TORCH TO A CONVENTIONAL ICP-MS

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KLOSTERMEIER and BUSCHER developed a new torch design for inductively coupled plasma optical emission spectrometry, which allowed to operate the plasma discharge at very low gas flow rates (SHIP, Static High Intensity (IC)P) [1]. The main characteristics of a SHIP-torch are a new geometry and an external air cooling system. With this system the total argon consumption of a 27.12 MHz plasma could be reduced to 0.6 Lmin⁻¹ while the obtained figures of merit were very well comparable to those obtained with a conventional ICP-OES system [2].

Based on this concept BUSCHER et al. investigated the analytical potential of the SHIP when coupled to a mass spectrometer [3]. Therefore the SHIP-torch, including the external air cooling system in the torch fastening, was modified to fit into a conventional ICP-MS-system (VG PlasmaQuad II). While the torch geometry was adjusted to fit the necessities of the interface to the mass spectrometer, the basic geometry of the torch remained the same as in the newly developed SHIP-OES-system. It was possible to operate the plasma discharge at 0.6 kW RF power and a plasma gas flow rate of 1.5 Lmin⁻¹ to investigate the mass spectrum of a multi elemental standard solution. An ultrasonic nebuliser was used as sample introduction system and the ion signals were observed for different nebuliser gas flow rates from 0.2 to 0.9 Lmin⁻¹. The results were compared to those obtained with the conventional ICP-MS setting.

It can be concluded that the SHIP is not only a promising system in optical emission spectrometry, but can be used also in ICP-MS allowing significant reduction of system operating costs.

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THE DIRECT DETERMINATION OF ARSENOLIPIDS IN BIOLOGICAL SAMPLES WITH HPLC-ICPMS

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Lipid soluble arsenicals (arsenolipids) occur in a wide range of biological samples where they may play a key role in the biosynthesis of organoarsenic compounds from inorganic arsenic. Although these lipid-soluble arsenicals can reach concentrations up to 95% of the total As, only very little is known about their chemical structure. So far, only one lipid-soluble arsenical has been rigorously identified, namely a phosphatidylarsenosugar isolated from a brown alga.¹ Further progress in this area of arsenic speciation has been hindered by lack of suitable analytical procedures – routinely employed analytical techniques such as HPLC-ICPMS are generally restricted to aqueous mobile phases, and hence are not suitable for the arsenolipids. The determination of lipid-soluble arsenicals is an analytical challenge but, if achieved, is likely to open up a new area of arsenic speciation research. We present our preliminary results on the analysis of arsenolipids in fish oils, including their direct determination by HPLC-ICPMS.

As a source of arsenolipids, we used 10 fish oils from various regions of the world and a lipid extract from a marine alga. Total arsenic analyses on the fish oils were performed by acid digestion with microwave-assisted heating followed by measurement with ICPMS, and gave concentrations from ~ 4 to 11 mg As kg⁻¹. Less than 5% of the total As was extracted (hydrolysed) with water at room temperature – extraction (hydrolysing) efficiency increased to 22% with hot water (70 °C). The dominant arsenic species in all water extracts was dimethylarsinate. Base hydrolysis experiments were then performed on one of the fish oils and the water-soluble products were analyzed by HPLC-ICPMS. Hydrolysis with 1 mol L⁻¹ KOH rendered water soluble about 90% of the total As. HPLC-ICPMS of these fractions produced two major peaks (dimethylarsinate and methylarsonate) that collectively accounted for 50% of the total As.

We then analyzed the intact arsenolipids with a modification of the method² developed for the determination of phospholipids with HPLC-ICPMS. Organic solvent load to the plasma was reduced by chilling the spray chamber to –5 °C, and oxygen was added to the plasma to prevent carbon deposition on the interface cones. All of the ten fish oils contained at least five major arsenolipids, but in varying amounts depending on the origin of the fish. The algal extract contained arsenolipids similar to those found in the fish oils in addition to some other arsenolipid species. This study shows for the first time the direct determination of intact arsenolipids with HPLC-ICPMS.

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DEVELOPMENT AND APPLICATIONS OF MULTIPLE ION COUNTING –
ICPMS AND -TIMS

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Laser Ablation in combination with MC-ICPMS has evolved to become a useful analytical technique for precise in situ isotopic analysis. The same is true for multicollector TIMS instruments coupled with the microdrilling technique to extract the sample volume from a small scale. However, most of today's multicollector instruments are still using Faraday detectors and for small sample sizes the attainable precision is limited by both: the noise level of the Faraday detectors and the stability of the background. Ion counting overcomes the noise limit and high mass resolution is the key to discriminate against molecular interferences to clear up the background. Both features open the door to expand the analytical power of these instruments to smaller sample sizes.

We have developed a special setup of miniaturized Multiple-Ion-Counters (MIC), which are identical in size to and interchangeable with the standard Faraday detectors of the multicollectors of both instruments, the Finnigan NEPTUNE multicollector ICPMS and the Finnigan TRITON multicollector TIMS. In total, 9 Faraday Cups plus 8 MIC channels can be installed simultaneously at any position in the collector array. The mass dispersion of the variable multicollector array is large enough to measure U isotopes on the high mass side and all Pb isotopes and Hg on the low mass side at unit mass separation. This makes the Finnigan NEPTUNE a powerful tool for in-situ analyses of zircons using multiple ion counting detectors and Laser ablation. An overview of other possible applications like Hf isotope systematics in old garnets, disequilibrium studies by precise determination of $^{234}\text{U}/^{235}\text{U}$ and $^{230}\text{Th}/^{232}\text{Th}$ on ng-sample sizes and forensic investigations of nuclear material. If proper cross calibration of the ion counters is ensured during the measurements precisions of 1‰ can be achieved.

IODINE SPECIATION STUDIES IN COMMERCIALY AVAILABLE SEAWEED
BY COUPLING DIFFERENT CHROMATOGRAPHIC TECHNIQUES WITH UV
AND ICP-MS DETECTION

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Iodine is an essential micromineral for human nutrition. Iodine deficiency leads to goiter and various disorders associated with growth and development like dwarfism, mental retardation and neuromuscular defects, commonly referred as Iodine deficiency disorders (IDD). In order to prevent iodine deficiency disorders, supplementation of foodstuff with iodine is commonly practiced. The consumer preference of natural products over artificial ones provides impetus for studying seaweed as source of iodine as seaweeds like *Hizikia* (Hiziki), *Undaria* (Wakame), *Laminaria* (Kombu) and *Porphyra* (Nori) are known to accumulate exceptionally high quantities of iodine available from the sea. As bioavailability and also toxicity of different form of iodine is species dependent, total analysis and characterization of iodine species in seaweed is an important pursuit.

In present study, speciation of iodine in commercially available commonly consumed seaweed samples was performed using a multidimensional chromatographic approach coupled with inductively coupled plasma mass spectrometry (ICP-MS) for element specific detection. Size-exclusion chromatography coupled to ICP-MS indicated the association of iodine in both high as well as low molecular weight fractions in Wakame while in case of Kombu, only low molecular weight iodine species were found. Likely association of iodine with protein as well as polyphenolic species was indicated in case of Wakame. Anion-exchange chromatography coupled to ICP-MS confirmed that the most predominant inorganic iodine species present in both type of seaweeds is iodide. Protein bound iodinated species were hydrolyzed by enzymatic digestion using Proteinase K. Analysis of the hydrolysate using reversed-phase HPLC-ICP-MS revealed the presence of monoiodotyrosine and di-iodotyrosine in Wakame, which was confirmed by matching the chromatographic retention time with the retention time of commercially available standards.

DEVELOPMENT AND APPLICATION OF HEADSPACE SPME-GC/ICP-MS FOR
ANALYSIS OF PHOSPHORIC ACID TRIESTERS IN HUMAN PLASMA

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Phosphoric acid triesters are widely used as flame retardants and plasticizers in variety of products ranging from electronic equipment, building-materials, lubricants, glues and poly(vinylchloride). This class of compounds consists of alkylated or arylated phosphate including the related compounds such as halogenated esters and related diphosphate esters. Their semi-volatile nature and non-covalent addition to materials make them an omnipresent pollutant. Some of the alkylphosphates, like tributyl phosphate and triphenyl phosphate are neurotoxic, while others like tris-(2-chlororethyl)-phosphate show carcinogenic properties.

One of the major uses of organophosphorus triesters such as triphenyl-phosphate is their use as flame retardant/plasticizer in synthetic plastic poly(vinyl chloride) which is commonly used in human plasma storage bags. In 2001 and 2003 Jonsson *et al.* reported the presence of triphenyl-phosphate and ethylhexyldiphenyl-phosphate in human plasma at ~100 parts-per-billion levels using rather time-consuming liquid-liquid membrane extraction combined with electron impact ionization GC/MS. Levels of phenylphosphates found in human plasma are of the same magnitude as their haemolytic EC₂₀ values, which is of enormous significance for the medical treatment of patients who have a large portion of their plasma exchanged for this type of donor plasma. With regard to this, a more thorough investigation of commercial whole blood collection bag systems is therefore needed.

Leaching of the triphenylphosphate and related species has not been extensively studied with the respect to the plastic bag contact time or blood type. In the present study solvent-free headspace solid-phase microextraction technique is used for the extraction and preconcentration of phosphate esters from the drug free human plasma samples previously stored in the standard poly(vinyl chloride) bags. GC coupled to ICP-MS for phosphorus specific detection of the compounds was performed for separation and monitoring the compounds. ICP-MS offers lower detection limits as compared to electron impact ionization MS among with the phosphorous-selective detection, which is an attractive alternative to the existing methods. Preliminary studies confirm the presence of triphenyl phosphate in drug free human plasma, which will be further validated by SPME-exact mass GC/time-of-flight mass spectrometry.

CLS-ICP-MS: COINCIDENCE LASER SPECTROSCOPY FOR ION DETECTION
IN ICP-MS – WILL IT WORK?

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The introduction of ICP-MS has brought about fundamental changes in the role played by atomic spectrometry within analytical science. The ability to determine isotopic composition and to provide molecular information when coupled to separation techniques has caused it to have a major impact in the bio-sciences and that role is about to expand further in the fields of genomics and proteomics. One could make the claim that ICP-MS has been responsible for the re-marriage of atomic spectrometry with main stream chemistry.

The ultimate limits on the performance of ICP-MS are set by the relatively poor transport of ions from the plasma to the detector and interferences. Much progress has been made in dealing with spectral interferences through the advent of high resolution instruments and chemical resolution employing collision/reaction cells. Each of these approaches has advantages and disadvantages and they are essentially complementary. Even so ICP-MS does not offer the kind of discrimination that techniques such as AMS or RIMS do where isobars are almost completely removed, and more importantly, abundance sensitivities approaching E-14 can be achieved (isotopic abundances of long lived radio isotopes often occur in the range from E-12 – E-16).

One way of addressing the issues of isobars and abundance sensitivity, and thereby extending the performance of ICP-MS, would be to introduce selectivity into the ion detection step. This paper describes a theoretical study of an instrument that employs coincidence laser fluorescence spectroscopy, CLS-ICP-MS, for ion detection. The modelling demonstrates the feasibility of this approach, but also the limitations, a key issue being the ion energy distribution of ions derived from the plasma.

THE ASSESSMENT OF NORMAL ELEMENTAL CONTENTS IN HUMAN HAIR

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Human hair is a sensitive indicator of the elemental status of an organism and can serve for medical diagnostics purposes. On the other hand it is well known that the lack as well as an excess of chemical elements in human organism leads to a serious problems in health disorder. Therefore a lot of doctors use an information about essential elemental content in biological substrates (blood, urine, hair etc.) for the diagnostic purposes. The most informative and available clinical substrates are a blood serum and hair. In the worldwide practice of serum blood and hair analysis an atomic-emission spectrometry with different sources of excitation is used to provide an overview data.

In frame of the present work an assays of Ca, Mg, Cu, Zn, Fe and P simultaneous determination in serum blood and hair by atomic-emission spectrometry with direct current plasma arc excitation DCP-arc AES has been developed.

The sample preparation a calibration procedure using a unified method of graphite collector analysis in the presence of intensifying additive has been elaborated.

The accuracy control was realized by the comparison with the results of independent method. The method allows simultaneously determine Ca, Cu, Mg, Fe, P and Zn at the level of 0.1-100 mg/L. Relative standard deviation was determined; it was 10-20% for different elements. The AES method may be recommended as a review method to evaluate the element at status of the organism.

The assessment of the levels of elements in hair and serum blood of 22 practically healthy individuals (blood-donors from the Meshalkin Institute of Pathology of the Blood Circulation). An elaborated method was applied for the estimation of the normal elemental status of human serum blood and hair. The ranges of the concentrations of a number of elements in the hair typical for this region are determined. Obtained data may be used for diagnostics of a number of the diseases originating from mineral exchange disturbance. The correlations between the Cu and Pb as well as between Fe and P contents in hair was revealed.

HOLLOW CATHODE ION SOURCE FOR THE ELEMENTAL ANALYSIS OF SOLIDS

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Still recently the glow discharge mass spectrometry was widely used for the elemental analysis of solids. However now interest to this analytical method has appreciably decreased. In article the reasons of such situation are analyzed. Main from them consists in imperfection of a used source with planar (or quasiplanar) electrodes configuration. For last 25 years it has not undergone essential changes.

In work the new glow discharge ion source on the basis of a hollow cathode is offered. The offered source can function at much big discharge currents, creating more dense plasma, than in earlier used source. In a combination with Pierce ion optics the source allows to increase a mass spectrometer illumination and, accordingly, sensitivity of a method approximately by two orders of magnitude.

In work the reasons of a high background of a glow discharge source are considered. It is established, that a background level of a source is determined by films of waters, gases and the hydrocarbons adsorbed on internal surfaces of a discharge chamber. It is offered for reduction of a background of hydrocarbons and adsorbed gases by 3-4 order to use a complex of methods: to increase a discharge current up to 100 mA, to use effect of plasma "stopper" in a hollow cathode, to apply a gettering effect in an ion source.

