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## ABSTRACTS

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- Plasma Spectrochemical Studies and Instrumentation
- Solid State Methods – GD Sources and Applications



and



**EUROPEAN COMMISSION**  
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# *Oral and Poster Sessions on Monday 19 February 2007*

## *Abstracts*

KN 01

PLASMA SPECTROMETRIC INSTRUMENTATION: NOT FOR JUST ATOMS ANYMORE

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In the atomic spectrometry community, the use of plasma sources has become associated almost exclusively with elemental analysis. This trend is not surprising; after all, inductively coupled plasmas, glow discharges, and microwave-induced plasmas offer outstanding figures of merit for the determination of metals and metalloids. However, in other fields, these same sources, suitably modified, and others such as corona discharges can be used not only to ionize samples but also to desorb and fragment them. These alternative plasmas therefore offer promise for molecular and speciation analysis.

In this presentation, the focus will be on alternative plasma sources that are capable of molecular characterization and speciation, and on spectrometers that take maximal advantage of these source features. The first new source is intended for the simultaneous emission-based examination of spots on a two-dimensional (planar) chromatographic plate, such as one from thin-layer chromatography or two-dimensional gel electrophoresis. Coupled with a monochromatic imaging spectrometer, the glow-discharge source enables the simultaneous detection and quantification of spots that hold metal-containing proteins or those stained with silver, gold nanoparticles, or metal-containing affinity tags used to identify functional groups. The device is anticipated to be an important tool in the emerging area of “metallomics”.

A second new source is based on the flowing afterglow produced by an atmospheric-pressure glow discharge (APGD). Simple in design, construction, and operation, this novel source can ionize vapor-phase samples or can be used to volatilize solution or solid samples directly and to ionize the resulting molecules. In all cases, the resulting mass spectra are amazingly simple, and consist mainly of the molecular ion or the protonated molecular ion. Because of this spectral simplicity, simple mixtures of compounds can often be characterized fully, without a prior separation. The plasma source is therefore useful for speciation analysis. It has been coupled to both time-of-flight mass spectrometers (TOFMS) and an array-detector mass spectrometer.

A TOFMS useful for molecular characterization and speciation will also be described. This spectrometer can be coupled to two or more ion sources at a time; here it is used with an ICP and an ESI source, the first to produce elemental mass spectra and the

second to be used for speciation information. This instrument is expected to be another important tool for metallomics.

#### Mo01

##### ION-MOLECULE REACTIONS TO OVERCOME SPECTRAL OVERLAPS IN ICP-MS

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Ion molecule reactions can provide a highly selective, highly efficient means to overcome spectral overlaps in ICP-MS. The current status of ion-molecule reaction methods to overcome the wide variety of spectral overlap types including molecular ions from the plasma, sample solvent and sample matrix will be assessed. Ion-molecule reaction chemistry and rates with different types of overlap ions and analyte ions will be discussed. Absolute ion-molecule reaction rates reported using selected ion flight tube measurements will be compared to relative reaction rates observed in the Dynamic Reaction Cell. The use of ion-molecule reactions for elemental analysis and isotope ratio measurements will be considered. Applications of ion-molecule reactions for elemental analysis, ICP-MS detection for elemental speciation analysis and laser ablation ICP-MS will be discussed.

#### Mo02

##### HIGH-FIELD ASYMMETRIC WAVEFORM ION MOBILITY SPECTROMETRY-MASS SPECTROMETRY FOR TRACE ELEMENT SPECIATION

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High-Field Asymmetric Waveform Ion Mobility Spectrometry (FAIMS)-Mass Spectrometry represent a very new approach for ion filtration/separation. The principles of FAIMS were first elaborated by Burakov *et al.* [1] and further described by Guevremont *et al.* [2]. FAIMS is a gas phase ion separation technique. The separation is based on the differential mobility of ions in high and low electric fields. It has been shown that FAIMS reduces background chemical noise and may resolve isobaric interferences thus improving detection limits while maintaining absolute signal intensities. Additionally, FAIMS can greatly reduce the time required for the analysis because the scanning of the transmission conditions specific for individual compounds is significantly shorter than the time required for LC separation.

In this presentation examples will be given for FAIMS MS based separation and detection of arsenic, selenium and platinum species [3-4].

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### MO03

#### ANALYTICAL PERFORMANCE OF A NEW RADially VIEWED CID-ICP-AES FOR ANALYSIS OF BRINES AND RELATED SAMPLES – SPECTROSCOPIC AND NONSPECTROSCOPIC INTERFERENCE EFFECTS.

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Radially viewed inductively coupled plasmas (RAD-ICP-AES) are ideally suited to the needs of earth and environmental science and related technologies. These analytical systems, specifically designed to provide elemental data for a wide range of complex geological, mineralogical and related raw materials, are generally considered to be more suited owing to easily ionized element interference effects in axially-viewed ICP-AES.

In this presentation we will describe the analytical performance of the new Thermo Electron (Cambridge, UK) radially viewed ICAP 6500 CID based spectrometer for major, minor and trace element determinations of high salt solutions, particularly natural and industrial brines and sediment extracts.

This instrument configuration features a versatile simultaneous spectrometer providing high spectral line selection for the analysis of complex brines and geological materials

Performance will be judged using conventional figures of merit, such as effect of Na and Ca concentrations on analyte spectral line intensity, linearity of the calibration functions, LODs, and recoveries from CRMs and spiked matrix samples. The MgII/MgI ratio will be employed to determine the robustness of the optimized analytical system (flow rate, observation height, RF power and injector diameter). These characteristics will be compared with various axially viewed ICP designs.

It is concluded that the performance of the robust radial plasma system is ideally suited for analysis of “difficult” brines and geological samples.

### Mo04

#### ELEMENT-SPECIFIC INVESTIGATION OF MICRO-CORROSION PROCESSES IN Al ALLOYS BY ICP-MS

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Different types of aluminium alloys are widely used in industry e.g. automotive industry or aircraft construction. Most of the industrially used alloys are called passive systems because of the formation of nm thick stable surface oxide layers. However, aluminium alloys are susceptible to pitting corrosion, since a local breakdown in the passive oxide layer can occur e.g. at inclusions or grain boundaries. This leads to local dissolution of the alloy material resulting in fast damages. Therefore, a detailed knowledge of spatially and time resolved rate of elemental dissolution is essential for the thorough investigation of corrosion processes and further prevention of surface degradation processes.

In order to obtain element-specific information on corrosion processes an ICP-MS feasibility study was performed. The data on elemental dissolution rate allow to evaluate whether a miniaturization of in-situ investigations is possible.

Main challenges of a novel hyphenated technique will be discussed. A special attention will be given to spectral interferences, correction strategies, matrix and background effects in ICP-MS analysis applied to Al alloys corrosion investigations.

Since the corrosion of Al alloys is a complex process dependent on a number of crucial factors such as variation of the corrosive media type and concentration, impact time, surface treatment, results displaying the influence of those factors on elemental dissolution will be presented. In addition, results of corrosion tests on several types of Al alloys demonstrate which secondary and trace element components can be detected besides the main alloying element.

## KN 02

### ICP-MS AND THE SECOND PUNIC WAR

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The general status of ICP-MS will be addressed briefly. The results of new experiments in the following areas will be presented:

Identification of polyatomic ions from accurate mass measurements, isotopic substitution, and theoretical calculation of their fundamental properties.

Further deduction of the origins of such ions from measurement of the gas kinetic temperature corresponding to their abundance.

Laser ablation for direct, spatially-resolved analysis of solids. High speed photographic studies of atomization during laser ablation in the ICP.

## Mo05

### HOW TO FAVOUR THE USE OF MULTILINE ANALYSIS IN CCD-BASED ICP-AES ?

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In order to take full benefit of the available information obtained with multichannel detection, several lines per element may be used so as to perform multiline analysis. In order to favour multiline analysis, HORIBA Jobin Yvon has developed a series of software tools to be used with the CCD-based ACTIVA ICP-AES system. The aim is to facilitate method development. The first tool is dedicated to multiline selection, and is called MASTER (Multi-element Analysis, Selection Tool for Enhanced Reliability). MASTER makes use of an ICP-based spectra database. Acquisition of this database has been performed with the ACTIVA under standard operating conditions and with an automatic interpretation of the data, in particular for line assignment. The database contains information about wavelength, excitation energy, line width, sensitivity, limit of detection (LOD), detector saturation, and background intensity. Based on this information, it is possible to select lines that can be used over a given concentration range, and to predict spectral interferences through a filtering procedure and an interactive display of the lines and their vicinity. There is obviously no need to prepare synthetic solutions and to perform tedious and time-consuming experiments. The next tool makes use of the SOS (Statistics for Outlier Survey) software. A detailed analysis of variance (ANOVA) is applied to the series of line concentrations so as to detect any possible outlier. A reliable, single concentration can be, then, deduced for each analyte.