The developed source allows expanding a circle of analyzed substances considerably. In particular it can be used for the elemental analysis of liquids and non-conducting solid substances with high sensitivity.

CHARACTERIZATION OF A VERY LOW POWER ARGON CAPACITIVELY COUPLED PLASMA

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The very low Ar capacitively coupled plasma (10 MHz, 5 – 70 W) at atmospheric pressure could be sustained at low gas flow rates (0.1 – 2 L.min⁻¹) on a sharp conducting electrode [1]. The plasma and the electrode are the intrinsic part of the resonant circuit of the free-running RF oscillator. The Ar plasma was characterized from four points of view: stability, plasma parameters (temperatures and electron number densities), spectral emission and the influence of the plasma on the waveform of the RF oscillations.

The stability diagram was obtained by observation of the behavior of the plasma as function of gas flow rate and plasma power. Six different regions were identified, the most important of them being the region of stable plasma. This state offers the optimum conditions for its characterization.

The characteristic temperatures (excitation, ionization, rotational and ion temperatures), electron number densities and intensity ratio of ion and atom lines were experimentally determined using Ar, Pb, Cu, Fe, OH and Ca emission lines. The influence of easily ionisable elements (Na, K, Li, Ca, Sr, Mg) on physical characteristics was also investigated. The OH molecular experimental spectra were compared to the computer simulated spectra using appropriated software.

The presence of the plasma inside the resonant circuit of the RF oscillator determines the change of the RF oscillations waveform. By Fourier analysis of the oscillations waveform in the absence and in the presence of the plasma were identified the high order harmonics absorbed by the plasma and was estimated the medium ion number density.

This plasma could be used as spectral source for the analysis of pneumatically nebulised liquid samples or direct analysis of nonconductive solid samples via atomic emission spectroscopy technique [2].

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INVESTIGATION OF A MEDIUM POWER RADIOFREQUENCY
CAPACITIVELY COUPLED PLASMA AND IT'S APPLICATION TO HIGH-
TEMPERATURE SUPERCONDUCTOR ANALYSIS VIA ATOMIC EMISSION
SPECTROMETRY

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A medium power radiofrequency capacitively coupled plasma (275 W, 27.12 MHz) sustained with low argon consumption (0.7 Lmin⁻¹) using a coaxial-annular geometry (Mo tube / two brass counterelectrodes, DRTRFCCP) [1, 2] was investigated to be used for the analysis of high critical temperature Bi based superconducting materials in order to determine their stoichiometric composition.

The optimum experimental parameters (observation height, Ar flow rate, matrix interference) were established. Matrix effect of Ca²⁺ and Sr²⁺ and their influence on analytical signals and detection limits of the significant metals (Pb, Bi, Ca, Sr, Cu) are presented. It was found that the Sr ion has a more significant influence on the studied parameters than Ca ions.

Each of the relevant metals from the superconducting materials could be analysed and determined successfully Under optimum operating conditions of the DRTRFCCP torch (6 cm between the ring electrodes) detection limits of 3 ng mL⁻¹ for Ca, 4.6 ng mL⁻¹ for Sr, 16 ng mL⁻¹ for Cu, 80 ng mL⁻¹ for Pb and 460 ng mL⁻¹ for Bi were found.

The operating parameters and figures of merit of the investigated plasma torch were compared to those of other plasmas used in atomic emission spectrometry for similar applications.

High critical temperature Bi baesd superconductors with certified chemical composition were analysed by DRTRFCCP-AES and a good agreement was obtained between analysis results and the certified values.

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A NEW HIGH PRESSURE GLOW DISCHARGE PULSED ATOMIZER FOR ZEEMAN SPECTROMETRY

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This work devote to investigation of a new glow discharge atomizer for Zeeman atomic absorption spectrometry. The atomizer can work with relatively high argon pressure. This case sensitivity of technique increases in high degree.

A sensitivity of the system in high degree is determined by rare gas pressure (dependence of the sensitivity from pressure is linear). But for longitudinal geometry of hollow cathode (cathode placed along optic axis, optical axis is orthogonal to magnetic field – the field is necessary to form analytical signal in Zeeman spectrometry) if pressure exceeds 16-20 (for Mo or Nb – the cathode was made from these metals) a temperature of Thin-Walled Metallic Hollow Cathode (TMHC) surface (and charged particles flows) in discharge become heterogeneous in high degree. This case rate of sputtering is decreased in many times. The heterogeneous is determined by thermoelectronic emission from TMHC surface and magnetic field influence. But heterogeneity of discharge can be decreased in high degree if cathode axis is turned on 90 deg. This case discharge pressure one can increase up to 100 torr, because this system have radial symmetry relatively cathode and magnetic field axis. Sensitivities were increased to – up to 5-7 times.

Liquid samples (10-20 ul) were introduced in cathode through quartz capillary placed in niobium capillary. Detection Limits were determined for As, Mn, Pb and Cd. Appropriate values are: As – 5 ppb, Mn – 0.3 ppb, Pb – 0.35 ppb, Cd – 0.04 ppb.

Besides solution this system was used for determination of the elements in air aerosols. Sampling air sucked through niobium capillary (rate – 0.75 l/min) and precipitated on inner cathode surface with aid of impact precipitation. Efficiency of precipitation was measured with aid of comparison with electrostatic precipitation technique. Appropriate values are in range 70 -75% for different elements. Detection Limits for some elements are: Mn – 0.2 pg/l, Pb – 0.3 pg/l and Cd – 0.15 pg/l. Appropriate precipitation time was 20 min.

Processes in pulse glow discharge in TMHC for relatively high pressure are discussed in the presentation.

SIGNIFICANCE OF ISOBARIC INTERFERENCES IN HF ISOTOPIC ANALYSIS OF GEOLOGICAL SAMPLES

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Isotopic composition of Hf in accessory minerals can be used as a tracer of various geological processes in the Earth's crust. Due to the high first ionisation potential of Hf, the ICP mass spectrometry is the method of choice for analysis of Hf isotopic composition. Natural variation of Hf isotopic composition, namely the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in geological materials, is primarily due to the ^{176}Lu decay to ^{176}Hf with a half-life of 35.7 billion years. High precision of isotopic measurements is often required because the Hf isotopic variations are commonly less than a fraction of permil. One of the most important factors affecting the precision and accuracy of $^{176}\text{Hf}/^{177}\text{Hf}$ measurements are the isobaric interferences of ^{176}Yb and ^{176}Lu on ^{176}Hf . The interferences can be avoided by chemical separation and purification of Hf prior to the Hf isotopic analysis on ICP mass spectrometer. Geological samples with high Hf/REE ratios, such as the mineral zircon, can also be analyzed without previous chemical separation of Hf (e.g. by laser ablation) with subsequent mathematical correction for REE isobaric interferences.

On-peak subtraction of ^{176}Yb and ^{176}Lu signal intensities from ^{176}Hf intensity is the most widely used procedure to correct for isobaric interferences. The non-interfering isotope intensities of ^{172}Yb and ^{175}Lu and the known isotopic abundance of Yb and Lu are used to calculate the signal intensities of ^{176}Yb and ^{176}Lu . The uncertainty in Yb and Lu isotopic abundance represents the main source of error on the interference-corrected Hf isotopic ratios. For example, Chu et al. (2002) obtained a value of $^{173}\text{Yb}/^{171}\text{Yb}$ of 1.132685 which is by $\sim 2.7\text{‰}$ different from the IUPAC value of 1.129552 and well outside the analytical uncertainty ($< 0.1\text{‰}$). Such variation might have a significant effect on the accuracy of Hf isotopic measurements, especially in samples with low Hf/Yb ratio.

We will demonstrate how the uncertainty in natural isotopic composition of interfering REEs can affect the accuracy of laser ablation ICPMS measurement of Hf isotopic composition in accessory minerals (such as zircon or baddeleyite) with high Hf/REE (Hf/Lu and Hf/Yb are ~ 1000), and low Hf/REE (Hf/Lu and Hf/Yb are ~ 20). We will also discuss the possible improvements in analytical precision and accuracy of laser ablation ICPMS measurements of Hf isotopes.

Chu NC, Taylor RN, Chavagnac V, Nesbitt RW, Boella RM, Milton JA, German CR, Bayon, G, and Burton K, JAAS 17, 2002, 1567.

THE USE OF DOPPLER BROADENING TO DETERMINE GAS TEMPERATURES IN A GLOW DISCHARGE SOURCE

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The profile of atomic spectral lines emitted by the plasma gas in a Grimm-type glow discharge is dominated by Doppler broadening, so that, in principle, the gas temperature can be determined from the line width. Some of the lines observed in the atomic spectra of argon and neon are transitions to metastable and quasi-metastable levels (the ArI $3p^54s$ levels and NeI $2p^53s$ levels) so that these lines are liable to self absorption and self reversal. Great care is therefore needed in the choice of lines used for temperature measurement.

Spectra emitted by a Grimm-type source using various plasma gases have been recorded with a vis-u.v Fourier transform (FT) spectrometer with a limit of resolution of 0.030 cm^{-1} . The limit of resolution of an FT spectrometer is independent of wavelength so that the chromatic resolving power falls at longer wavelengths. It was therefore necessary to make a correction for the instrumental profile when measuring argon lines above about $\sim 600\text{ nm}$; below this wavelength and for all neon lines the correction was negligible. Some of the argon lines and many of the neon lines exhibited self-reversal when pure inert gas was used, but, as has previously been reported, when small amounts of hydrogen or nitrogen (up to 2 % v/v) were added to the plasma gas, the self reversal was reduced, indicating a reduction in the metastable population.

In the present work, we have measured the "half width" (i.e. full width at half maximum intensity, FWHM) of many atomic lines of inert gases, using a pure inert gas as the plasma gas, and have calculated the gas temperature from those lines whose profile appears to be Gaussian. The values show a large scatter. We have compared the results obtained using controlled additions of nitrogen and hydrogen, between 0.01 and 2 % v/v. The gas temperature calculated from the narrowest lines is independent of the added gas, i.e. the molecular gas does not change the gas temperature, and the temperatures calculated from other lines fall towards this value as the amount of molecular gas is increased. This shows that even where lines apparently fit a Gaussian profile well, the peak intensity may be reduced by self absorption, leading to a higher FWHM.

These studies allowed us to choose the lines most suitable for temperature measurements with pure plasma gases and showed that, under typical operating conditions for a Grimm source, the Ar I 696 nm line, used in some work for the measurement of gas temperature, may give a value higher than the true temperature. The chosen lines have been used to investigate the dependence of gas temperature on discharge conditions and, using side-on observation, the distance from the cathode.

PERFORMANCE OF A TUNABLE CONCENTRIC PFA NEBULIZER FOR ICP-MS SPECTROMETRY

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Low-flow (100 microliter/min or less) nebulizers are widely used for liquid sample introduction for ICP-MS spectrometry. This low-flow capability combined with inert construction of fluoropolymer components such as PFA (perfluoroalkoxy) is very useful for volume-limited and / or highly corrosive samples such as in the semiconductor industry or geology.

Important operational issues with low-flow nebulizers include clogging of the narrow capillary, stoppage of sample uptake due to trapped air pockets, and the difficulty or impossibility of capillary adjustment relative to the nebulizer gas orifice. In the event of an intractable nebulizer problem, replacement of the entire nebulizer can be expensive.

A new tunable concentric PFA nebulizer design incorporates a novel adjustable outer body, while the capillary remains in a fixed position. This feature allows simple adjustment of the nebulizer gas orifice relative to the fixed capillary. In addition, a clogged or damaged capillary can be easily replaced with a new one; the original nebulizer body can be retained at a considerable cost savings versus a complete new nebulizer.

Figures of merit to be presented for the nebulizer include raw ICP-MS sensitivity, signal stability, and detection limits. Data will also be shown with the nebulizer coupled to a desolvating membrane system.

A COMPARISON OF THE PERFORMANCE OF KINETIC ENERGY
DISCRIMINATION AND REACTIVE INTERFERENCE REMOVAL FOR THE
DETERMINATION OF TRACE AND ULTRATRACE ELEMENTS IN
SEAWATER BY COLLISION/REACTION CELL ICP-MS

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Seawater is a complex matrix for analysis by ICP-MS as it typically contains around 3.5% of total dissolved solids, mostly as common salt. This causes analytical problems in the form of physical and polyatomic interferences. Dilution is normally necessary in order to overcome the physical interferences, exacerbating the problem of confident determination of the typically exceedingly low concentrations of analytes of interest. Polyatomic interferences remain after dilution and can severely hamper accurate determination of many analytes.

The use of collision/reaction cell can be applied to this analysis in order to improve many interference situations. In recent years two distinct cell operation approaches have become well documented: reactive removal and removal by kinetic energy discrimination. The former utilises ion-molecule reactions between the polyatomic interference species and a reaction gas flowing into the cell. The aim is for the reactions to result in a change of mass-to-charge ratio of the interfering species so that it no longer coincides with the mass of interest, or to promote the loss of charge from the interfering species to prevent its observation. The latter process often utilises an inert gas such as helium. It differentiates the plasma-based polyatomic ions from the analyte ions by taking advantage of ion energy differences attributed to differing collision frequency along the cell path-length caused by larger ionic radii for polyatomic ions. The transmission of the lower energy polyatomic species can be discriminated against by the use of a stopping potential between the cell multipole and the analyser quadrupole.

The two approaches were evaluated and compared for the analysis of seawater samples. The use of the reactive approach is highly effective at removing specific interferences, but since the removal is dependent upon reaction chemistry, the performance is highly dependent on the cell gas of choice for a particular interference. The use of kinetic energy discrimination is also shown to be extremely effective with the use of an inert gas and has the advantage of offering a single set of conditions that can produce benefits for multiple analytes. The combination of both approaches is also demonstrated to give excellent results since kinetic energy discrimination provides a simple method of stopping the transmission of charged cell-reaction products.