## Mo06

### DEVELOPMENT OF A UNIVERSAL PROCEDURE FOR COMPENSATION OF PLASMA-RELATED MATRIX EFFECTS 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. The presence of matrix effects, without the awareness and subsequent correction by an analyst, will lead to an analytical error. A plasma-related matrix effect is probably the most troublesome type of interference in the ICP for two reasons. First, it is not always easy for an analyst to spot the presence of such an interference. Second, the degree of interference usually depends on the characteristics of the analyte and its emission line; as a result, it is not possible to use a single internal standard for universal correction in a multi-element analysis. Currently, the most commonly used compensation techniques for matrix effects are matrix separation, matrix matching, internal standardization, and standard additions. While all these methods will reduce the problem when correctly applied, they require either some prior knowledge about the sample (e.g., matrix separation, matrix matching), the approximate concentration of the analyte in the sample (e.g., standard addition) or even a separate study (e.g., internal standardization), and are time-consuming and laborious in most cases.

A novel and more universal methodology that can flag the presence of matrix interferences and simultaneously compensate for their effects is developed in the present study, with an aim that the method will be widely applicable for a range of samples and without any knowledge of their matrix compositions. In this presentation, the theoretical

basis of this novel matrix-effect correction method will be discussed and its effectiveness will be evaluated.

#### Mo07

##### CHARACTERIZATION OF THE ICP-MS CAPABILITIES USING METHANE ADDITION

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The analytical performance characteristics of sector field ICP-MS (Finnigan ELEMENT 2) can be significantly improved by adding methane to the argon gas flow (Field et al, Rodushkin et al). Especially when samples of high matrix content are analyzed, methane addition minimizes drift effects and certain spectral interferences, beside that the sensitivity for analytes with high ionization potentials are significantly improved. The current work has investigated to which extend these findings are transferable to Quadrupole ICP-MS using a collision cell (X-Series 2) for the minimization of spectral interferences. In-depth analysis and comparison between the two ICP-MS technologies have been carried out to evaluate the benefit of Methane addition for Quadrupole ICP-MS. Different samples types ranging from high matrix samples to ultra-pure water (UPW) and isotopes of different ionization energies have been assessed.

#### Mo08

##### ULTRA-TRACE SPECIATION ANALYSIS OF MERCURY IN ANCIENT ANTARCTIC ICE

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This work deals with the development of an analytical method for speciation analysis of mercury ( $\text{CH}_3\text{Hg}^+$  and  $\text{Hg}^{2+}$ ) at ultra-trace levels and its application to the analysis of ancient Antarctic ice (time span between ~10,000-200,000 years). The method is based on (headspace) solid-phase microextraction (SPME) combined with multi-capillary gas chromatography hyphenated to inductively coupled plasma time-of-flight mass spectrometry. By using a 75  $\mu\text{m}$  carboxen-polydimethylsiloxane SPME fiber, method detection limits (MDL) of 0.03  $\text{pg g}^{-1}$  (as Hg) for  $\text{CH}_3\text{Hg}^+$  and 0.3  $\text{pg g}^{-1}$  for  $\text{Hg}^{2+}$  were obtained. The analytical repeatability in terms of relative standard deviation was below 5% for 10 successive injections of a standard mixture of 10  $\text{pg g}^{-1}$   $\text{CH}_3\text{Hg}^+$  and  $\text{Hg}^{2+}$ . The highest concentrations of both mercury species occurred during the last glacial age, presumably due to enhanced atmospheric circulation from the Southern Ocean to

Antarctica. Levels close to the MDL were obtained preponderantly during the last glacial-interglacial transition. The detection of  $\text{CH}_3\text{Hg}^+$  in the Antarctic ice may constitute the first direct indication of the Southern Ocean's contribution of mercury to Antarctica. The speciation data are evaluated on the basis of geo-chemistry and emissions sources and may contribute to the elucidation of the transport mechanisms of mercury species into remote environments such as the poles.

#### Mo09

##### PROS AND CONS FOR INERT AND REACTIVE CELL GASES IN COLLISION/REACTION CELL ICP-MS

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

For routine purposes, separation should be fast (below 15 minutes), sensitive (quantification limits below 0.5ppb) and must allow the separation of all the toxic inorganic and organic forms of As in urine - AsIII, AsV, MMA, DMA - from the non toxic AsB..

Work has been performed on an Agilent 7500ce ICPMS equipped with an octopole collision/reaction cell, which may be necessary to resolve residual Cl-based overlaps on As with some separations.

Different separations and mobile phases have been tested. Using a newly developed column and a mobile phase composed of 2mM phosphate buffer solution, 10mM  $\text{CH}_3\text{COONa}$ , 3mM  $\text{NaNO}_3$ , 1% EtOH, adjusted to pH=11, the desired separation can be achieved in 12 min using an isocratic elution and injecting 5 $\mu\text{l}$  of undiluted urine. Moreover, the elimination of the main interferent of As, which is ArCl, can be achieved either by separating the elution of Cl from As species or eliminating ArCl using octopole reaction system. Detection limits vary between 0.035 and 0.1 $\mu\text{g/L}$  depending on the species. Repeatability of peak area and retention time on 15 urine samples ranges respectively between 0.95 and 1.8% and between 0.08 and 0.11%. The method has been validated analyzing NIES certified reference material no.18.

The developed method offers new possibilities for routine monitoring of arsenic speciation in urine.

#### KN 03

##### COMPREHENSIVE SPECIATION USING A GLOW DISCHARGE IONIZATION SOURCE: WHO WOULD HAVE THOUGHT . . . ? **R. Kenneth Marcus**, Tim M.

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This laboratory has been following a line of research wherein we are looking to provide tools for what we have termed “*comprehensive speciation*”. That is, we look to

couple a chromatographic separation (typically liquid chromatography) with a single ionization source capable of producing both elemental and molecular mass spectra. A secondary criterion that we look to maintain is the ability to sample LC effluents under a variety of elution conditions including reversed-phase, ion exchange, and hydrophobic interaction. To this end, we have chosen to use a particle beam (PB) LC/MS interface to convert the solute/solvent mixtures to dry analyte particles for delivery into a low-pressure ion source. In doing so, the interface serves to enrich the analyte concentrations and totally remove deleterious solvent effects within the ion source.

Glow discharge (GD) ion sources have a long history of effective use in the elemental analysis of solid samples. The low pressure (~1 Torr), inert gas plasma provides an environment where thermal degradation of molecular species takes place, yet with sufficient energetics to yield meaningful molecular and elemental mass spectra. The development of the LC/PB-GDMS instrument has been funded specifically for use in the characterization of botanical extracts (i.e., nutraceuticals). The analytical challenges in this area are immense as one must first distinguish between toxic, carcinogenic, adventitious, and benign forms of the elements. On a secondary level, one would also like profiling of active ingredients and additives. Finally, one would need to perform these analyses across the broad spectrum of sample forms, including raw materials, ethanolic and aqueous extracts, and a number of solid tablet matrices.

We will describe here the design and operation aspects of the LC/PB-GDMS system as is applied to a variety of botanical materials including echinacea, green tea, ephedra, kelp, and bladderwrack. The ability to perform comprehensive speciation will be demonstrated in the case of arsenic components in the kelp and bladderwrack. Identification and quantification of active ingredients in the green tea will also be presented, particularly in light of the now cult-like sales of the drink. It is believed that the coupling of HPLC, the PB interface, and GDMS analysis is a powerful approach that can indeed deliver *comprehensive speciation*.