COMPARISON OF DRC AND HR ICP-MS TECHNIQUES IN THE
DETERMINATION OF PLATINUM IN URINE

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In recent years the increasing use of Pt both in medical and industrial applications caused its growing anthropogenic emission and spread in the environment.

In fact, Pt is released in the atmosphere by exhaust catalytic converters and Pt-compounds are often used in antitumoral therapies and, as consequence, significantly present in the waste waters of the hospitals. This fact could bring to a general increasing exposure to Pt, especially in the urban areas.

It is therefore evident the necessity of determining the reference values of Pt in the normal population, with suitable procedures able to achieve adequate analytical performances.

Many authors have already reported Pt data, but methods of Pt determination in biological fluids very often lack of information about the uncertainty of the results, in particular if we consider the low concentration of Pt in urine of non-exposed subjects.

In this work, urine Pt levels in the general population of a north Italian region were determined by means of both DRC and HR ICP-MS systems. The two procedures were validated and the respective expanded uncertainties were calculated.

The detection limits of the procedures adopted were about 0.5 ng/L in urine samples.

The average concentration observed was below 20 ng/L, while the relative combined uncertainty at these levels of concentration resulted 25-30%.

These data are in good agreement with those reported in literature for similar studies.

DETERMINATION OF REFERENCE VALUES OF BA, CS, SB AND W IN
URINE BY MEANS OF HR AND DRC ICP-MS INSTRUMENTATION.
COMPARISON OF ANALYTICAL PERFORMANCES AND MEASUREMENT
UNCERTAINTIES.

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The determination of reference values in biological fluids is a hard task for analytical laboratories for many reasons:

- Very low detection limits are required
- Analytical methods should be adopted in order to reduce the sample manipulation
- Low levels for the blanks have to be assured both in terms of absolute value and variability

Many authors have reported the possibility of determining the metallic species in biological fluids by ICP-MS, but very few articles could present their data with a robust evaluation of the analytical performances of the proposed methods, in terms of assessment of the uncertainty of measurement.

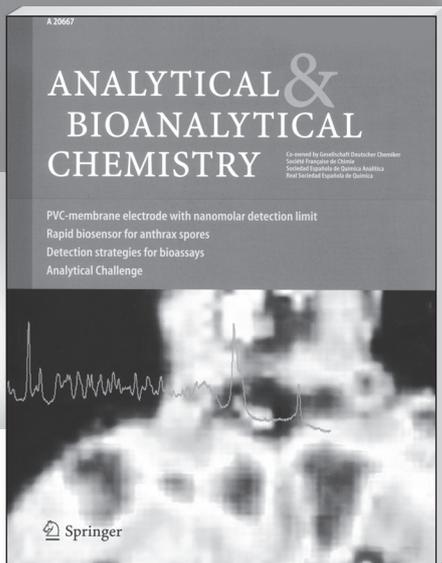
In the present work, the reference values for Ba, Cs, Sb and W (for which very few data are available in literature) in the general population of a north Italian region were determined by means of two ICP-MS instruments (DRC and High Resolution systems).

These procedure were evaluated according to the procedures recommended by ISO1 and Eurachem/CITAC2 Guides for estimating measurement uncertainty.

The reported results show that the contribution due to the instrumental calibration (often not considered in the method validation procedures) is significantly high, so considering only the contribution due to the short time repeatability can underestimate the uncertainty data, especially at the low concentrations, typical of these kind of samples.

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ICP-MS TECHNIQUE APPLICATION TO SOLVE OF IAEA TASKS

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Control over the undeclared nuclear activity is one of the important tasks of International Atomic Energy Agency (IAEA) analytical investigations. Measurement of uranium and plutonium isotope concentration in samples can give objective information about undeclared nuclear activity. The analysis of single microparticles is most interesting and informative because among hundreds and thousands particles one only can obtain by impotent isotope information.

The operation with extremely small amounts of substance is needed to solve similar analytical problems. Thus, in typical samples contain sub-picogram quantities of plutonium. Such measurements require high sensitivity mass spectrometric methods.

Traditionally similar measurements were carried out by a method of thermal ionization mass spectrometry (TIMS). However, recent developments in inductively coupled plasma mass spectrometry (ICP-MS) have shown considerable promise to use it in detecting of U and Pu at ultratrace levels.

The comparative analysis of various mass-spectrometer methods of U and Pu isotope concentration definition is presented in report. The basic attention is paid to ICP-MS method. Experimental data on measurement of U and Pu isotope concentration at ultratrace levels by ICP-MS method in different samples is presented.

ANOMALOUS PROFILES OF HYDROGEN SPECTRAL LINES AND THE IMPLICATIONS FOR ANALYSIS

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The presence of hydrogen in the argon plasma gas of a glow discharge (GD) source causes significant changes in the intensities both of the argon atomic and ionic spectral lines and of the lines arising from the cathode material (sample)^{1,2}. The hydrogen may be present in the sample as a compound (e.g. a metallic hydride) or as occluded gas, may arise from contamination in the source, or may be deliberately introduced as a gas.

When the hydrogen arises from contamination, the amount present in the discharge (which may be ~ 0.01 % v/v) changes with time. This is not a serious problem with bulk samples, but presents major difficulties for depth profiling, particularly of very thin layers. One solution is to use a premixed gas, containing, say, 2% v/v hydrogen in the argon. The small amount of hydrogen arising from contamination then has a negligible effect on the intensities and a stable discharge is rapidly obtained. Alternatively using pure argon, a correction linked to the amount of hydrogen present at any instant may be used. One approach is to base this on the intensity of a hydrogen line³, together with predetermined data on the effect of hydrogen on the spectral lines used for analysis.

However, all hydrogen lines exhibit anomalous Doppler broadening, leading to extremely wide line profiles; the wings of the H α line (656.3 nm) may extend over almost 1 nm, compared with the normal Doppler half-width of ~ 0.03 nm⁴. When a commercial GD polychromator is used, typically with a spectral bandwidth of ~ 0.03 nm, only the central part of the line is measured. Using a Grimm source with an 8 mm anode tube at constant voltage (700 V), the profile normalised to peak intensity is broadest at the lowest current (Fig 1), although the peak intensity increases with current. The changing profile leads to the effect that plots of measured intensity vs. current will depend on the spectral bandwidth used. Moreover the profile also depends on the concentration of hydrogen present; at 0.1 % v/v H₂, the line wings are not significant; at 2% v/v, the profiles shown in Fig. 1 are obtained. This means that plots of intensity vs. hydrogen concentration also depend on the spectral bandwidth.

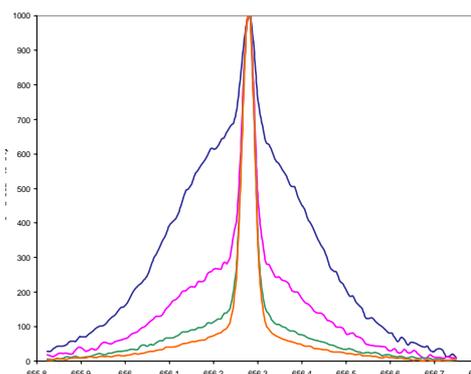


Fig.1. Effect of current on normalised H α line profile

Great caution is therefore needed when using data obtained on a particular instrument on the effect of hydrogen on spectral intensities, in particular the relationship between the changes and the hydrogen signal, to derive a generally applicable correction.

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ANALYSIS OF PHOSPHORUS CONTAINING MICRO POLLUTANTS IN AQUATIC
SAMPLES BY LC-ICP-SFMS AND LC-ICP-DRCMS

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Phosphorous containing micro pollutants are emitted into the environment as a harmful effect of intensive agricultural and industrial human activity. On the one hand the compounds cover a part of herbicides as glyphosate and its metabolite aminomethylphosphonic acid (AMPA). On the other hand chelating agent nominated to phosphonates forms the other part of the micro pollutants of interest.

Glyphosate is one of the most frequently used herbicide in the world. However, in generally the toxicity of herbicides for mammals is low, the widespread use of the compounds has raised the potential for accumulation and therefore has increased the need of analytical methods for monitoring the level of glyphosate and its metabolite in food, in surface or in drinking water. The maximum allowable concentration of glyphosate in drinking water is 0.1 $\mu\text{g L}^{-1}$, set by the European Community. Unfortunately the conventionally used analytical methods for the analysis at this low level are available only with pre-concentration and derivatisation steps prior to measurement, which increase time, cost and uncertainty of analysis.

The most commonly used phosphonates are structural analogues to ethylenediaminetetra acetate (EDTA) and are worldwide used as chelating agents or as inhibitors of mineral precipitation in paper and textile industry, water treatment procedures or in laundry detergents (consumption in Europe was 16000 tons in 1994). All of these compounds contain one or more phosphonic acid groups and are expected to form AMPA as degradation product. Unfortunately very little is known about the fate of phosphonates in the environment due to the lack of a sensitive method for the determination at natural level (concentration in waste water is found to be 28-960 $\mu\text{g L}^{-1}$).

Aim of the present study was the development of a highly sensitive and selective method, which makes possible the analysis of glyphosate, phosphonate and their degradation product AMPA in surface water without any pre-concentration step. During the study a novel HPLC method capable of simultaneous analysis of all investigated compounds was developed. The phosphorous content of analytes was used for quantification employing ICP-MS detection. To overcome the difficulties during determination caused by polyatomic interferences on mass 31P ($^{14}\text{N}^{16}\text{O}^{1}\text{H}^+$, $^{15}\text{N}^{16}\text{O}^+$) both dynamic reaction cell technology (DRC) and high resolution mass spectrometry were employed. The two ICP-MS based detection methods are discussed in terms of analytical performance. Moreover, analysis of surface water samples was carried out in order to investigate the fate of the compounds in the aquatic environment.

Acknowledgement

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THE STUDY OF MAGNETICALLY TAILORED DIRECT CURRENT ARC
PLASMA WITH AEROSOL SUPPLY FOR ANALYTICAL APPLICATION

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Direct current (DC) arc plasmas in inert gas atmospheres have sufficiently high temperature to be used as atomization and excitation sources for elemental analysis by atomic emission spectroscopy. Atmospheric pressure DC arc plasma with aerosol supply still attracts considerable attention as spectrochemical tool for analysis of samples of different origin. For many elements, its analytical capabilities are comparable to the features of ICP.

However, demixing effect existence inside the plasma volume causes partial depletion of some elements free atoms and ions in the arc core region [1]. Ordinary way to reduce the demixing effect and increase the density of analyte is by using easily ionisable elements (EIE) as spectroscopic buffer.

This work describes possibility of reducing demixing effect by imposing DC argon arc plasma with aerosol supply to the transverse oscillatory magnetic field. The magnetic field, oriented perpendicularly to the arc current in the plasma, causes the arc column to move as a whole with respect to the surrounding atmosphere. Arc core depleted of analyte species, driven by magnetic field, run on the surrounding gas, which is richer with respect of analyte compared to the partially depleted radiation zone of stationary arc plasma. The enhancement effect could be expected if the velocity of the lateral movement of the arc column become comparable with radial component of drift velocity of analyte ions. Magnetic fields strengths used are up to 90 mT and frequencies up to 600 Hz.

Emission enhancements up to two orders of magnitude, is observed for some of spectral lines. Enhancement depends on the first ionization energy of analyte atoms, magnetic field strength and frequency, presence of easily ionized elements in nebulized solutions, and observed plasma zone. The obtained results are promising for improving limits of detection of many elements.

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VALIDATION OF TOTAL ORGANIC CARBON (TOC) ANALYSIS WITH
ICPMS

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Evaluation of the capability of ICPMS for the quantification of total organic carbon (TOC) in natural freshwater samples has been carried out. Emphasis was laid on developing a method that is easily applicable together with trace metal analysis, when TOC is an important parameter in speciation or fractionation studies. Citric acid and potassium hydrogen phthalate were compared for the use in calibration standards with both ICPMS and standard TOC analysis (with high temperature catalytic oxidation instrument). The standards were comparable regarding repeatability, linear range and long-term stability but the phthalate was slightly more stable over time. Different elements were tested as internal standard for C in samples with varying salt content, but no suitable internal standard was found. The source of the high C background in ICPMS was investigated, and was mainly assigned to impurities in the argon gas. The method was evaluated for different natural water samples with different concentrations and composition of TOC. This was done both through standard addition and by comparison with a standard TOC.

SEASONAL VARIATIONS IN SEAWATER TRACE METAL FRACTIONATION
AND COLLOIDAL SIZE DISTRIBUTION STUDIED BY FLFFF-HR ICPMS

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Seawater samples were taken in a depth profile from surface to the 50m depths on six occasions from January to June in a Swedish fjord. Trace metal concentrations in unfiltered and 0,45 µm prefiltered samples were measured by High Resolution ICPMS. Calibration was done with non matrix-matched standards, where matrix induced sensitivity variations were corrected for by using 9 different internal standards. The continuous size distributions of the small colloidal material (1-50 nm) were studied by Flow Field-Flow Fractionation (FIFFF). Trace metal composition and concentrations of the colloidal material was investigated by online coupling to High Resolution ICPMS. The colloids in samples from the surface down to the pycnocline were dominated by fluorescing organic material in the size range 1-5 nm, high in Cu concentration and originating from freshwater runoff from land. Larger, Fe-containing colloids appeared after the spring blooms, most frequent at the depths with the highest chlorophyll fluorescence.

DETERMINATION OF TRACE ELEMENTS IN COW MILK BY Q-ICP-MS

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The cow milk belongs to the fundamental foodstuff of human diet due to its high content of essential nutrients, vitamins and trace elements. However depending on the geological and environmental background, as well as the feeding procedures of the agricultural area, different toxic trace elements can also appear in the milk. Therefore, in addition to its dietetic function milk can be used for biomonitoring too [1,2].

The raw cow milk contains approximately 87.5% water and 12,5% dry matter including 3.8% fat, 3.3% proteins and 0.8% inorganic compounds. From analytical point of view the fat content is critical since its total decomposition is difficult applying the conventional digestion procedures. The residual organic compounds can stick to the wall of PTFE bombs resulting in inhomogeneous sample as well as the dissolved organic compounds have an influence on the droplet size distribution of aerosols transported into ICP source. Therefore the sample preparation step should be optimized by checking the total organic (TOC) content of solution after the microwave assisted acidic digestion. [3,4,5]

In our work the sample preparation was carried out by MW-system (Milestone Ethos Plus). 2 ml nitric acid and 0.8 ml hydrogen-peroxide were added to 2 ml milk and 10 samples were digested simultaneously at 200 °C for 30 minutes. Following this procedure as internal standards In, Ge and Tl were added to the solutions in concentration of 200 ppb. In order to decrease the memory effect of mercury, gold was also added at the same concentration.

For quantitative determination of Cr, Mn, Co, Cu, Zn, Se, Cd, Pb and Hg in the digested samples were analyzed by a quadrupole ICP-MS (Thermo Elemental X-series). The analytical procedure was validated by investigation of a milk powder certified reference material (BCR No. 150). The deviation between the certified and found concentration values are less than 6% for Cd, Cu and Pb, however, for Hg more than 30% (Table 1.)

Table 1. Certified and found concentration data (mg/kg) of milk powder CRM (BCR No. 150)

Element	Certified conc.	Found conc.	uncertainty, (\pm)
Cd	0,0218 \pm 0,014	0,0220	0,0090
Cu	2,23 \pm 0,08	2,16	0,14
Hg	0,0094 \pm 0,0017	0,0061	0,0016
Pb	1,00 \pm 0,04	0,942	0,011

132 cow milk samples collected in 7 regions of Hungary were analyzed and the average concentration values were compared to Spanish results. The differences of elemental concentration are higher than one order of magnitude only in case of Ni and Sb. In the EU legislation the maximum tolerance level is determined only for Pb which amounts to 20 ppb. All measured Pb concentrations remained below this limit.

Table 2. Trace element concentration ($\mu\text{g/l}$) in Hungarian and Spanish raw cow milk samples

Element	<i>Hungary, 2003-2004</i>		<i>Spain, 2001-2003</i>
	Average value	(<i>min.-max.</i>)	Average value
⁵² Cr	98,6	(<i>n.d.-479,3</i>)	1,1
⁵⁵ Mn	34,5	(<i>8,0-116,7</i>)	53
⁶⁰ Ni	52,4	(<i>n.d.-257,5</i>)	9,5
⁶⁵ Cu	43,9	(<i>12,9-126,9</i>)	60
⁶⁶ Zn	4012	(<i>1969-5366</i>)	3800
⁸² Se	30,0	(<i>6,1-62,5</i>)	12,8
⁸⁸ Sr	883	(<i>312-2488</i>)	675
¹¹¹ Cd	1,37	(<i>n.d.-6,29</i>)	0,47
¹²¹ Sb	0,37	(<i>n.d.-4,62</i>)	7,14
²⁰² Hg	0,38	(<i>n.d.-7,67</i>)	n.d.
²⁰⁸ Pb	3,73	(<i>n.d.-13,53</i>)	1,8

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TWO DIMENSIONAL SEPARATION SCHEMES FOR INVESTIGATION OF
THE INTERACTION OF AN ANTICANCER RUTHENIUM (III) COMPOUND
WITH PLASMA AND CYTOSOL PROTEINS

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In the past years, increased efforts have been made to detect and identify metalloproteins and ligand-metal complexes in biological samples, as they are involved in transport, storage and detoxification of trace and toxic elements. Furthermore, the bioavailability and the pharmacokinetic profile of metal-based drugs, which are used in about 50 % of cancer patients' therapy schemes, are affected by their interaction with serum proteins. Currently only platinum coordination compounds are routinely applied in clinics. The search for metal complexes comprising several advantages (lower side effects, higher selectivity, broader activity spectrum) over the established drugs led to the development of ruthenium coordination compounds with indazolium trans-[tetrachlorobis(1H-indazole)ruthenate(III)] (KP1019) being one of the most promising representatives. KP1019 is thought to exhibit its activity via the transport into the cell mediated by the transferrin cycle followed by reduction in the hypoxic tumoral environment. In in vitro and in vivo tests the therapeutic potential was proven against a number of tumors, e.g., in chemically induced autochthonous colorectal carcinoma of the rat a reduction of the tumor volume of 95 % was observed (compared to the control group).

However, metal speciation analysis in biological samples is a challenging task, because trace concentrations of metal species have to be determined in a complex matrix. The application of hyphenated techniques is one approach to meet the analytic requirements: Multidimensional chromatographic methods (mostly size exclusion followed by ion-exchange or reversed phase) are preferred for the separation of the analytes from the matrix and from low molecular metal species, as they show increased resolution and a decreased time consumption compared to gel electrophoretic methods. As concerns the detection of the analytes, ICP-MS enables - beside its other well-known advantages - species unspecific element selective quantification. This is of extreme importance since the unavailability of standards is considered to be a major problem in the analysis of metalloproteins.

In this work, size exclusion followed by ion exchange chromatography was coupled to ICP-MS with dynamic reaction cell technology to investigate the interaction of KP1019 with plasma- and cytosol-proteins. A pharmacokinetic study in human plasma was performed using human apo-transferrin incubated with KP1019 for the calibration of the ruthenium-sulfur ratio.

ON-LINE DESALTER-ICPMS SYSTEM FOR THE DIFFERENTIATION OF
CR(III,VI) IN NATURAL WATERS

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Chromium is extensively used in industrial processes; large quantities of chromium compounds are discharged into the environment and ultimately have significant adverse biological and ecological effects. Cr(III) and Cr(VI) are the most common species in the environment. Cr(III) is a trace element essential for the proper functioning of living organisms. On the other hand, Cr(VI) is a known mutagen and carcinogen. Thus, speciation analysis of chromium is a prerequisite for health and environmental considerations.

In this study, a method for the determination of Cr(III) and Cr(VI) in natural waters using on-line Desalter-ICPMS system was developed. Owing to Cr(VI) and Cr(III) are present as negatively-charged ions (HCrO_4^- or CrO_4^{2-}) and positively-charged ions (Cr^{3+} , CrOH_2^+ , or $\text{Cr}(\text{OH})_2^+$), respectively, quantitative retention of Cr(VI) and nearly complete removal of Cr(III) and sodium matrix could be achieved in the use of proposed on-line desalting process. To determine the total concentration of Cr, H_2O_2 was used as oxidant to convert Cr(III) to Cr(VI) prior to the separation. Thus, the amount of Cr(III) can be obtained by subtracting the amount of Cr(VI) from the total amount of chromium. In order to overcome the spectral interference resulting from extremely high concentration of chloride ion in saline samples, cool plasma has been successfully employed to suppress the molecular ion ($\text{Cl}^{35}\text{O}^{16+}$) interferent in the ICP-MS measurement. In view of the notable elimination of those interferences resulting from cationic and anionic matrices prior to the ICP-MS measurement, it indicated that the direct determination of chromium species in saline samples is possible by proposed on-line Desalter-ICP-MS system.

GLOW DISCHARGE SOURCE ASSOCIATED WITH OPTIC AND MASS
SPECTROMETRY

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GD-OES and GD-MS are very well suited to perform in-depth elemental chemical analyses of materials. Both techniques are complementary ones. GD-OES is able to measure simultaneously relative or quantitative concentrations (in the last case, calibration curves are needed) of nearly all chemical elements. GD-MS is able to perform isotopes analyses, quantitatively and with a very high sensitivity, but has to be restricted, for technical reasons, to study simultaneously elements with close atomic masses.

We have developed a new source that permits to use both techniques during the same experiment. This new "source" has been connected to an echelle spectrometer (GD-AES) and to a mass spectrometer (GD-MS). The optical spectrometer allows to study emission lines located between 200 and 750 nm. This broad spectral band allows to study most of the elements. The mass spectrometer uses an electrostatic sector field followed by a magnetic field one and allows to study nearly all isotopes (resolution about 3500). This experiment will be described. Operating conditions leading to a stable analytical signal will be discussed. As an example, results on a multi-layer sample will be shown.

COMPARISONS OF LIBS AND ICP / AES TECHNIQUES

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Standard and robust techniques such as ICP / AES or ICP / MS are largely spread in laboratories and give analytical results with very good confidence. But when the access to the sample is difficult or when its toxicity is very high, an interesting way to overcome these problems is to use the LIBS technique. With this goal [1], the feasibility of LIBS to analyse multi elemental solutions has been investigated. A particular ablation cell was built and optimised. The liquid jet configuration was used. The laser was guided up to the cell by mirrors. The plasma emission was collected by an optical fibre. An interesting way to obtain quite all the plasma emission spectrum is to use an echelle spectrometer for both techniques LIBS and ICP / AES. For multi elemental analysis echelle spectrometer [2] has been used since it can display simultaneously a large domain of the emission spectrum even with high resolution (typically $1/D1 = 10\ 000$ for LIBS technique).

As an example, this set-up was used to analyse a solution containing 20 different chemical elements. To compare the results with a “standard” technique, the same solution was also analysed using two ICP / AES (OPTIMA 2000 Perkin Elmer DV and a Jobin Yvon system). Results will be discussed. The capability of LIBS to analyse liquids in-situ remote analyses will be highlighted.

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RAPID AND PRECISE PB ISOTOPIC ANALYSIS WITH MULTIPLE
COLLECTOR ICP-MS AND ITS APPLICATIONS TO GSJ REFERENCE ROCKS
AND ARCHEOLOGICAL BRONZES

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Thermal ionization mass spectrometer (TIMS) has been successfully employed for the acquisition of high precision isotopic data for elements with relatively low first ionization potentials, such as Sr and Nd. TIMS is also applied to Pb isotopic analysis and the ionization with silica-gel drastically improved the precision and sample amounts required compared to electron impact ionization of gaseous tetramethyl lead. Pb has only one stable isotope Pb-204, however, and the correction of mass fractionation applied for Sr and Nd isotopic analyses is impossible. This problem is resolved by stable or radioactive double-spike method or by calculating “zero time intercept”, but both methods are not simple and not suitable for a rapid routine analysis. In recent years, inductively coupled plasma mass spectrometer (ICP-MS) with multiple collectors (MC) has been introduced for the precise isotopic analysis. The mass discrimination in MC-ICP-MS is independent of time but depend on mass number, and the correction of the discrimination is possible with elements in near mass range from analyte. This normalization is applied to many elements to detect mass-dependent fractionation in natural samples, and Pb isotopic analyses are performed through a normalization with Tl-203/Tl-205 isotope ratios as reference by several authors.

In our presentation, we develop a rapid routine Pb isotope analysis with Tl normalization for ordinary igneous rocks. This rapid analytical point of view is different from the previous reports which mainly discussed the accuracy. Three Pb isotopic data can be acquired per hour with a reproducibility of 0.01 % by optimizing several analytical parameters. We applied this Pb analytical technique to GSJ (Geological Survey of Japan) reference rocks and to archeological Japanese bronze samples. Resultant Pb isotope ratios will be compared to previous TIMS results, and advantages and limitations of the ICP-MS method will be discussed.

DETERMINATION OF ^{135}Cs AND ^{137}Cs IN SOIL AND SEDIMENT BY
DYNAMIC REACTION CELL ICP-MS

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The radiocaesium isotopes, ^{135}Cs ($t_{1/2} = 3$ million years) and ^{137}Cs ($t_{1/2} = 30$ years) are present in the environment primarily from anthropogenic sources, such as nuclear testing and radioactive spills. Determination of ^{135}Cs : ^{137}Cs isotope ratios in soil and sediment samples provide an indication of the source of radioactive contamination, due to differences in abundance of the short-lived, volatile precursors, and potentially enable the distinction of recent contamination from global fallout due to the significantly longer half-life of ^{135}Cs than ^{137}Cs . While ^{137}Cs can be easily detected by gamma counting, ^{135}Cs is a pure beta emitter and radiometric detection is limited by its slow decay rate. In this study, ^{135}Cs and ^{137}Cs were determined by dynamic reaction cell (DRC) ICP-MS, to examine radiocaesium isotope ratios in contaminated samples.

Determination of ^{135}Cs and ^{137}Cs in soil and sediment samples by mass spectrometry encounters several analytical challenges. Complete dissolution of the sample is required, as Cs binds strongly to the silicate fraction of soil. This is achieved by several cycles of reflux and evaporation with HNO_3 , HF and HCl , in a high pressure microwave digestion system. Extraction of Cs from the sample matrix, and separation from the isobaric, stable Ba isotopes ^{135}Ba and ^{137}Ba , having 7% and 11% natural abundance, respectively, is also necessary. Ammonium molybdophosphate is used to selectively extract Cs from the sediment matrix, and suppression of residual Ba in the sample solution is achieved by gas phase collision with N_2O in the DRC. Energy discrimination is employed to suppress polyatomic interferences caused by sequential reactions with the collision gas and gas impurities in the DRC. Contaminated samples from both Chernobyl and a nuclear waste facility were analysed, and the method was validated using standard reference materials.

CAN INTERNAL STANDARDISATION IN PLASMA SPECTROCHEMISTRY
ASSIST IN IMPROVING CLINICAL AND
ENVIRONMENTAL MEASUREMENTS OF TOXIC ELEMENTS?

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For quantitative ICP-OES and ICP-MS analysis, calibration is most commonly achieved by external standardisation. Although modern instruments generally provide relatively stable signals for extended periods of time, instrument drift (i.e. temporal variations of the analytical signals) does occur and has to be corrected for in order to ensure optimal analytical quality. This drift-correction may be achieved by internal standardisation, i.e. the normalisation of all data to a non-analyte signal present with the same mass in all samples and standards. In both ICP-OES and ICP-MS the use of internal standards has become well established as a technique of reducing such random errors from variations in sample introduction and instrumental parameters.