## Mo10

### EXCITATION BEHAVIOUR OF IRON ATOMIC LINES HAVING VARIOUS EXCITATION ENERGIES EMITTED FROM GLOW DISCHARGE PLASMAS USING ARGON, NEON, AND ARGON-HELIUM GASES

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The emission characteristics of 62 iron atomic lines having the excitation energy of 3.4 - 6.9 eV are investigated by means of the excitation temperature as well as their Boltzmann plots, when the discharge voltage and the gas pressure are varied. The emission lines in the range of 3.4 - 4.8 eV are well fitted to a straight line of the Boltzmann plot, which is almost independent of both the discharge voltage and the gas pressure. The excitation temperature estimated from these Boltzmann plots is little changed by the discharge parameters. However, the emission lines having the excitation energy of more than 5 eV deviate from the linear relationship upwards, implying that they are over-populated compared to the expected ones under thermodynamic excitation process. It is therefore considered that, in addition to thermal excitation processes such as electron collision, any

additional excitation channel would exist for iron atomic lines having larger excitation energies in the glow discharge plasmas.

#### Mo11

##### ELEMENTAL SURFACE IMAGING WITH A PULSED RADIO-FREQUENCY GLOW DISCHARGE.

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Glow discharge atomic emission spectrometry has become an important surface elemental analysis technique in part because of its outstanding depth resolution (on the order of single nanometers). However, the ability of the glow discharge to provide laterally resolved information has been explored in very few studies. Presented here is the coupling of an end-on viewed pulsed radio-frequency glow discharge to a monochromatic imaging spectrometer to provide lateral surface imaging. The performance of the instrument is demonstrated with etched copper on fiberglass targets. Several operating parameters are shown to affect the lateral surface resolution, including pressure, pulsed-mode operation, and time-resolved detection. In addition, the ability of a pulsed radio-frequency glow discharge to provide elemental information from non-conducting samples is exploited by applying the technique to the surface elemental imaging of proteins on blotting membranes. Several additional sample types are also examined, such as glass and photographic film.

#### Mo12

##### BREAKTHROUGHS IN RF GD FOR THE CHARACTERISATION OF THIN FILMS

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Radio Frequency Glow Discharge with Optical Emission Spectrometry detection is now an established technique capable of Ultra Fast Elemental Depth Profiling of thin films down to the nanometre.

The theoretical and experimental characterisations of the RF GD plasma and of the interaction plasma/sample are permitting some important knowledge based breakthroughs that will be described.

The first series of results that will be presented are about fragile thin films (polymers and glasses) where the optimisation of the RF coupling efficiency and the minimisation of induced heat are key aspects.

The second topic will introduce the possible use of RF GD as a preparation tool for Scanning Electron Microscopy. Recent results published on ultra thin films featuring molecules adsorbed on surfaces have shown the minimal surface damage that the technique induces and have given birth to this idea at the cross road of two domains. Adequate sample preparation methodology will be described using the technique developed for glasses.

#### KN 04

##### DEVELOPMENT AND APPLICATION OF MASS SPECTROMETRY FOR CURRENT SOLID STATE AND MATERIALS RESEARCH

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The introduction of spark source mass spectrometry (SSMS) offered a technique whereby solid samples could be atomised and ionised by an energetic spark. Unfortunately, the instability of this source meant that large integration times were necessary to average out the signal, and therefore photographic plates were used as the detection system. Because of the comparably simple evaluation of the measured spectra, fast and easy preparation techniques for many kinds of samples, like powders and chips and sensitivity factors within one order of magnitude, SSMS is still unique, e.g. at semi-quantitative survey analyses. Additionally, the use of a high vacuum system allows the determination of light elements far below 1 µg/g, which is difficult or impossible for most other analytical methods. The lack of an instrument manufacturer and the need of photographic plates limit the use of SSMS nowadays to universities and research institutes and SSMS is only used in a few laboratories of the world for special applications. However, the development of new electronic detectors could cause a revival of this technique. Also the use of laser ionisation and time of light mass spectrometers offer ways to overcome the present limitations of SSMS including the possibility to analyse nonconductors and to perform laterally resolved elemental analysis.

In practice, glow discharge mass spectrometry (GDMS) has become the industry standard for the analysis of trace elements in metals and semiconductors. A review of its history is followed by a picture of the present situation and a look to where the future may lie. Since the introduction of a new GDMS instrument by Thermo Finnigan in 2005, new features exist and the corresponding new possibilities will be discussed. Finally, recent work about the “fast flow” source and pulsed glow discharges is presented.

#### Mo13

##### COMPOSITIONAL DEPTH PROFILE ANALYSIS BY GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY – APPLICATIONS AND RECENT DEVELOPMENT.

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The Grimm [1] type glow discharge source was originally designed for bulk elemental analysis of metals and alloys. While it has proven to be a highly useful tool for this purpose, the most important application area for GD-OES has become compositional depth profiling (CDP) of surfaces and layers. Metallic coatings, surface segregation, oxides, PVD coatings, polymers etc. are typical application areas. It is well established that GD-OES has proven to be a very fast, powerful and versatile technique for CDP, with state-of-the-art systems it is also quantitative. The purpose of the analysis can be R&D for product development, quality control of a production line, or just “trouble-

shooting” when there is a technical problem that may be related to surface chemistry. In this work, examples of a few applications illustrating the impressive versatility of the technique are presented:

- The Zn layer on a batch of hot dipped galvanised steel sheet peeled off in various spots. The GD-OES analysis shows a strong oxygen peak in the interface, the absence of carbon shows that this is due to an oxide layer.
- A shiny aluminium panel plate was slightly discoloured as delivered from the manufacturer. A near-surface analysis, and comparison with an acceptable surface of the same type of material, revealed that some alloying elements had segregated to the top surface of the discoloured plate.
- The extremely thin passivation layers on high purity cold-formed stainless steels. The difference between a material that was bright annealed and one with a proprietary cleaning and passivation treatment will be shown and discussed.
- A white polyester paint on anodised aluminium sheet was analysed using the RF (radio frequency) source to check the thickness and composition of the complete coating. The analysis shows a homogeneous polyester coating, but strong enrichment of S in the anodised layer underneath.

The most recent development in quantification techniques will be presented; hydrogen correction [2,3] and subtraction of background from molecular emission [4]. Both of these techniques have been shown to be very important in order to improve the analytical accuracy in applications to organic coatings and very thin films. The potential for further improvements in correcting for these and related phenomena will be discussed.

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#### Mo14

##### THE INFLUENCE OF SAMPLE MATRIX ON PROCESSES IN A GLOW DISCHARGE WITH DIRECT SOLUTION SAMPLING.

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The electrolyte-cathode discharge (ELCAD) takes the constituent atoms from a solution phase to electronically excited atoms in a small (~1 mm) distance. The source operates in open atmosphere at relatively low power (~60 W). Advantages of this strategy include simplicity, low cost, lack of a gas flow, and compactness. Detection limits are mostly in the 10s of ppb, and the dynamic range extends over more than 4 orders of magnitude for some elements. Combined, these attributes give the ELCAD potential as a field instrument, but further exploration of the source's processes and performance are necessary before this potential can be met. Because the sample is an integral part of the source, there is substantial coupling of processes along the path from solution to excitation. In this work, we explore the influence of sample composition on ELCAD behavior. This leads to knowledge of limitations in the discharge's conventional

operation, deeper understanding of the its mechanisms, and strategies for improving its function.

## Mo15

### CHALLENGES AND SOLUTIONS OF SEPARATION TECHNIQUES COUPLED TO DC-PULSED GLOW DISCHARGE TIME OF FLIGHT MASS SPECTROMETRY.

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Pulsed glow discharges are ionization sources that provide to time dependent formation of elemental, fragmented and molecular ions within one plasma pulse.

Coupled to gas chromatography and in combination with mass spectrometry, quantification of organic analytes is possible and the figures of merit of today's GD-TOFMS instruments are improved compared to early instruments in terms of mass resolution, sensitivity and data acquisition speed.

Coupling the pulsed glow discharge to separation techniques like gas chromatography or other methods nevertheless remains a challenge due to the lack of adequate interfaces which is limiting the achievable sensitivity.

Moreover the huge amount of data acquired during measurements in less than a second still is exceeding the performance of current personal computer hardware.

The properties of the pulsed glow discharge plasma are highly sensitive to quenching agents as H<sub>2</sub>, water or organic solvents.

Especially the population of the metastable argon species, which is responsible for the "soft" Penning-ionization, is dependent on the plasma operating parameters. However thresholds for a maximum plasma load with quenching agents, until the molecular information in the afeterpeak vanishes, have not been reported.

The quenching by organic solvents was studied and quantified in detail with respect to the impact on the performance of coupling techniques.

Different concepts for interfacing different sample introduction systems suitable for gaseous, liquid and solid samples will be discussed.