One important prerequisite for internal standardisation in plasma spectrochemistry is that the internal standards are affected in the same way as the analyte emission lines and or isotope counts.

The choice of internal standards is thus dictated by several criteria: in addition to that internal standards should be soluble in all solutions and absent in detectable amounts in the original samples, spectral and mass factors as well as ionization and excitation behaviour should also be examined and optimised.

For characterisation of workers exposure to toxic elements the analysis of workroom air filters and whole blood/urine requires high precision and accuracy. In order to apply ICP-OES and ICP-MS for this task, sophisticated procedures for sample preparation, measurement optimisation and data correction and evaluation, such as multi-line and multi-isotope measurements for each analyte element, optimum calibration and recalibration, and internal standardisation, have been developed.

Procedures and results are demonstrated for selected major, minor and trace elements measured in human placenta, serum, urine and workroom air filters by ICP-OES and ICP-MS. Improved long-term reproducibility and calibration stability (in average 0.5% RSD) in ICP-OES have been obtained by analyte-matched internal standardisation. This performance is superior in contrast to ICP-MS measurements where typical long-term stabilities of 5% RSD are experienced.

APPLICATIONS USING A NEW CCD SIMULTANEOUS ICP SPECTROMETER
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Various applications have been performed using a new simultaneous CCD spectrometer. This paper will describe some of those applications done in our laboratory. The use of the spectrometer, that has an 8pm optical resolution up to 440nm, can be advantageous for the rare earth elements that pose serious problems due to the similar and complex spectrum. We will show application work done with metals and other complex matrices including organics using this new ICP-OES. We will also demonstrate the performance on the various figures of merit on a variety of elements and a variety of matrices that have entered this laboratory. A comparison with classical detector high resolution ICP spectrometer will also be made on some of these applications. Finally, this paper will also present design criteria for the research and development programme of this new CCD ICP-OES spectrometer and the analytical work performed in our laboratories.

LASER ABLATION ICP-OES FOR BULK ANALYSIS OF STEELS AND
REFRACTORY GEOLOGICAL SAMPLES

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Utilization of Laser ablation for direct solids bulk analysis using ICP-OES is less common than ICP-MS. The coupling of a laser ablation system to ICP-OES has several advantages for rapid determinations in refractory samples that are difficult to decompose.

In this study, we will describe the performance for analysis of certified steels, glass and pelleted refractory silicate samples using a combination simultaneous/sequential ICP-OES with a UV macro laser ablation system. The overall performance is evaluated using conventional figures of merit such as short and long-term precision, and detection limits for a wide range of elements.

Analytical data obtained using a high resolution spectrometer with a multi-channel polychromator operating simultaneously shows superior detection limits for the monochromator due to its 5 pm resolution.

The LA-ICP-OES combination produces accurate data when samples are homogeneous & thus any pellet preparation required, plays an important role in the final analysis. We will critically compare advantages vs. disadvantages of LA-ICP-OES and solution techniques.

SOLID STATE DETECTOR OR CLASSICAL HIGH RESOLUTION ICP-OES?
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In this paper we will critically review a comparison of spectrometers showing applications where both systems can have advantages & also disadvantages. In this comparison we will compare a new CCD ICP with comparative medium & high resolution classical ICP spectrometers.

High resolution is synonymous with minimal spectral interferences, high accuracy & best LOD's, however, it is accepted that for some applications high resolution is not necessary, thus "good" resolution will suffice. Comparisons with high & medium resolution classical ICP as well as with the CCD ICP spectrometer will be described.

The Ni base alloys presented to this laboratory gave some on-line interferences of Mo & Nb on Cu & Si specifically & this posed interesting problems that once observed could be resolved by the suitable use of alternative Cu & Si lines. We will present both the problems & the answer to these problems utilizing high optical resolution of 5 pm. We also show a comparison of the same solution with high resolution (5pm) & comparison with medium (16pm) resolution Fig 1 & 2.

We will present the analysis was done on many elements & many different lines to compare values & the effect of interferences on a variety of sample types.

CHARACTERISATION OF A NEW ANALYTICAL HYPHENATED TECHNIQUE:
GC-SPLITTED EFFLUENT-FID/ICP-MS FOR THE DETERMINATION OF
PESTICIDES

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Inductively coupled plasma mass spectrometry (ICP-MS) equipped with a collision/reaction cell hyphenated with gas chromatography (GC) is recently growing to an attractive alternative for investigating elements that are traditionally difficult to analyse with the ICP-MS such as P, S etc. This new promising approach opens the door for example to the element-specific determination of heteroatom containing organic substances such as pesticides using ICP-MS detection.

The main account of GC-ICP-MS for pesticide analyses is the higher sensitivity of the ICP-MS with respect to other detection methods used such as nitrogen-phosphorus detection, atomic-emission detection or flame ionization detection (FID).

However, GC-ICP-MS provides better sensitivity for a couple of pesticides based on the element specific determination of the heteroatom contents of the investigated substances, but doesn't yield any information of the non-heteroatom containing compounds eluting from the GC. This drawback of the mentioned hyphenated analytical technique can possibly be eliminated by a novel analytical approach based on the followings. The effluent coming from the gas chromatographic column is splitted to a predetermined ratio. A part of the effluent is transmitted to the ICP-MS, while the rest of the effluent is driven into a FID in parallel with the ICP-MS.

In this study this novel coupled system, the GC-splitted effluent-FID/ICP-MS is characterised.

DEPTH PROFILING OF ZINC-COATED SHEET USING LASER-INDUCED
BREAKDOWN SPECTROSCOPY

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Laser-induced breakdown spectroscopy (LIBS) is based on imaging laser microplasma, which arises at interaction between focused laser beam and sample. LIBS is widely used for rapid on-line bulk analysis of various materials (soils, metals, powdered materials). However, this method is also applicable for depth profiling. LIBS is an appealing technique for fast analysis of micrometer-sized layered structures. Sampling depth can be reduced using suitable beam focal conditions and angle-resolved LIBS.

Nd:YAG laser operated at fundamental wavelength (1064 nm) and fourth harmonic frequency (266 nm) was used for formation of microplasma. Emitted radiation of the microplasma was collected with a fiber optic system and transported onto entrance slit of the monochromator. The monochromator was equipped with a photomultiplier gated by a laboratory-built control unit. Time-resolved signal was recorded by the digital storage oscilloscope.

In this work, depth profiles were observed on zinc-coated sheets. Obtained results were compared with LA-ICP-OES and GD-OES. Depth profiles were measured in various surrounding gases (air, helium, argon). LIBS results show better correlation with depth profiles obtained by GD-OES than using LA-ICP-OES technique.

The authors wish to express their thanks to the Grant Agency of the Czech Republic for the support of this research within the grant: 203/02/P097 The study of interaction of laser radiation with solid materials by plasma spectrometry methods.

SIMULTANEOUS ANALYSIS BY TIME-OF-FLIGHT MASS SPECTROMETRY
AND ATOMIC EMISSION SPECTROSCOPY TO STUDY DIFFERENCES IN
LASER FLUENCE THRESHOLDS FOR IONIZATION AND PLASMA
FORMATION PROCESSES IN METALS

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The amount of energy reaching a solid sample greatly influences the type of phenomena occurring at the sample surface. While at high irradiance extensive fragmentation, particle emission, and plasma formation is the predominant situation, at low irradiance levels, surface desorption and thermoemission are the common processes. The energy threshold for both situations is not well-defined. Several attempts to study the energy threshold for plasma formation have been done, and the dependence with sample type and laser wavelength is described. However, to our knowledge, it has not been done a systematic study trying to determine the energy density region where no plasma formation (or photon emission) occurs while ion thermoemission or desorption takes place.

The presented work is facing this challenge by simultaneous monitoring of the process using two multichannel detectors: an intensified optical spectrometer that monitors the events capable of generating measurable photons, and a time-of-flight mass spectrometer that detects any generated ion.

SPECTROSCOPIC CHARACTERIZATION BY OPTICAL EMISSION
SPECTROMETRY OF LASER INDUCED PLASMAS ASSISTED BY GLOW
DISCHARGE SPUTTERING IN CONTINUOUS AND PULSED REGIME
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The amount of energy reaching a solid sample greatly influences the type of phenomena occurring at the sample surface. While at high irradiance extensive fragmentation, particle emission, and plasma formation is the predominant situation, at low irradiance levels, surface desorption and thermoemission are the common processes. The energy threshold for both situations is not well-defined. Several attempts to study the energy threshold for plasma formation have been done, and the dependence with sample type and laser wavelength is described. However, to our knowledge, it has not been done a systematic study trying to determine the energy density region where no plasma formation (or photon emission) occurs while ion thermoemission or desorption takes place.

The presented work is facing this challenge by simultaneous monitoring of the process using two multichannel detectors: an intensified optical spectrometer that monitors the events capable of generating measurable photons, and a time-of-flight mass spectrometer that detects any generated ion.

REACTIVE CHEMISTRY OF URANIUM ION WITH AMMONIA IN THE
BANDPASS REACTION CELL

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Recently we have reported high reactivity of uranium ions, generated under ICP-MS conditions, in the dynamic reaction cell (DRC) pressurized with oxygen or ammonia [1,2]. The reaction product of U^+ with oxygen was identified as uranium dioxide ion UO_2^+ . The reaction between U^+ and ammonia yielded an array of ions with the major product possessing m/z 270. Two possible isomeric structures with empirical formula $UN_2H_4^+$ retain this mass-to-charge ratio of 270. One is a bidentate condensation product ion $U(NH_2)_2^+$ and the other is a cluster ion $UNH^+ \cdot NH_3$. These isomeric ions have, obviously, different precursors: UNH_2^+ and UNH^+ , respectively, and are formed through alternative pathways. Experiments with deuterated ammonia (ND_3) were performed in order distinguish between NH_2^+ ions and isomeric UO^+ , contributing greatly to the NH_2^+ signal, and establish correct products ratio. UNH^+ ion was found to be the major primary product thus leading to formation of the cluster ion $UNH^+ \cdot NH_3$. Scanning of axial field AFT voltage from 0 to 500V provided additional insight into the structure of uranium containing ions.

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USE OF CHEMICAL RESOLUTION IN A DYNAMIC REACTION CELL (DRC)
IN LASER ABLATION – ICPMS

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Especially since the introduction of UV-lasers, laser ablation – ICP – mass spectrometry (LA-ICPMS) has evolved into a powerful technique for bulk and spatially resolved analysis of solid materials. Of course, also when using LA for sample introduction, the occurrence of spectral overlap may jeopardise the accuracy of the results obtained. It is the aim of this presentation to illustrate at hand of real-life applications from the authors' lab that also under these conditions, the use of selective ion – molecule chemistry (chemical resolution) in a dynamic reaction cell (DRC) may be used to create interference-free conditions (or at least to alleviate the effect of the spectral interference).

A method was developed for the quantitative determination of the economically most important platinum group metals PGMs Pt, Pd and Rh in Pb buttons obtained by fire assay of platiniferous ores. Chemical resolution using NH₃ as a reaction gas was used to overcome the spectral overlap of the 103Rh⁺ analyte signal and that of 206Pb²⁺.

A combination of 2-dimensional gel electrophoresis and LA-ICPMS was used to study the incorporation of Se into yeast (*Saccharomyces cerevisiae*) proteins. Chemical resolution using CO as a reaction gas was used to avoid spectral interference from the 40Ar²⁺ signal and hence, permitted the use of the most abundant 80Se nuclide.

Depth profiling analysis of printing plates required monitoring of traditionally difficult elements, such as S (interference from O₂⁺), P (interference from NOH⁺) and K (interference from 38ArH⁺ and the wings of the signals from 38Ar⁺ and 40Ar⁺). The use of O₂ as a reaction gas enabled simultaneous determination of all of the elements of interest via the signals of condensation product (SO⁺ and PO⁺) or atomic (K⁺) ions.

Finally, the depth profiling analysis of car paints will be used to illustrate that not in all instances, chemical resolution suffices to solve all interference problems encountered.

MICRO-COLUMN OFF-LINE MATRIX SEPARATION FOR PGE
DETERMINATION IN ENVIRONMENTAL SAMPLES

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In the last two decades since cars were fitted with catalytic converters, harmful automobile emissions have been reduced but at the same time due to surface abrasion of the catalysts the concentrations of the platinum group elements (PGEs) have increased resulting in a new possible risk for the human health. Nevertheless, their concentrations are still very low, therefore very sensitive instrumentation and careful sample handling is essential. An inductively coupled plasma sector field mass spectrometer (ICP-SFMS) has the advantages of very high sensitivity with low detection limits and low sample demand. Coupling with a micro-flow nebulisation/desolvation sample introduction system has two benefits, it increases the signal-to-background ratio and reduces most of the spectral interferences (mainly the oxides) which hamper the PGE determination. In many cases, especially in environmental samples, some further sample preparation (matrix separation or preconcentration) is necessary because of the heavy matrix. In the work presented here, off-line matrix separation by a strong cation exchange microcolumn was studied. It was observed that the PGEs pass through, while most of the matrix elements are retained on the column. Different acid concentrations were studied in order to optimise the separation. The precision and accuracy was studied using a BCR-723 road dust standard reference material digested in an acid mixture of HCl, HNO₃ and HF in a microwave oven. The samples collected off-line were then analysed by the ICP-SFMS coupled with the desolvation sample introduction system. For quantification, different calibrations were studied (i) without matrix separation: an external calibration made up in 1% HNO₃ and in the acid mixture used for the digestion, respectively, and (ii) with matrix separation: as well as using the above mentioned external calibration solutions, the digested samples were spiked before and after digestion. The results obtained together with the advantages and also the disadvantages will be discussed during the presentation. The method was successfully applied to PGE determination in sediment samples the results of which will be also demonstrated.