Finally, applications of pulsed glow discharge time of flight mass spectrometry in the field of chemical speciation of Se compounds with respect to the elemental, structural and molecular information will be presented.

*Poster Session Monday 19 Feb 2007*

**MoPo1.** OPTIMIZED FLOW BLURRING NEBULIZER-BASED SAMPLE INTRODUCTION SYSTEM AS A GENERAL ATTEMPT TO REMOVE NON-SPECTROSCOPIC INTERFERENCES PRODUCED BY HIGH CONTENT OF MINERAL ACIDS ON ICP-AES

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Aqueous solution is still the most common way of presenting samples to ICP-based atomic spectroscopic techniques (*i.e.*, ICP-AES and ICP-MS). Both techniques are sufficiently robust to analyze a wide variety of samples (*e.g.*, biological, clinical, environmental, forensic). However, in many cases it is necessary to use specific methodologies for successful determinations (*e.g.*, matrix matching, internal standard, standard addition, numerical methods) because sample solution properties are different from standard aqueous solutions. Matrix's components affect the characteristics of the analytical signal finally obtained. Mineral acids belong to this kind of matrix's components and it seems that, under robust plasma conditions, a fraction of this commonly negative interference effect occurs during aerosol generation and transport to the plasma. To aspire of solving this problem, an alternative to the methodologies mentioned above is the sample introduction system improvement.

Hence, the present work will show the optimization of a new sample introduction system using a Flow Blurring Nebulizer (FBN) and evaluating some spray chambers of different design, material and internal volume with the aim to remove, or at least reduce, the non-spectroscopic interferences caused by mineral acids. To this end, solid real samples digested in both, closed and open microwaves systems, using concentrated acids will be analyzed by ICP-AES, being compared with calibration aqueous standards.

**MoPo2.** INTRODUCING THE T2100 – A NEW HIGH SOLIDS / SLURRY NEBULIZER

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The new high solids T2100 nebulizer has been run in comparison with several other industry standard nebulizers. While most high solids nebulizers have much poorer sensitivity and stability than standard ICP nebulizers, the T2100 has results comparable to standard glass concentrics and much better results than the compared cross flow nebulizers. A brief description of how the design works will be presented along with comparison charts showing stability and sensitivity compared to several other nebulizers.

**MoPo3. MICROCAPILLARY ARRAY NEBULIZER – A FLEXIBLE TOOL FOR LIQUID AEROSOL GENERATION FOR OPTICAL AND MASS SPECTROMETRY**

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A novel microcapillary array pneumatic nebulizer has been designed and constructed for use in dedicated spectrometric techniques. Our criteria for this development included the ability to working at different gas flow rates and at low sample consumption as well as to produce fine aerosol with high efficiency. A very localized aerosol generation surface is formed by microcapillary array technology. Basic operating parameters and characteristics have been studied for ICP dedicated nebulizer (NAR-1) to determine how this new nebulizer may be applied to both OES and MS. The performance and nebulization characteristics of the nebulizer depend on microcapillary array parameters. At low flow rates (20-200  $\mu\text{l min}^{-1}$ ), the mean droplet size is approximately 1  $\mu\text{m}$ , and over 50% of the sample is converted to usable aerosol. Generally good stability, precision and reproducibility are observed for emission signals of some metals at all flow rates without desolvation. The results of preliminary comparison with the conventional Meinhardt nebulizer with cyclonic spray chamber indicate several notable advantages. The NAR-1 nebulizer produces a smaller droplet size distribution and has the higher sample transport efficiency. The operation of NAR-1 is controlled by microprocessor to improve sampling, measuring and washing stages. The wash-in and was-out times are acceptable for routine practice.

Analytical characteristics include ICP-OES, ICP-MS and MIP-OES detection limits for some elements at  $\text{ng ml}^{-1}$  level and signal stability of between 0.5 and 2%. The ability to provide high analyte transport efficiency at low flow rates suggests good potential for the NAR-1 use as microsample introduction technique. The nebulizer should be readily applicable to FAAS, ICP-OES, ICP-MS and MIP-OES/MS.

**MoPo4. SPECTROSCOPIC DIAGNOSTICS FOR EVALUATION OF THE ANALYTICAL POTENTIAL OF ARGON + HELIUM MIP WITH SOLUTION NEBULIZATION.**

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Spectroscopic diagnostics is used to predict mixed (Ar+He) plasma conditions and a possible improvement of analytical performance of microwave induced plasma with solution nebulization. All measurements are performed using one experimental setup based on a  $\text{TE}_{101}$  integrated cavity, hence, the results are easily comparable. The analyte solution was introduced by means of microcapillary array pneumatic nebulizer in the form of wet aerosol. Rotational temperature is determined to study the analyte

vaporization capacity of the MIP as well as  $T_{ion}$  to evaluate the ionization degree. Radial profiles of electron number density and electron temperature as well as excitation temperature are obtained. Emission profiles and limits of detection for some elements are determined. Additionally, the influence of operating conditions on plasma parameters and matrix effects caused by easily ionized elements are investigated. Fundamental plasma parameters for both pure argon and helium MIP are determined and compared to those obtained for the PN-MIP-OES. The presence of aerosol causes a substantial increase of all plasma parameters for argon plasma, while in the case of helium a slight increase of electron number density and the effect of plasma cooling are observed. Argon plasma exhibits high tolerance for water loading up to  $250 \text{ mg min}^{-1}$ . The helium MIP is more robust as changes in operating parameters and EIE concentration affect slightly plasma parameters and analytical figures of merit. The mixing of argon and helium is assumed to be more favorable for sample excitation and as a result for analytical performance of the MIP.

Remarkable differences in fundamental plasma parameters are observed when helium has been introduced to the argon plasma. The electron number density in the mixed plasma is slightly lower than that in argon (about  $2 \cdot 10^{15} \text{ cm}^{-3}$ ). However, a considerable increase of rotational temperature (3700 K) and Ar excitation temperature (7500 K) is observed. This leads to improvements in DLs for some metals. The addition of sodium causes a considerable improvement in DLs for ionic lines and relatively low changes for atomic lines of some metals. This indicates a robust plasma conditions and possibility of minimizing matrix effects caused by EIE.

#### **MoPo5. CALIBRATION STRATEGIES FOR DIRECT DETERMINATION OF MAJOR AND TRACE METAL CONTENT BY CONTINUOUS POWDER INTRODUCTION MICROWAVE INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY**

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Calibration is a crucial problem of solid sample analysis using any spectrometric method. Accurate results can be achieved using calibration with solid standards if only the matrix composition of the sample and the calibration standards are almost identical. The availability of reference materials of the similar matrix composition and containing analytes in a wide range of concentration is limited. Moreover, it has been shown for most spectrometric techniques that the particle size of standards and samples is a very important parameter. Matching similar particle size ranges is necessary for improved accuracy.

Despite calibration with solid reference materials, there are few approaches, which may be considered for the calibration in direct solid analysis by continuous powder introduction plasma optical emission spectrometry. For determination of major contents of analyte external calibration is adequate with using calibration standards prepared by dropping of standard analyte solution on a suitable powdered support with matrix matching. The determination of some metals (Co, Mo, V, Ni) at the concentration level of several percent in alumina and silica based catalysts by CPI-MIP-OES is shown as an example.

For determination of trace metals standard addition technique with aqueous standard solutions seems to be attractive because standard solutions are readily available and inexpensive. This calibration technique is strongly recommended for multielement determinations. However, it should be noted that the addition of aqueous standards to solid samples raises problems related to the different chemical form in which the analyte is added and that in which it is present in the sample. Moreover, differences in vaporization efficiency are possible between surface impurities (analytes added) and bulk traces (analyte originally present in the sample). The standard addition method was successfully applied for determination of some elements in alumina powder.

The use of external calibration is also suitable for determination of trace metals by CPI-MIP-OES. In particular, it is attractive when coupled with preconcentration and separation of the analytes. The proposed procedure was used for heavy metals determination in water samples and for precious metals in the platinum ore. A sensitive direct spectrometric method for the determination of total fluorine content in a wide variety of geological materials has been also developed and presented on the separate poster.

**MoPo6.** COMPARISON OF EXCITATION CONDITIONS IN INDUCTIVELY COUPLED PLASMA AT VARIOUS SAMPLE INTRODUCTION SYSTEMS

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Inductively coupled plasma optical emission spectrometry (ICP-OES) despite of great progress in development and wider application of inductively coupled plasma mass spectrometry is still not only very popular and recommended technique of trace analysis but is also considered worthy to be of subject of fundamental and inquisitive studies.

Sample introduction systems used in the ICP-OES have significant influence for plasma excitation conditions and in a consequence for analytical figures of merit.

In the present study inductively coupled plasma combined with various analyte introduction systems was investigated. The analytes were supplied into plasma as aerosol and/or gas phase. The gas phase was produced using a hydride generation system with and without phase separation. Multielemental solutions with various inorganic and organic matrices were used.

Lines of elements being components of the samples analyzed, lines of argon and hydrogen, as well as rotational lines the OH  $A^2\Pi - X^2\Sigma^+$  0-0 band and the  $H\beta$  half width were measured at various sample introduction systems.

The ion-to-atom intensity ratios, electron density, excitation and ionization temperatures were determined to search differences in plasma characteristics. In addition to lines of iron (considered commonly as a standard thermometric indicator), lines of light and heavy elements were employed for the temperature determination.

Excitation conditions were discussed in point of view non-equilibrium state of plasma and analytical performance.

**MoPo7.** ATOMIZER FOR SPECTROCHEMICAL ANALYSIS

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The universal design of the atomizer may be perspective for the realization of the different spectrochemical problems and the intellectual multielemental analysis. In this item may be used the atomizer which was proposed by Prudnikov E.D. and Shapkina Y.S. (Patent of Russia n. 2018806. Pub. 30.08.94. Inventions. 1994. n. 16, p. 115).

The measurements are produced in the tube with the inner diameter from 10 up to 20 mm. The length of the tube comes up to 150-200 mm but the length and the diameter of the atomizer may vary in the dependence of the type of the determined problems. The tube has of the offset in the center of the atomizer. We use the quartz for the preparation of this atomizer but on can apply the various refractory materials.

The analyzed samples with the gases are given in the atomizer into the both hands of the tube and go out from the central offset. For the atomization of the samples it is possible to use the different flames, the combiner flame-plasma sources of the atomization and also the ICP high frequency discharge. It is possible also to determine the elements by the methods of the cold vapor and the hydride methods.

The universal character of this atomizer is provided by the possibilities of the multi elements analysis of the different analytical methods without the replacement of the atomizer. And more this atomizer allows passing at the same time the multi elements analysis by atomic emission flame spectrometry, absorption flame spectrometry, ICP AES and ICP MS. In this case we can to take into account of the different reciprocal interferences of all component of the analyzed sample in the full volume, and to pass intellectual process of the element determination most complete.

The possibilities of proposed atomizer was investigated for the atomic absorption of the elements in the flame and the determination of the mercury by the cold vapor methods. The analytical characteristics of this atomizer don't yield another types of the atomizer and analytical methods.

#### **MoPo8. LASED-BASED AEROSOL DESOLVATION SYSTEM FOR LIQUID SAMPLE INTRODUCTION IN ICP-OES AND ICP-MS: A VIABILITY STUDY**

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Nebulization is, nowadays, the preferred way for sample introduction in ICP-AES and ICP-MS. When liquid samples are nebulized, a great quantity of solvent is injected to the ICP together with the sample, which leads to problems like plasma instabilities or spectral and non-spectral interferences.

Desolvation systems are commonly used to reduce the solvent load to the plasma. Normally, these systems consist on a first stage for particle heating and a second one for solvent vapor removal., Conduction/convection-based methods are usually used for particle heating; however, due to the various drawbacks associated with them (poor

signal, high memory effect), alternative systems based on radiative heating have also been proposed.

In this work, a viability study of a laser-based desolvation system is presented. Aerosol particles were generated by a conventional nebulization system. For particle heating, a Nd:YAG laser emitting at 1064 nm was focused by a lens into a glass tube, through which the aerosol stream flowed, to create a high-temperature laser plasma. For solvent vapor removal, a two-step condensation unit was used. The aerosol desolvation efficiency was evaluated by measuring, with and without laser heating, the analyte and solvent transport efficiencies of the system for different aerosol nebulization conditions ( $Q_g$  and  $Q_l$ ).

#### **MoPo9.** ICP-MS AND X-RAY ABSORPTION SPECTROSCOPY STUDIES OF THE ARSENIC UPTAKE AND SPECIATION IN CORN PLANTS

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The uptake and speciation of arsenic was determined in corn plants grown in hydroponic medium supplied with As(III) and As(V) (using  $As_2O_3$  and  $As_2O_5$ , respectively). ICP-MS analyses showed that the As concentrations in roots were 110 and 90  $mg\ kg^{-1}\ d\ wt\ mass$ , when As was supplied as As(III) and As(V), respectively; while the As concentrations in shoots were 10 and 15  $mg\ As\ kg^{-1}\ d\ wt\ mass$ . XANES studies showed that the As in roots remained as the supplied As(III) while most of the As(V) was reduced to As(III). EXAFS studies confirmed the presence of As(III) and As(V) bound to sulfur and oxygen ligands, respectively. In addition, the iron concentration was found to increase 4 fold in roots of plants exposed to As(V) and 7 fold in roots of As(III) treated plants. Conversely, the iron concentration in shoots was reduced 3 fold in both arsenic species. The concentration of manganese in shoots was 4.7 and 2.7 times lower in plants exposed to As(III) and As(V) respectively. Both As species reduced phosphorus and potassium concentrations in roots (about 2.4 and 0.3 times, respectively). However, the total sulfur in plants was found to remain relatively constant.

#### **MoPo10.** COMPARISON OF EXCITATION CONDITIONS IN ICP-OES AND THEIR USE FOR OPTIMIZED ANALYSIS

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We propose a new versatile optimization method for ICP-OES, which is based on fundamental physical plasma conditions such as rotational temperature, electron number density and electron temperature. The method is based on measurements with a standard commercial ICP-OES instrument.

The influence of height above load coil, nebulizer flow and rf power on the electron temperature and element detectability were investigated. To obtain a general overview a wide range of device parameters was chosen with respect to height above load coil (1 to 20 mm), nebulizer flow (0.2 to 2.0 L/min) and rf power (1100 to 1700 W). In the

electron temperature map three clearly separated areas at low, mid and high temperatures have been identified corresponding to atomic excitation energies up to 3 eV, 3 to 6 eV, and 6 eV and above, respectively.

The position of the optimum signal-to-noise-ratios for specific element lines in the device parameter space showed excellent correlation to the electron temperature, and allows good prediction of optimum single- and multi-element (compromise-) conditions.

**MoPo11.** NEW APPLICATION POSSIBILITIES OF HIGH RESOLUTION-CONTINUUM SOURCE AAS (HR-CS AAS) CLOSING THE GAP BETWEEN SEQUENTIAL ICP-OES AND AAS

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Atomic absorption spectrometry (AAS) is universally employed to detect elements in trace and ultra trace range. Despite of the advantages like low operational costs, fast measuring readiness and to be mainly free of interferences it is a single method with the must of an element specific light source. However, with the introduction of the principle of high resolution continuum source AAS, the multielement barrier is overcome. It is now possible to perform fast and sequential analysis using one single source for all elements and is undoubtedly the greatest innovation in AAS in the last 45 years.

HR-CS AAS allows fast sequential multielement analysis, operational simplicity, robustness, speed (similar to sequential ICP-OES) and flexibility. Because of simplicity of the absorption spectra, compared to emission spectra, method development is very easy. Operating costs are much lower than the RF plasma that uses more than 20L Ar /min.

The HR-CS AAS series of Analytik Jena uses a Xenon short arc lamp as continuum light source. Operating in a special "Hot-Spot" mode this light source shows the required high light intensity over the whole wavelength range from 189 up to 900nm, which is important in field of AAS. The resolution of the high-resolution double Echelle monochromator is much better to that of standard ICP-OES. Complete spectra in the vicinity of the absorption line, about 200 pm left and right and right of the analyte profile are generated. In this way the entire environment around the analytical line becomes visible and gives a lot more information than current AAS. This way HR-CS AAS combines the data acquisition and data evaluation of ICP-OES array spectrometers with the AAS advantage of simple spectra and method development because of the low risk of line overlap. HR-CS AAS is therefore bridging the gap between AAS and ICP-OES. The use of a low noise linear CCD array detector for signal detection in combination with high-intensity lamp ensures best signal-to-noise ratio resulting in improved photometric precision and detection limits. It allows a truly simultaneous background correction. The combination of these parts of the spectrometer guarantees a high number of new and unique features, unknown in the atomic absorption so far.