DETERMINATION OF TRACE ELEMENTS IN HUMAN LIVER BIOPSY
SAMPLES BY ICP-MS AND TXRF

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Chronic diffuse liver disease (CDLD) is frequent in Hungary and its incidence is increasing continuously. CDLD includes a variety of liver diseases with similar ultrasonographic signs ("bright liver"). A quantitative ultrasound attenuation measurement was elaborated based on a comparison of attenuation of patient's liver with attenuation of a homogeneous tissue-equivalent reference phantom. Two basic groups of bright liver can be differentiated according to attenuation: the low and the high attenuation types. Effect of water content of liver samples on attenuation type was investigated but hardly any dependence could be found. The primary aim of this study was to determine element concentrations in human liver biopsy samples, moreover to explore possible correlation between medical diagnostics and concentrations of microelements.

Biopsy samples were collected from 69 individuals under the supervision and permission of ethical committee from MI Central Hospital Budapest. Parts of biopsy samples, not used for histopathological investigations were immediately freeze-dried for conservation. Considering the proposed sample preparation procedures in the literature and our earlier studies on human tissues a modified microwave digestion method was developed suitable for very limited amount of tissue samples (typically 0.5-2.5 mg dry mass). Microwave-assisted nitric acid digestion resulted in 0.3 cm³ total volume of sample solutions.

Each biopsy samples were unique, therefore the precision of the measurements was tested by the analysis of homogenised and freeze-dried pig liver. Inductively coupled plasma mass spectrometry (ICP-MS) exhibiting favourable detection limits was applied for the determination of micro and trace elements in biopsy samples. Total reflection X-ray fluorescence spectrometry (TXRF) is a suitable technique for the analysis of small mass biopsy samples, since it requires small amount of substance. 25-100 mL of sample solution was used to prepare specimens for the TXRF analysis. Yttrium was employed as an internal standard, made by the dissolution of 5N purity yttria (Y₂O₃) in our laboratory. Control measurements were performed to prevent misinterpretation of data. All materials, solutions and tools used during sampling and sample preparation were tested. The steel parts of disposable biopsy needles were also digested and analysed. It was proved that no measurable contamination originated from our laboratory. The accuracy was tested by the analysis of standard reference materials. Intraindividual variability of elemental concentrations was determined by the analysis of autopsy samples taken by the same disposable tool as biopsy samples. Comparison of analytical results using ICP-MS and TXRF technique are presented in the lecture.

INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY –
INFLUENCE OF THE ICP-FREQUENCIES AND SPECTROMETER TYPE ON
THE DETECTION LIMITS IN THE DETERMINATION OF Y, Zr, Nb, Hf, Ta AND
Th IN GEOLOGICAL MATERIALS

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The progress in the study of the occurrence and distribution of different elements in geological materials depends on the possibilities of its quantitative determination in wide concentration range. The determination of the metal content of yttrium, zirconium, niobium, hafnium, tantalum and thorium in rocks is of outstanding relevance for the solution of problems in the geochemistry.

A radial – viewing Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used in the determination of above-mentioned elements in geological materials. The Q-concept, as proposed by Boumans and Vrakking, was applied for quantification of spectral interferences in the presence of multi-component geological matrix.

The general purpose of the present study is to derive comparative data for spectral interferences dependant on the ICP-frequencies and spectrometer type: 40.68 MHz and 27.12 MHz ICPs; spectrometers with practical spectral bandwidths 5 pm, 10 pm or 15.6 pm, respectively. To this purpose the following data were compiled: 1. Spectral data of Al, Ca, Mg, Fe, Ti, Mn, Na, K and P as interferents around prominent lines of the analytes; 2. Data base of Q-values for line interference and for wing background interference; 3. Detection limits for the analytes in the presence of complex geological matrix by using the 'true detection limits' criterion. The lines with the lowest values of true detection limits were selected for analyte determination.

The comparative data derived under approximately the same excitation conditions (the Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio is equal to 11.0 for the different ICP-AES equipment), show that the Q-values strongly depend on the spectral resolution of the spectrometer. The detection limits (in g g⁻¹) obtained by 40.68 MHz ICP and 5pm spectral bandwidth are as follows: Y-0.013; Zr-0.07; Nb-0.3; Hf-0.065; Ta-0.23; Th-0.3. These values are up to one order of magnitude lower than the corresponding values acquired by 27.12 MHz ICP and 15.6 pm spectral bandwidth.

The data base of Q-values were used for background correction at the wavelength of the analysis lines, when Q-values for line interferences is equal to 0 without a separate matrix blank. By this way the errors in the measurement of net analyte signals resulting from erroneous background determination can be eliminated.

THE STUDY OF HEAVY METAL ENVIRONMENTAL POLLUTION USING
THE INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION
SPECTROMETRY METHOD

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The estimation of the pollution level and of the dangers presented by this phenomenon, implies some analyses in which the concentrations of heavy pollutant metals should be determined in samples of dusts from the air, samples of soil and plants. The analytical techniques used must have low detection limits, the lowest matrix effects possible and they must allow the determination, as precise as possible, of the major components as well as of the minor ones in traces. The methods that respond to these requirements are from the category of atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES). The area in which the researches were done is characterized by the existence of some industrial units of extraction of some ores which contain as major components Pb, Cu, Zn and as minor components or in traces Cr, Mn, Ni, Co, Ag, Au, Al, Fe. The presence of these metals in the air, water and soil has negative effects on human health, plants and animals. This study analyzes these aspects in a zone of Romania strongly polluted with heavy metals.

DEVELOPMENT OF HELIUM RADIO-FREQUENCY GLOW DISCHARGE
PLASMA SOURCE ASSOCIATED WITH LASER ABLATION SAMPLING

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This paper describes a new excitation source for emission spectrometry consisting of an r.f. helium glow discharge plasma and a laser-diode pumped Q-switched Nd:YAG laser. The Nd:YAG laser works dominantly as a sampling source for introducing sample atoms into the helium plasma, because the laser irradiation causes laser ablation but cannot produce the laser-induced plasma due to its high repetition rate and thus the small peak power. On the other hand, the helium glow discharge plasma mainly acts as an excitation source, because small amounts of sample atoms can be introduced due to the low sputtering rate. However, excited species of helium have the excitation capability for sample atoms requiring large excitation energies. From these characteristics in this combined emission source, the sampling process and the excitation process could be controlled independently.

ISSUES AFFECTING THE MASS BALANCE OF ARSENIC AND SELENIUM
SPECIATION IN COMPLEX INDUSTRIAL PROCESS WATERS

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Speciation determines the environmental cycling and fate of trace elements in natural and industrial environments, and the mass balance between the total element concentration present and the sum of the determined species should be used as an important geochemical tool and analytical QA criterion in speciation studies.

As part of an ongoing project studying the mobility and release of trace elements from coal combustion by-products (CCBs), we determined total arsenic (As) and selenium (Se) concentrations in waters that had been in contact with CCBs by inductively-coupled plasma-dynamic reaction cell-mass spectrometry (ICP-DRC-MS). Simultaneously, As and Se speciation in these samples was measured using anion-exchange chromatography- anion self-regenerating suppression-ICP-DRC-MS (AEC-ASRS-ICP-DRC-MS). Contrary to our experience in other types of waters, we found that the mass balance for As and Se in these samples did not work well; i.e. the sum of the measured species was usually significantly lower than the independently measured total element concentrations. In this contribution, we present investigations on several aspects affecting these mass balances, aimed at resolving the observed discrepancies.

The first set of experiments studied artifacts in the total element determinations by ICP-DRC-MS, and led to the elimination of several interferences causing artificial high total As and Se results. A variety of DRC reaction gases (none, methane, ammonia, methane plus ammonia, and oxygen) were used to measure As, various Se isotopes, and several internal standard (IS) elements in this set of samples. While the reaction gases were effective at eliminating specific known spectral interferences on the analytes, we also encountered a number of new interferences, most of which were apparently created in the DRC by reaction between the gas and major constituents of the complex water samples. These generated interferences were eliminated by kinetic discrimination. We also detected spectral and non-spectral interferences on several IS elements, which prevented their use in the analysis of these samples.

The second set of experiments addressed the question if these samples contained any As or Se species that may not be detected by AEC-ASRS-ICP-DRC-MS. To test for the presence of colloidal As and Se species, samples were subjected to ultrafiltration to < 500 nominal molecular weight, and total As and Se were measured before and after filtration. Likewise, potential precipitation losses of As and Se species were checked by comparing total element concentrations measured in cryofrozen samples (for speciation) to those measured in parallel samples acidified with HCl (for speciation) or HNO₃ (for total element determinations). Finally, potential chromatographic artifacts were investigated by establishing the As and Se mass balance during AEC-ASRS-ICP-DRC-MS analysis in preserved and unpreserved samples, with and without using the ASRS eluant suppression, and during mixing of the samples with the chromatographic eluant. Results of these experiments will be presented and discussed with respect to potential species losses or discrimination during storage or analysis.

DETERMINATION OF THE HEXAFLUOROARSENATE ION IN INDUSTRIAL PROCESS WATERS

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It has long been known that arsenic (As) forms the stable hexafluoroarsenate anion $[\text{AsF}_6]^-$. However, to date this compound has received little to no attention in environmental As speciation studies, probably because the conditions for its formation in natural systems are usually not given. Recently, $[\text{AsF}_6]^-$ has increasingly been used in the production of batteries, and there may also be industrial process waters and certain ground waters that contain high concentrations of fluoride, warranting the speculation that $[\text{AsF}_6]^-$ might occur and constitute a significant fraction of the total As concentration in such specialized scenarios.

Common As speciation methods do not allow the determination of $[\text{AsF}_6]^-$, mostly because this compound was not included in the method development. It has been shown that $[\text{AsF}_6]^-$ does not react with borohydride under normal hydride generation (HG) conditions, so HG-based speciation approaches are not suitable for its positive determination; however, one might attempt to interpret the difference between total and HG-active As as $[\text{AsF}_6]^-$. In this study, we have attempted to determine $[\text{AsF}_6]^-$ by anion-exchange chromatography coupled to inductively-coupled plasma mass spectrometry (AEC-ICP-MS).

Separation of $[\text{AsF}_6]^-$ from all other As species routinely analyzed in our group, including arsenite, arsenate, mono- and dimethylarsenate, as well as various As-sulfur species, was tested using gradient elution with hydroxide. Stability of $[\text{AsF}_6]^-$ during separation under these conditions was assessed by its chromatographic behavior, by the mass balance between total As and the detected species, and by molecular mass spectrometry. The results of these experiments will be discussed, and the feasibility of $[\text{AsF}_6]^-$ determination in industrial process waters from a site where this compound might be expected to occur will be evaluated.

DETERMINATION, PRESERVATION AND STABILITY OF METHYLARSENIC SPECIES IN SALINE GROUND WATERS

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The methylated arsenic (As) species monomethylarsenate (MMAs(V); $\text{CH}_3\text{AsO}_3^{2-}$; also known as methylarsonate) and dimethylarsenate (DMAs(V); $(\text{CH}_3)_2\text{AsO}_2^-$; also known as dimethylarsinate or cacodylate) are encountered in most natural systems when As speciation is studied. Under typical circumstances, these species constitute only a small fraction of the total As concentration, and because they are considered non-carcinogenic and are also less toxic than the inorganic As oxyanions arsenite and arsenate, they are usually not paid much attention in these studies. However, since MMAs(V) and DMAs(V) are used extensively as biocides, their relative importance can change dramatically at sites where they are either produced or used.

Determination of MMAs(V) and DMAs(V) is routinely accomplished using either batch hydride generation (HG) followed by cryogenic gas chromatography coupled to a suitable atomic spectrometry detector, or by liquid chromatographic separations coupled to the same array of detectors (with or without HG as an intermediate step). It has been reported, though, that the first approach may sometimes cause artifacts in the observed As speciation patterns, namely cross- and demethylation of various species, so the second approach appears favorable.

In this study, we investigated As speciation in highly saline ground waters at a site impacted by methylarsenic compounds. Anion-exchange chromatography coupled to inductively-coupled plasma-mass spectrometry (AEC-ICP-MS) was used as the analytical technique with hydroxide as the eluant. Separation of MMAs(V) and DMAs(V) from inorganic As oxy- and thioanions was accomplished. Unfortunately, eluant elimination using an anion self-regenerating suppressor (ASRS) could not be employed, because DMAs(V) was partially lost in this step, so detection limits and long-term stability were compromised. Also, the impact of the high chloride and sulfate concentrations encountered at the site on the chromatographic separation and ICP-MS detection were studied and eliminated as far as possible.

While several studies on preservation and stability of MMAs(V) and DMAs(V) were conducted in the early days of As speciation analysis, this body of knowledge has been largely forgotten, so we conducted an experiment in which samples from the site as well as synthetic samples containing a mixture of As species were preserved and stored under different conditions (cryofreezing, acidification with HCl or HNO_3 , and unpreserved for comparison) for a period of four months. Stability of As speciation under these different conditions will be discussed. Finally, we will show a number of different As speciation patterns encountered at the site as the result of varying emission scenarios and hydrogeochemical conditions.