The lecture will describe the introduction of the new kind of continuum source spectrometer and some interesting applications demonstrating the new available information content for the user.

**MoPo12.** MATRIX EFFECT OVERCOMING IN ENVIRONMENTAL DCP-ARC-ATOMIC EMISSION ELEMENTAL ANALYSIS

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It is well known that environmental analysis is one of the most important fields of modern analytical chemistry due to a growing interest of a man to the transformation and transport of substances in nature. It was developed a great variety of new powerful instrumental methods for elemental analysis, nevertheless DCP-arc-atomic-emission spectrometry stays one of most simple and available tools for trace elements determination. The main advantage of DCP-arc-AES consists in it's suitability for the direct analysis of solid samples without previous dissolution. But the main disadvantage is connected with a strong matrix and third element's influences.

The goal of the present investigation was an elaboration of the approach to eliminate those effects using a successive dilution method. Earlier a similar way has been applied by P.T.Gilbert for the evaluation of the results in atomic-absorption spectrometry, but no attempts have been done in AES.

This developed method demonstrates it's acceptability for environmental analysis. It allows a correct determination of analytes in any type of unknown samples without additional information about major components contents, moreover the detection limits of minor elements in the sample under analyzing may be reduced sufficiently due to the use of a series of the most suitable dilution (pre-concentration) factors

**MoPo13.** EMISSION CHARACTERISTICS OF OKAMOTO-CAVITY MICROWAVE-INDUCED PLASMA IN DIRECT INTRODUCTION OF ORGANIC SOLVENTS AND ITS APPLICATION TO ANALYSIS OF MIBK EXTRACTED FROM IRON-MATRIX SAMPLES

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An Okamoto-cavity microwave-induced plasma (MIP) with a nitrogen-oxygen gas mixture was employed as an atomization and excitation source for the emission analysis when organic solvent samples were directly aspirated. The mixed gas plasma could be maintained with a high robustness against the loading of organic solvents such as ethanol and 4-methyl-2-pentanone (MIBK). Also, the introduction of the organic solvents exerted little influence on the emission characteristics: the atomic-to-atomic and the ionic-to-atomic intensity ratios of various emission lines were a little varied by introducing organic solutions containing different compositions of ethanol. This is probably because the organic solvent can be easily removed due to reactions with active oxygen species in the MIP. After test solutions containing Al, Co, Cr(III), Cu, Fe(III), Ni, and Pb were extracted with MIBK, both the aqueous and the organic phases were aspirated into the MIP, yielding calibration curves having a good linearity, either from

the aqueous phase for Al, Co, Cr, Ni, and Pb or from the organic phase for Fe and Mo. This effect can be explained from the partition coefficients of these elements between in MIBK and in water.

**MoPo14.** ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR DIRECT SOLID SAMPLING: POTENTIAL FOR CHALLENGING APPLICATIONS

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Among the different methods that allow the direct determination of metals at trace and ultratrace levels in solid samples, electrothermal vaporization-inductively coupled plasma mass spectrometry (ETV-ICPMS) has proved to be very suitable. This technique shows interesting advantages such as a high sample throughput, an increased sensitivity and a reduced risk of analyte losses or contamination. Of course, it also shows some disadvantages, such as relatively high imprecision values (5-15% RSD) and the need to carry out some method development for best performance. Taking these characteristics into consideration, and after years of development, it seems evident that the fate of this technique is not to completely replace digestion approaches in routine labs. However, it is also obvious that the technique can be particularly useful for some specific applications, which can hardly be carried out using traditional solution approaches, but may be not so difficult for ETV-ICPMS.

In principle, there are two prospective fields of application for this technique: multi-element analysis of materials that are very difficult to bring into solution (e.g., industrial materials such as carbonfluoropolymers, silicon carbide, titanium dioxide, etc...) or elemental analysis when the aim is to determine very complex analytes (e.g., Si, B, ...). In the present works, several examples of both situations will be presented. Particular attention will be paid to the coupling of an ETV device to a high resolution-ICPMS unit, in order to overcome C-based interferences, as well as to the potential of isotope dilution for calibration.

**MoPo15.** COMPUTATIONAL FLUID DYNAMIC RESULTS FOR SEVERAL (NEW) SPRAY CHAMBERS IN ICPMS

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The quality of ICPMS analysis is strongly affected by the performance of the sample introduction system whose main components in most cases are a nebulizer and a

spray chamber. Typically, the quality of the aerosol is improved by removing the large droplets via a spray chamber to enhance precision and to reduce interferences.

Computational fluid dynamics (CFD) allows one to predict the physical events that occur in the flow of fluids around and within designated objects. These events are related to the action and interaction of phenomena such as dissipation, diffusion, convection, shock waves, slip surfaces, boundary layers and turbulence.

From all effects describing the aerosol modification in the spray chamber turbulent dispersion, gravitational settling, gas phase compressibility and evaporation are taken into account.

The main problem for the poor mass transport efficiencies is that the bulk flow close to the wall changes its direction as a result of recirculation and therefore most of the aerosol is deposited on the inner cylinder of the spray chamber. An attempt to overcome the deposition behavior concerning the inner cylinder is to model its geometry. The first numerical experiment is made with a conical shape of the tube under consideration whereby the chamber lengths is kept constant and the diameter of the outer tube is enlarged. From the result of the simulation it can be derived that both, for the cooled new chamber and the new chamber at room temperature, about 50 % more droplets are able to leave the chamber compared with the Scott-type spray chamber. At present several new geometrical variations of the inner cylinder are under investigation.

**MoPo16.** SAMPLE PRESENTATION IN MICROWAVE INDUCED PLASMA OPTICAL EMISSION SPECTROMETRY: EVOLUTION AND FUTURE TRENDS

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Since the preparation of samples is often dictated by the form in which they can be presented to the instrument, development of new methodologies and improvement of existing techniques for regulatory elemental determinations in analytical matrices constitutes a major challenge for analytical chemists. A profusion of instrumental approaches has been brought to bear on analysis problems. Of available sources for use in atomic spectrometric techniques include microwave plasmas. Forecasts suggesting an enhanced role for laser and spark ablation, direct sample insertion, electrothermal vaporization, direct powder sampling and slurry sample introduction techniques in microwave induced plasma optical emission spectrometry (MIP-OES) have been made for many years. In light of these forecasts, discussions about the “future” of MIP-OES for elemental analysis will include advances in related technical areas, in addition to those of instrumental itself.

Two additional factors will arise in closing discussion: the methodological blank and the “value” of the data produced.

**MoPo17.** A MICRO-CAPILLARY SYSTEM COUPLED TO AN ICP-MS AS A NOVEL TECHNIQUE FOR INVESTIGATION OF MICRO-CORROSION PROCESSES.

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Detailed information on corrosion processes provides the key to effective prediction and minimization of corrosion damages. The initiation stage of material decomposition plays a special role, since the corrosion starts mainly on weakest locations such as surface defects, grain boundaries, segregations or inclusions. However, surface analysis or electrochemical methods commonly used in corrosion research can not present local element-specific and online in-situ information at the same time.

As a solution a combination of a device for localized investigations of corrosion based on a micro-capillary system coupled to an ICP-MS has been proposed. The online coupling of the micro-capillary system with controllable solution flow to an ICP-MS should allow continuous or time-dependent introduction of investigated in-situ samples and enable both element specific as well as spatially and time-resolved investigations of corrosion processes and mechanisms. The hyphenated technique can become an excellent tool to obtain essential data for reliable modelling of local surface degradation processes and mechanisms.

The minimization of the micro-capillary spot diameter is essential in the investigation of initiation stage of complex corrosion processes. However, the development of a suitable flow cell is challenging and requires a careful optimization. Detection sensitivity is limited by several factors such as blank levels of used materials and chemicals, dissolution rates of the materials of interest, matrix content of the investigated corrosive media, possible dilution factors and maximum salt charge for the ICP-MS.

Strategies for suitable interelement correction equations as well as detector calibration (e.g. custom resolution, dual detector calibration) will be discussed. Investigations on method development and first results, which were achieved on different aluminium alloys, will be presented. These results should enlighten how far the wetted surface area can be reduced and provide information about the spatial resolution capabilities of the technique.