FURTHER EXPERIMENTAL DATA CONCERNING THE CONCEPT OF ‘ABSOLUTE’
EMISSION YIELDS IN GD-OES

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In a recent paper [1], a formalism was proposed to describe line spectra in the Glow Discharge Emission Spectrometry (GD-OES), according to which the intensity $I_{X,\lambda,M}$ of an emission line with a wavelength λ , belonging to an element X, in the analysis of a material M, can be expressed as

$$I_{X,\lambda,M} = R_{X,\lambda}^{abs} \xi(\lambda) c_{X,M} q_M \quad (1)$$

where $c_{X,M}$ is concentration of the element X in the matrix M, q_M is the sputter rate of M, $\xi(\lambda)$ is the spectral responsivity (instrument function) of the spectrometer (i.e. of the optics and the detection system) and $R_{X,\lambda}^{abs}$ is the ‘absolute’ emission yield of that line. The intensity in the above formula is supposed to be background-corrected and non-affected by self-absorption. In the same paper, a hypothesis was formulated, suggesting that the ‘absolute’ emission yields reflect excitation conditions in the glow discharge source and fundamental parameters of the observed transition in the following way :

$$R_{X,\lambda}^{abs} = h \frac{c}{\lambda} A_{ik} g_i k_X f_{exc}(X,i) \quad (2)$$

where h is the Planck’s constant, c is the speed of light, k_X is a proportionality factor related to the transport of the element X in the excitation source, A_{ik} is the Einstein probability coefficient of spontaneous emission for the observed transition, i denotes its upper level, g_i is statistical weight of that level and $f_{exc}(X,i)$ is excitation function, i.e. population factor of the upper level.

In this contribution, experimental evidence will be presented, showing to which extent the above described concept reflects reality in different situations, on different instruments and with different analysed matrices.

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DETERMINATION OF INTERFERENCES IN THE ANALYSIS OF ELEMENTS
IN FOODSTUFFS WITH ICP-MS USING COLLISION CELL TECHNOLOGY
(CCT)

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One of the main tasks of the Food and Consumer Products Safety Authority is enforcement of the food and consumer product laws. In these laws maximum levels of harmful and toxic compounds are set. A specific group of compounds are (heavy) metals and minerals. Due to the fact that maximum levels are set for several compounds in the laws, ICP-MS might be a very useful technique for analysing these compounds. Examples of product groups are: toys, cosmetics, (contaminated) food, fortified food, supplements, tobacco, etc.

To develop ICP-MS methods for the wide variety of elements and matrices it is helpful to know which of the theoretically interferences occur and how they can be reduced.

To investigate which interferences in food occur, solutions have been measured which simulate real food sample solutions. This was performed by addition of different levels of several elements in order to create \"simulated food solutions\". These solutions contained for instance carbohydrates, phosphates, sulphates, etc. After analysis of the solutions it was determined which of the theoretical interferences really did occur. Then the set-up of the instrument was adjusted in such a way that the interference was reduced to a minimum. Changes, which were made, were for instance: use of different cones, change in plasma conditions, selection of other isotopes and/or by using Collision Cell Technology (CCT). With CCT three different mixtures of gases were examined, Helium with 1% Hydrogen, Helium with 1% NH₃ and Helium with 1% Xenon.

Based on the results obtained it was clear that many of the theoretically possible interferences (about 90) actually do occur in \"simulated food solutions\" (measuring in the standard mode, about 50 polyatomic interferences were visible). By using CCT with different gases the existence of the polyatomic interferences were reduced to less than 20. The 3 different gasmixtures used, showed differences in the remaining interferences (some interferences disappeared using one gasmixture, but not with the others), however some interferences (about 10) still remain independent of the gasmixture used and might thus cause incorrect results. In order to get correct results each measurement must be checked for remaining interferences and if any are present a correction equation must be applied.

The advantage of having this knowledge is that it is possible to predict interferences for different types of food products / food supplements analysed with ICP-MS, thus reducing the time necessary for method development.

ANALYSIS OF PBDES BY GC-ICP-MS - THE CHROMATOGRAPHIC
ADVANTAGES OF USING ICP-MS AS A GC DETECTOR

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ICP-MS has been shown to be a sensitive, highly selective GC detector for volatile brominated compounds including pesticides and alkylbromides. As a bromine-specific detector for gas chromatography, ICP-MS exhibits several advantages over other halogen-specific detectors. Since it is an elemental mass spectrometer, it is absolutely selective among the halogens, suffering no interference from fluorine, chlorine or iodine. Because of the high-power, high-temperature argon plasma, ICP-MS does not exhibit the suppression of response from co-eluting compounds typical of some other elemental detectors. For the same reason, ICP-MS can tolerate a range of GC carrier gas options and flows, greatly increasing the chromatographic flexibility. It is this ability to tolerate high flows and a variety of carrier gases which makes ICP-MS a powerful tool in the gas chromatographic analysis of PBDEs. PBDEs, particularly the higher brominated congeners (7 to 10 bromines), are high-boiling, yet thermally labile compounds which are difficult to recover quantitatively by GC. Good recovery requires a highly inert chromatographic system (injector, column, transfer line and detector) and excellent temperature control. It also requires that the time the sample is exposed to the heated components of the system must be minimized. This can best be accomplished through the use of short, large-diameter, thin film columns at high carrier gas velocities. However, since there are 209 possible PBDE congeners, in addition to other possible brominated contaminants, good chromatographic resolution must be maintained. Initial work using a 5-meter DB-5MS column with either He or H₂ carrier at ~7 ml/min gave excellent separation of the 14 congeners tested and good recovery of the difficult deca congener (BDE-209). Other column/flow combinations are examined. Since it has been shown that the elemental response of ICP-MS is compound independent, it is possible to estimate the chromatographic recovery of the higher congeners compared to the lower ones by comparing response factors. For the same reason, it is also possible to quantify congeners for which there are no standards, if the degree of bromination can be deduced from the retention time.

In this work, the suitability of GC-ICP-MS for the detection and quantification of PBDEs in standards and mixtures containing PCBs is examined. Figures of merit include detection limits and response factors for various PBDE congeners, linear range as well as chromatographic conditions and retention times.

RAPID SIMULTANEOUS SPECIATION OF MULTIPLE METALS USING ION
CHROMATOGRAPHY COUPLED TO ICP-MS

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ICP-MS has been shown to be a powerful tool for the measurement ionic species of single elements separated by ion chromatography. However, simultaneous speciation of multiple elements has been challenging for a number of reasons. Chromatographic elution and separation of elements with widely varying ionic properties can be difficult. This is especially true when extreme care must be taken to maintain species integrity as in the case of chromium (III) and (VI). Additional chromatographic difficulties arise when some of the species exist as cations while others are anionic. Furthermore, detection limits can be compromised when polyatomic interferences overlap one or more of the analytes of interest.

By combining simple anion chromatography with chelation using EDTA, species preservation and efficient separation multiple species of 13 elements was achieved simultaneously under a single set of conditions. Polyatomic interferences that would normally interfere with the measurement of several elements including Cr, As, Se were eliminated using the Octopole Reaction System of the Agilent 7500ce ICP-MS.

Figures of merit will include ion chromatographic and ICP-MS operating conditions as well as sample chromatograms and limits of detection for several elements. Results for two common bottled mineral waters are presented.

USE OF NEW ELECTRICAL SIGNALS FOR QUANTITATIVE
MEASUREMENTS OF INSULATING SAMPLES BY RF-GD-OES

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Radio frequency glow discharge optical emission spectroscopy (RF-GD-OES) is routinely used for the chemical analysis of solid samples. For quantification two independent electrical signals of the discharge are required. These are provided in real time by the glow discharge source with integrated voltage and current sensors [1]. The available time dependent voltage and current is evaluated by a plasma equivalent circuit [2]. It was shown that the cathode voltage and active cathode current describe the sputtering and excitation well. The measurements of standard reference materials at constant cathode voltage and cathode current result in linear calibration curves [3]. We present RF-GD-OES measurements of thick insulating samples and thin insulating layers.

For insulating samples the discharge voltage $u_p(t)$ is calculated using the coupling capacity C_f , the electrode voltage $u(t)$ and the discharge current $i_p(t)$ [1]. Because the coupling capacity of insulating samples is usually not known, a procedure is developed to determine it by an electrical measurement without discharge. We present current-voltage characteristics sputtering 0.35 mm thick sintered aluminium oxide. The Bouman formula describes the dependence of the sputtering rate of insulating samples on cathode voltage and cathode current well. Sputtering all samples at constant cathode voltage and current, it is found that the emission yield of an Al line (396.152 nm) for thick insulating samples deviates only 25% from the emission yield of conducting samples. The measurement of a 0.35 mm thick aluminium oxide is compared to that of a 5 μm thick aluminium oxide layer on aluminium.

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INCREASING THE LINEAR DYNAMIC RANGE OF SECTOR FIELD ICP-MS

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Sector field ICP-MS is widely used in various demanding application fields mainly due to its capability for interference-free multielement determinations in complex sample matrices, because of the potential to measure precise isotope and elemental ratios at lowest concentrations, and its suitability to be a detector for laser ablation experiments and for chromatographic couplings. Especially for laser ablation the linear dynamic range is of immense importance, since a wide range of elements and concentrations has to be analyzed in a single analysis and often in a single laser pulse. Typically sector field ICP-MS incorporates a discrete dynode detector with a linear dynamic range of 9 orders of magnitude. However, to analyze matrix elements and ultra-trace elements in one analysis, this dynamic range is not sufficient. Thermo Electron developed a new detector system for the Finnigan ELEMENT2 which is tailored for the tasks of geochemical, clinical and environmental applications: the new detector incorporates 3 modes of operation, which automatically switches the detection mode depending on ion signal. The new detection system consists of a discrete dynode detector and a faraday detector and covers a linear dynamic range of 12 orders of magnitude, capable to analyze matrix and ultra-trace elements in one analysis. Due to a fast detection system, sample times down to 1 ms can be used. The presentation will describe the technical concept and its operation and demonstrate its capability for multielement analysis as well as coupling the sector field ICP-MS Finnigan ELEMENT2 with a laser ablation system.

2006 Winter Conference on Plasma Spectrochemistry

Tucson, Arizona, January 8 - 14, 2006

The 14th biennial international Winter Conference will be held at the Hilton Tucson El Conquistador Golf and Tennis Resort (www.hiltonelconquistador.com) in Tucson, Arizona (www.visitTucson.org). More than 600 scientists are expected, and over 300 papers on modern plasma spectrochemistry will be presented. Six plenary lectures and 22 invited speakers will highlight critical topics in 12 symposia.



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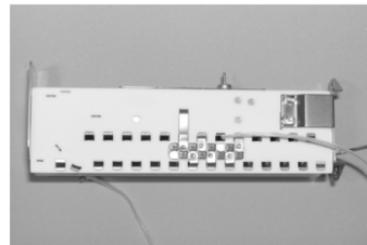
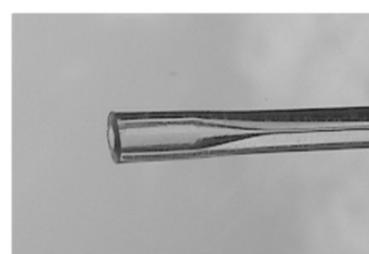
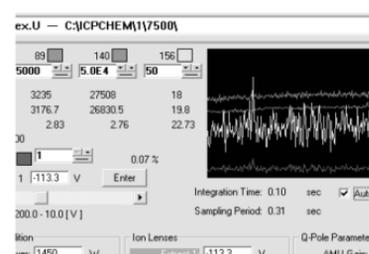
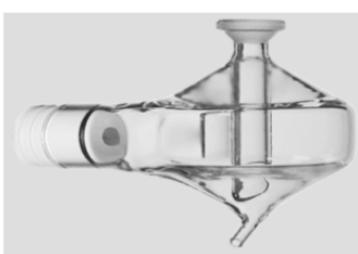


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- Continuing Education Short Courses, Friday - Sunday, January 6 - 8
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- Plasma Spectroscopy Instrumentation Exhibition, Tuesday-Thursday, January 10-12
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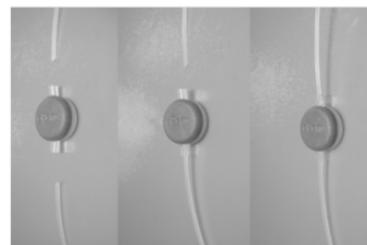
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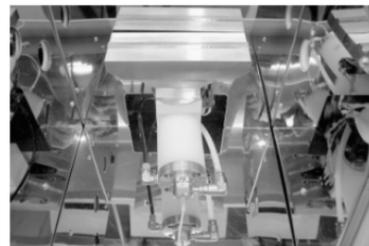
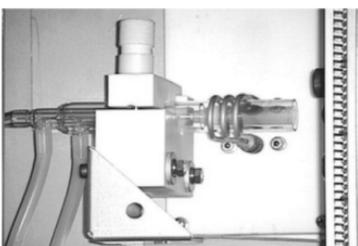
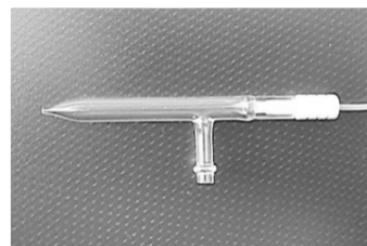
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THE ANALYSIS OF DNA BY COLLISION CELL ICP-MS

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Phosphorous is an element particularly important in biological processes and is a vital component in the DNA helix. The analysis of the ^{31}P isotope by quadrupole inductively coupled plasma mass spectrometry (ICP-QMS) is complicated by interference from polyatomic ions originating from atmospheric and matrix species. Polyatomic ions, such as $^{14}\text{N}^{16}\text{O}^{1}\text{H}^+$ ($m/z = 31$) appear at the same mass to charge ratio as the ^{31}P isotope and the two species cannot be separated due to the low resolution of the quadrupole.

The employment of a collision/reaction cell, O_2 reaction gas and the ion kinetic energy effect (IKEE)¹ allows the oxidation of the ^{31}P isotope to form the $^{31}\text{P}^{16}\text{O}^+$ ion that can be measured at the little interfered $m/z = 47$ ratio. This approach allows the measurement of the ^{31}P isotope at a limit of detection of approximately $1 \mu\text{g l}^{-1}$.

The work presented here describes the study of DNA by ICP-QMS, in solid and liquid samples, incorporating a collision/reaction cell. The presence of DNA is determined by measuring the concentration of the ^{31}P isotope at the $m/z = 47$ ratio by the approach mentioned above.