**MoPo18.** DEVELOPMENT AND CHARACTERIZATION OF A LOW ARGON CONSUMPTION TORCH FOR INDUCTIVELY COUPLED PLASMA SPECTROMETRY **C. Engelhard**<sup>1</sup>, A. Scheffer<sup>1</sup>, S. Nowak<sup>1</sup>, T. Maue<sup>2</sup>, G. Y. Chan<sup>3</sup>, G. Gamez<sup>3</sup>, G. M. Hieftje<sup>3</sup>, W. Buscher<sup>1</sup> <sup>1</sup>University of Münster, Institute of Inorganic and Analytical Chemistry, Corrensstr. 30, D-48149 Münster, Germany <sup>2</sup>The Münster Chamber of Handicrafts, Bismarckallee 1, D-48151 Münster, Germany <sup>3</sup>Department of Chemistry, Indiana University, Bloomington, IN 47405, USA [Carsten.Engelhard@uni-muenster.de](mailto:Carsten.Engelhard@uni-muenster.de)

The inductively coupled plasma (ICP) is a popular and powerful tool in elemental and speciation analysis. Recent advances in ICP instrumentation have produced greater spectral resolution, lower detection limits and have made hyphenated techniques easier available. However, the basic setup of the ICP source itself has been retained unchanged

over the years. As a consequence, the main drawback of this technique, the high argon gas consumption of up to 20 L min<sup>-1</sup> - resulting in high operating costs - is still persistent. In this presentation an overview of recent developments of the Static High Sensitivity ICP (SHIP) and its characterization will be given. This low argon consumption torch is a new plasma excitation source with competitive figures of merit and a total argon consumption of only 0.6 L min<sup>-1</sup> in optical emission spectrometry.

Fundamental studies of the new source with several plasma diagnostic tools and an overview of the current analytical performance will be presented. Additionally, infrared thermography as a fast and easy technique for the optimization of external torch cooling devices and torch geometries will be discussed.

This source is expected to become an important tool in optical emission spectrometry and mass spectrometry. It offers new possibilities when these techniques are used as detectors for gas chromatography (GC) or high performance liquid chromatography (HPLC) and low gas flows are required.

**MoPo19.** INFRARED THERMOGRAPHY: A FAST AND EASY TECHNIQUE FOR OPTIMIZATION OF NEW TORCHES FOR INDUCTIVELY COUPLED PLASMAS

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Infrared thermography is an excellent tool for the monitoring of temperatures and thermal patterns. Applied to inductively coupled plasmas, the technique allows for measuring of torch temperatures and thermal patterns while the ICP is operating and despite strong background emission from the plasma itself. It is a fast and easy method for determining temperature distributions and stress features within the torch.

Here, this method was applied to the characterization of the Static High-Sensitivity ICP Project (SHIP), a spherical inductively coupled plasma torch that operates at unusually low Ar flows. The limits of detection (LOD) for the SHIP are comparable to state-of-the-art LODs of a conventional setup. However, the lifetime of the SHIP torch is limited mainly by the efficiency of the external flow of cooling air. Accordingly, infrared thermography was employed to investigate different setups of the new torch and to identify quartz regions in it that approach critical temperatures. Recent results on torch geometries variations and cooling-flow optimization will be presented. Moreover, a conventional ICP torch was studied and inhomogeneous temperature distributions were found.

**MoPo20.** TIME-OF-FLIGHT MASS-SPECTROMETRY WITH PULSED DISCHARGE IN COMBINED HOLLOW CATHODE

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New analytical mass-spectral system for solids (as conductive, as semiconductive and dielectric) direct analysis is developed. It is based on time-of-flight mass-spectrometer with ionization at pulsed glow discharge in combined hollow cathode (combined cathode consists of a flat sample and a cylindrical wall made of high-purity metals – Nb or Al.). Pressure, voltage, pulses duration and frequency optimizations, and mathematical processing are reported. Influence of Helium and Hydrogen additions to the discharge gas is discussed. Hydrogen addition allowing decreases in high degree intensities of gases components (O<sub>2</sub>, O, N<sub>2</sub>, N, Ar, ArH, Ar<sub>2</sub>, H<sub>2</sub>O, H<sub>3</sub>O). Parameters of the analyzer (repelling pulse delay, pulse frequency, pulse width, pressure) were optimized. Experimental data are compared with computer discharge pulse model. Using PGD-TOFMS system, different samples (copper, lead, steel, nickel, slag produced on lead plant, alloys and different glasses) were analyzed. Appropriate standards were used for calibration of analyzer. Spectra and measurement concentrations for different samples and samples standards are presented. Measured detection limits are approximately 0.2–0.8 ppm for wide range of elements with reproducibility 1–10%.

**MoPo21.** USEPA200.7 CANNOT BE USED FOR COMPLAINT MULTIELEMENT ANALYSIS OF DRINKING WATER – IS EPA 200.5 AN ALTERNATIVE? A CRITICAL EXAMINATION OF RADially (RV) AND AXially VIEWED (AX) ICPS

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The group of so-called heavy metals is renowned for their toxic effects on human health. Recent published permitted concentrations of these elements are usually only slightly above and in many cases below Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) instrument detection limits (IDLs). While this technique is used for routine compliant analysis of wastes, the significant lowering of regulation concentration limits of several toxic elements in drinking water poses a serious challenge for ICP-AES.

ICP-AES IDLs can be improved by a factor of 5-10 using ultrasonic nebulization depending on the element and the spectral line. However, as a result of enhanced aerosol formation and desolvation, high plasma loading results in easily ionized element interference effects. Axially viewed (AX) ICP-AES could be an alternative because IDLs are enhanced by factors of 5-20.

Because radially viewed (RV) ICP-AES fails to meet recent new concentrations, USEPA recently published a new procedure (EPA 200.5) detailing analysis of drinking water using AX-ICP-AES. However, perusal of the 200.5 document indicates that IDLs were obtained using an obsolete tuned photomultiplier-based multichannel spectrometer. Since most commercially available systems are based on CT technology, it is important

to examine whether the IDLs listed in USEPA 200.5 are attainable using these spectrometers.

Accordingly, currently available IDLs obtained using conventional pneumatic sample introduction and multielement conditions of several commercially available axially viewed CT ICPs were critically examined to determine if these data meet the 200.5 criteria. Data were also compared to those obtained using a high resolution PMT-based RAD-ICP-AES.

Data in this presentation indicate that none of the commercially available instruments meet EPA 200.5 regulation IDLs for 30 s multielement integration periods, failures varying from about 25-60 % (critical toxic element failures varying from 1-5 elements). Of interest is the score for the high resolution RAD-ICP-AES, which was among the high performers with only two element failures.

It can be concluded that if this evaluation represents the current performance of AX-CCD-CID-ICP-AES, these instruments do not meet EPA 200.5 compliant limits and therefore cannot be used for determination of trace elements in drinking water in accordance with this procedure. An AX-high resolution instrument might meet all the defined 200.5 limits; however, such an instrument is not available.

The pragmatic alternative is inductively coupled plasma quadrupole ICP-MS, the IDLs easily meeting stringent drinking water requirements.

## **MoPo22. COMPARISON OF ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA TIME AND DC ARC ATOMIC EMISSION SPECTROMETRY FOR MULTIELEMENT ANALYSIS OF GEOLOGICAL AND RELATED SAMPLES**

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Although in the recent past DC arc OES was widely employed as a powerful analytical method for direct solids elemental analysis in a range of applications, due limitations of photographic detection, the technique went into a technical slumber. On the other hand, the use of ETV for direct solid sample introduction presents several advantages over conventional solution nebulization. Very high sample transport efficiencies can be attained, and as a result lower limits of detection can be achieved.

A comparison is made of the analytical performance of ETV-ICP-AES and Direct Current Carbon Arc Plasma (DC arc-AES) coupled to a CID atomic emission spectrometer for direct solids multielement analysis of refractory geological and related materials. The ability of the CID spectrometer to record complete atomic emission spectra throughout the various stages of the thermal vaporization cycle is shown to be a major advantage. Variation of background interferences throughout the temperature program were quantitatively measured and compensated. An optimized temperature program was selected to volatilize the various species in the DC arc and in the ETV and the transient signal generated during the vaporization stages were acquisitioned by the CID spectrometer.

In this study we addressed spectral line selection for trace, minor and major element determinations. Spectral line interferences were minimized by taking into consideration differences in vaporization characteristics of the elements. Figures of merit for both systems include dynamic range of calibrations, burn-to-burn precision, detection limits for volatile, involatile and refractory elements and analysis of certified reference materials.