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SPECIES-SPECIFIC ISOTOPE DILUTION ANALYSIS FOR DETERMINATION
OF IONIC ORGANOLEAD COMPOUNDS WITH GAS CHROMATOGRAPHY
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Organolead compounds are released into the environment through the anthropogenic activities, such as automobiles, industries, incinerations. For example, tetraalkyllead is still used as antiknock agent for automobile in many developed countries in spite of the large efforts to eliminate and reduce its use in developing countries. Its degradation compounds such as tri-, dialkyllead, which have much higher toxicity to human and animals than inorganic lead, are unintentionally produced in automobile engines and emitted into atmosphere through exhaust gas as free molecules or adsorbed on particle matters. However, the research on the mass flux of ionic organolead compounds in environment has rarely been reported, because of difficulties in their reliable determination. Thus, it is necessary to develop a reliable analytical method and construct a monitoring system for the organolead compounds.

The GC-ICP-MS system has the advantage of the sensitivity and identification of volatile organic compounds, and also has capability to apply for species-specific isotope dilution analysis (SSIDA). The combination of both methods makes it possible to accomplish highly accurate and sensitive determination of organometallic compounds. Therefore, in this presentation, the development of species-specific isotope dilution analysis with GC-ICPMS for determination for ionic organolead compounds in atmospheric particle matter will be discussed. ²⁰⁶Pb-labeled trimethyllead chloride and diethyllead chloride were synthesized from ²⁰⁶Pb enriched Pb (NIST SRM 983), iodomethane, and iodoethane as spike reagents for SSID/GC-ICPMS. Organolead compounds adsorbed on particle matter sample were extracted with acetic acid / methanol solution by using a mechanical shaking. The extracted organolead compounds were derived to volatile compounds for GC-ICPMS measurements using Tetrabutylammonium tetrabutylborate. The present method was applied to the analysis of urban dust certified reference material (BCR 605).

SPECIATION OF CATIONIC SELENIUM COMPOUNDS IN LEAVES OF
BRASSICA JUNCEA BY SCX-ICP-MS
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Brassica juncea (Indian mustard) is categorized as selenium (Se) accumulating plant and is used extensively for phytoremediation. In the present study, wild type Brassica plants were supplemented with sodium selenite and analyzed after five weeks of growth. Cationic selenium species present in the leaf extract of these plants were separated by strong cation exchange (SCX) chromatography and detected using inductively coupled plasma mass spectrometric (ICP-MS) detector. Major cationic species found were methylselenomethionine (MeSeMet) and methylselenocysteine (MeSeCys). Selenomethionine (SeMet), which is a selenium analog of methionine, was found in minor amounts in the leaf extract. Presence of these species in the leaf extract was confirmed by spiking experiments, using commercially available standards of SeMet and MeSeCys and an in-house synthesized standard of MeSeMet. The synthesized standard was characterized by molecular mass spectroscopy using soft ionization technique.

Presence of MeSeCys supposedly prevents incorporation of seleno amino acids in protein biosynthetic pathway. SeMet forms MeSeMet, which is an intermediate involved in formation of volatile dimethylselenide (DMeSe), a less toxic form of Se compared to inorganic Se species.

SPECIATION OF ALUMINIUM IN SILICON CARBIDE BY ETV-ICP-AES METHOD

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Aluminium is the only one metallic element which can be found in the SiC-lattice. Material properties of SiC like strength, brittleness and hardness are strongly influenced by the aluminium content. This is especially important for SiC-grains in case of abrasive applications and production of sintered SiC. In order to achieve better elasticity and better fracture toughness Liquid Phase Sintered-Silicon Carbide (LPS-SiC) is produced by adding and mixing Y-Al garnet (1-7%) as binder phase. During the sintering process aluminium migrates into the SiC-lattice, however, yttrium remains in the binder phase. Since the distribution of aluminium between the lattice and the binder phase, as well as the total concentration of aluminium in these phases play a decisive role in the properties and by them in the applicability of SiC, it was necessary to develop a rapid and reliable analytical technique for direct determination of aluminium in different phases of LPS-SiC.

The traditional wet chemical method is based on dissolution of the binder phase in concentrated hydrochloric acid at 220 °C for 20 hours in Teflon vessels. Following this acidic dissolution step and a filtration, the solution was analysed by ICP-AES resulting in information about the aluminium concentration in the binder phase. The total concentration of aluminium was determined after an alkaline melt decomposition. These analytical procedures are time consuming and complicated.

A shortest way offers the ETV-ICP-AES technique. Applying an electrothermal vaporization unit and argon atmosphere the different aluminium compounds were separately evaporated from the solid sample at different temperatures. Aluminium evaporates from the binder phase and lattice in temperature range of 1300-1800 °C and 2100-2400 °C, respectively. The aerosol formed by heating of ~1 mg SiC sample was introduced into the ICP and the time-resolved analytical signals of aluminium and silicon were detected by CID system. The calibration was carried out by means of home-made standards analyzed by wet chemical method. The calibration curves of Al were linear in the concentration range of 0.1-4.0% and 0.1-2.5% for the binder+lattice phase (total Al) and lattice phase, respectively, which is crucial from the technological point of view.

Analytical results of real samples determined with the two methods deviated from each other by maximum 5%.

ON-SITE FRACTIONATION OF TRACE ELEMENTS IN KARSTIC
GROUNDWATER BY MEMBRANE FILTRATION AND CHELATING
EXCHANGE

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An operationally defined on-site preconcentration and fractionation scheme was developed to distinguish between the different metal forms in cave water based on thermodynamic and kinetic behavior of trace element species. In the field the sample was pressed through a membrane filter (0.22 μm) coupled to an imino diacetic acid – ethyl cellulose (IDAEC) chelating exchanger minicolumn by means of a syringe. The filtrate was collected in a PE tube containing chelating cellulose fibers for batch enrichment. The fractions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). By membrane filtering beside colloids (Fe, Al, Ti) Cr, Pb, Co, Zn and Sn were also partly separated presumably as colloid-adsorbed forms, but Ba was not retained. Reactive part of trace elements namely their ionic and complex forms with lower stability but fast ligand-exchange was partitioned by complex formation with the chelating exchanger in dynamic mode. In spite of the high stability of carbonato complexes of U and the expectable anionic form of Mo at that pH their predominant fraction was the resin-active part. Exchangeable complexes with slow ligand-exchange such as Cr were enriched in batch method. Species remained in solution include strongly complexed forms and ions not chelatable with IDAEC (main part of Se, As, Ag). The distribution was compared to that of river water.

Verifying the reliability of the method the batch and/or dynamic steps were skipped. The agreement between the different procedures proved the validity of fractionation process.

DETERMINATION OF SR-90 AND PU ISOTOPES RATIO MEASUREMENTS IN
CONTAMINATED GROUND WATER SAMPLES BY INDUCTIVELY
COUPLED PLASMA MASS SPECTROMETRY

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The precise and accurate determination of concentration as well as isotope ratios of long-lived natural and artificial radionuclides is required for different application fields [1, 2]. In particular, the determination of 90Sr and plutonium isotopes (e.g. 239Pu, 240Pu) at sub-fg concentration level are of increasing importance [2, 3]. Inductively coupled plasma mass spectrometry (ICP-MS) with its ability to provide the sensitive and fast multielemental analysis is one of the most suitable methods for the measurements of long-lived radionuclides in the trace and ultra-trace concentration range [4].

In the present study a sensitive analytical method for the determination of artificially produced radionuclides 90Sr, 239Pu and 240Pu at ultratrace level in ground water samples by double focusing sector field inductively coupled plasma mass spectrometry (ICP-SFMS) was developed. In order to avoid possible isobaric interferences at m/z 90 for 90Sr determination, (e.g. 90Zr+, 40Ar50Cr+, 36Ar54Fe+, 58Ni16O2+, Hf++ etc) the measurements were performed at medium mass resolution under cold plasma conditions. The separation of Pu from the uranium was achieved by means of extraction chromatography using Eichrom TEVA resin with a recovery of 82%. The limits of detection for 90Sr, 239Pu and 240Pu in water samples were determined to be 11 fg ml⁻¹, 0.12 fg ml⁻¹ and 0.1 fg ml⁻¹, respectively. Concentrations of 90Sr in contaminated ground water samples ranged from 18 to 32.3 fg ml⁻¹, while concentrations of 239Pu from 28 to 856 fg ml⁻¹ were measured. The 240Pu/239Pu isotopic ratio in water samples was found to be 0.17. This isotope ratio indicates that the most probable source of contamination of the investigated ground water samples was the nuclear weapons test in the sixties.

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DETERMINATION OF RADIUM-226 IN MINERAL WATERS AT
ULTRATRACE LEVEL BY SECTOR FIELD INDUCTIVELY COUPLED
PLASMA MASS SPECTROMETRY

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Determination of long-lived radionuclides in environmental samples and foods at ultratrace level is a challenging task of analytical chemistry [1, 2]. Among the artificially produced actinides (e.g. ²³⁶U, ²³⁹Pu, ²⁴⁰Pu, ²³⁷Np, ²⁴¹Am etc) naturally occurred long-lived radionuclides such as ²²⁶Ra in drinking water and foods is in particular interest [3, 4].

An analytical procedure for determination of ²²⁶Ra in low femtogram per ml concentration level in mineral water samples has been proposed. For the pre-concentration and separation of radium from the water matrix a tandem of laboratory prepared filter, based on MnO₂, and Eichrom "Sr-specific" resin was used. The recovery of the method was found to be 71.5%. Determined limit of detection and limit of quantification for ²²⁶Ra were 0.02 and 0.06 fg ml⁻¹ respectively, assuming pre-concentration factor of 10. In addition uranium concentration and uranium isotope ratios were measured. Generally, the radium and uranium concentrations in analyzed mineral water samples were not considerable, except of two samples where the concentration of ²²⁶Ra were 10.3 fg ml⁻¹ and 14.2 fg ml⁻¹ and the concentration of U were 17.3 ng ml⁻¹ and 19.2 ng ml⁻¹, respectively. The effective dose of contribution was calculated using the radionuclide concentration and dose conversion factors from the World Health Organization WHO (1993). Assuming the mineral water consumption of 2 l d⁻¹ a slightly higher calculated doses than suggested limit for drinking water (0.1 mSv y⁻¹) in some samples were found.

MICROLOCAL (15-50 μm) ISOTOPE RATIO MEASUREMENTS OF URANIUM
ON BIOLOGICAL SURFACE BY LA-ICP-MS WITH A COOLED LASER
ABLATION CHAMBER

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Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful analytical technique for the determination of element concentrations at the trace and ultratrace level and isotope ratio measurements of long-lived radionuclides in solid samples [1, 2]. In addition, this technique can also be applied as the surface analytical technique, in particular, for the surface analysis of biological samples (e.g. brain, liver). However, due to the presence of water in different biological sample (more than 30%) the stability of laser ablation process will be altered, that, therefore, leads to decrease of RSD of the measurements [3].

The aim of the present work was to study a method utilizing LA-ICP-MS with cooled laser ablation cell in order to improve precision and accuracy of direct microlocal uranium isotope ratio measurement at the ultratrace level on the surface of biological samples. A cooled laser ablation chamber using a Peltier element was developed in order to analyze element distribution in thin cross sections of frozen tissues with a lateral resolution in the μm range. In order to study the figures of merit of LA-ICP-MS with the cooled laser ablation chamber, one drop (20 μl , U concentration 200 ng mL^{-1}) each of the certified isotope reference materials NIST U350 and U930, the uranium isotopic standard CCLU 500 and also a drop of uranium with a natural isotopic pattern was deposited and analyzed on the biological surface (flower leaf). The precision and accuracy of isotope ratio measurements are significantly improved using cooled laser ablation chamber in comparison to non-cooled chamber. The precision of isotope ratio measurements in the range of 2.0-1.6 % for $^{234}\text{U}/^{238}\text{U}$, 1.3 to 0.4 % for $^{235}\text{U}/^{238}\text{U}$ and 2.1 – 1.0 % for $^{236}\text{U}/^{238}\text{U}$ in selected uranium isotopic standards reference material were determined by microlocal analysis (diameter of laser ablation crater: 15, 25 and 50 μm) using LA-ICP-MS with a cooled ablation chamber. The accuracy of $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ isotope ratio measurements varied in the range of 4.2 – 1.1%, 2.4 – 0.5% and 4.8 – 1.1%, respectively, and were dependent on the diameter of the laser beam used.

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ICP-MS ANALYSIS OF TRACE ELEMENTS IN THE DIFFERENT REGIONS OF
HUMAN BRAINS INFECTED WITH ALZHEIMER DISEASE VS. CONTROL
BRAIN

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Potential role of trace elements on the progressing of several brain diseases (e.g. Alzheimer, Schizophrenia, Epilepsy) have been increasingly studied in the past years [1, 2]. The physiological function of trace elements in the human brain samples depends on their binding properties to different proteins and their concentration [3]. So it is important to determine not only the distribution of the elements in different proteins, but also the total element concentration in analyzed sample. Moreover, determination of toxic elements (e.g. Hg, Cd, Pb) may of additional importance.

In present study comparative multielemental analysis of the different regions of human brain samples infected and non-infected with Alzheimer's disease was performed by ICP-SFMS. In measured samples the presence of the elements such as Al, Si, P, S, Mn, Fe, Ni, Co, Cu, Zn, Y, Cd, Hg, Pb, and U was found. Elevated concentration of the phosphorus, sulfur, iron, copper and zinc was detected and was different in the sample infected and non-infected with Alzheimer disease (e.g. phosphorus concentration of 0.9 and 0.1 mg ml⁻¹ was determined, respectively). Some elements, such as Al and As were found only in Alzheimer disease brain sample, whereby V, Cr, and Th were below the detection limits in both samples. Obtained limits of detection for selected elements ranged from 0.0005 to 17 ng mL⁻¹, depending on the element analyzed.

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