**MoPo23.** CLOUD POINT EXTRACTION AS A PRECONCENTRATION PROCEDURE FOR DETERMINATION OF TRACE METALS IN HIGH SALINE EFFLUENTS FROM PETROLEUM INDUSTRY BY USING ICP OES WITH ULTRASONIC NEBULIZATION

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In the present work an analytical methodology for simultaneous extraction of cadmium, lead, copper and nickel in high saline effluents from petroleum industry and determination of low levels of these metals by inductively coupled plasma optical emission spectrometry - ICP OES using ultrasonic nebulization was developed. The methodology was based on cloud point extraction of the metals as diethyldithiocarbamate (DDTC) complexes, in micellar media of non ionic surfactant octylphenoxypolyethoxyethanol (Triton X-114). Statistical multivariate methodologies (factorial design and Doehlert matrix) were used to optimize the experimental variables. Limits of determination of 0.03; 2.1; 0.62 and 0.27  $\mu\text{g L}^{-1}$  and enrichment factors of 20.0; 20.4; 19.5 and 20.6 were achieved for cadmium, lead, copper and nickel, respectively. The proposed methodology has been applied for quantification of these metals in sea water and high saline produced water from off shore and onshore oil producing operation facilities in Brazil, being suitable for attending regulations concerning environmental quality guidelines for surface saline waters and Brazilian permits for effluent discharges.

**MoPo24.** IMPROVING LABORATORY THROUGHPUT AND QUALITY BY MEANS OF ASSISTANCE SOFTWARE TOOLS TO ACHIEVE RELIABLE RESULTS IN BOTH ROUTINE OR COMPLEX APPLICATIONS.

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Multi-line analysis principle being the efficient method to provide reliable results, dedicated software tools have been developed on the ACTIVA CCD-based ICP-AES

instrument to take full benefit of it. The first tool is dedicated to multiline selection, and is called MASTER (Multi-element Analysis, Selection Tool for Enhanced Reliability). The next tool makes use of the SOS (Statistics for Outlier Survey) software to detect any possible outlier.

These software tools are described in another presentation (1).

The potential of these tools will be illustrated with environmental or chemistry applications. For applications where the element concentrations can easily vary from one sample to another one and where unexpected spectral interferences can occur, this global procedure facilitate the work of the operator, while ensuring the quality of the results. It enhances then the potential of the multi-line analysis.

(1) HOW TO FAVOUR THE USE OF MULTILINE ANALYSIS IN CCD-BASED ICP-AES ? (Agnès Cosnier, Yves Danthez, Sébastien Velasquez, Emmanuel Fretel, Jean Michel Mermet, Olivier Rogerieux)

#### **MoPo25.**

THE OPTIMASS ICP-oTOF-MS: THE NEXT STEP IN ELEMENTAL TRACE ANALYSIS

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The progress of elemental analytical instrumentation from Atomic Absorption through ICP optical emission to ICP mass spectrometry has been dictated by the pursuit of lower detection limits, multi-element capability and high sample throughput.

Interest in using a time-of-flight mass spectrometer to further advance the ICP-MS technique and expand laboratory capabilities has grown in recent years. The true and greatest advantage of a time-of-flight mass spectrometer is simultaneous sampling mass analysis. The simultaneity allows for the most precise internal standard and isotope ratio correction, transient signal multi-element analysis, elemental fingerprinting and advance retrospective analysis techniques. Examples of design, routine data from commercial laboratories, isotopic ratio results and transient signal application will be presented.

**MoPo26.** BUILDING AND ANALYZING MODELS FROM DATA BY STIRRED TANK EXPERIMENTS FOR INVESTIGATION OF MATRIX EFFECTS AND SELECTION OF INTERNAL STANDARDS IN ICP-AES

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Matrix effects caused by inorganic acids and easily ionized elements in ICP-AES have been modelled by regression analysis of experimental data obtained using the "stirred tank method". The main components of the experimental set-up were a magnetically-stirred container and two peristaltic pumps, which allowed gradual and automatic variation of matrix composition before its introduction into the plasma source, whereas

the analyte concentration remained unchanged throughout the experiment. An ICP spectrometer with multichannel detection based on coupled charge device was used to simultaneously measure the emission signal at several wavelengths with changing the matrix concentration. Up to 50 different concentrations were evaluated in a period of time as short as 7 min.

Both single interfering species (nitric acid, hydrochloric acid, sulfuric acid, sodium and calcium) and their mixtures (*aqua regia*, sulfonitric mixture, sodium+calcium and calcium+nitric acid) were investigated.

In order to fit the experimental data, different regression models were used depending on the interfering specie. For inorganic acids and their mixtures, the dependence of the emission signal on acid concentration was well-fitted by simple logarithmic models. Conversely, for the easily ionized elements, polynomial models were more suitable to describe the trends.

Then, the coefficients of the models were used as "signatures" of the matrix-related signal variations and analysed by principal component analysis. Similarities and differences among the emission lines have been highlighted and discussed. It was clearly showed that the analysis of the score plot allows an easy choice of the optimal internal standard, for each analyte and interfering specie.

#### **MoPo27. IN SITU MONITORING OF HELIUM CONCENTRATIONS USING VISIBLE EMISSION SPECTROSCOPY OF ATMOSPHERIC PLASMAS**

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Monitoring helium concentrations in situ is important for various scale experiments using helium gas as a hydrogen simulator. Helium concentrations are attempted to be estimated from the visible line emission of atmospheric plasmas without separate sampling and drying processes. Reliable continuous discharges are generated at atmospheric pressures between two disc-shaped electrodes powered by AC leakage transformer (15kV, 20mA, 20kHz). Spectral line intensities in the visible range are measured with a PC plug-in 5-channel spectrometer from Ocean optics. Among various visible lines atomic helium lines of 587.56nm HeI and 501.57nm HeI are identified to have a strong linear dependency on helium concentrations with good reproducibility. Helium concentrations are estimated from those line intensities by following the correlation. Errors from the calibrated values are very small, i.e. less than 0.5%, demonstrating that accurate measurements of helium concentration are possible down to a percent with good time resolution. Moreover, intensities of those two lines are not influenced even by the presence of humidity. A compact prototype detector has been fabricated and tested successfully in actual helium test facility. Test results will be presented. This optical technique may be used as an environmental monitoring system not only for helium gas but also for other hazardous gases.

**MoPo28.** ION CHROMATOGRAPHY COUPLED WITH ICP-OES: OPTIMIZATION AND VALIDATION. APPLICATION TO THE ANALYSIS OF IMPURITIES IN PLUTONIUM.

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Spectra interferences encountered while analyzing impurities in nuclear matrices (especially plutonium) were the incentive for coupling ion chromatography (IC) to inductively coupled plasma-optical emission spectroscopy (ICP-OES) in a glove box.

The interface was optimized by investigating the influence of several introduction systems (conventional and micro-nebulizers and chambers) and of different parameters on the performances (sensitivity, repeatability, chromatographic efficiency and resolution) of the coupling. The Aspire nebulizer was selected among all the micronebulizers tested because this one gives the best sensitivity.

This coupling was next validated by participating in an ion chromatography interlaboratories comparison organized within six laboratories of CEA group. Consistent and satisfactory results were obtained for an unknown solution containing  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$ . Moreover several figures of merit (linearity, limits of detection, precision and accuracy) were determined.

Finally, this new technique was applied to the analysis of impurities in plutonium matrices. The speciation of plutonium was realized and interpreted thanks to specific interaction theory and solution chemistry. A suitable IC separation enabled to perform quantitative analyses of impurities in the plutonium matrix. The method was validated by comparing the results with reference materials.

**MoPo29.** SPECTROSCOPIC CHARACTERISATION OF THE SLIDING SPARK PLASMA FOR TRACE ELEMENT ANALYSIS IN SOLID DIELECTRICS

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**MoPo30. MICROWAVE INDUCED PLASMA SPECTROMETRY (MIP) AS DETECTOR FOR CARRIER GAS HOT EXTRACTION (CGHE)**

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Helium operated CGHE with infrared and heat conductivity detection for the measurement of oxygen and nitrogen is a well established measurement technique for inorganic matrices. Besides blanks, typical problems are stability, sensitivity, broad signals due to catalysts and reagent installations and problems related to the gas species released. Detection with a helium operated MIP looks very suitable to overcome these problems. A HP AED 5921A originally developed for capillary GC was coupled to a LECO-TC436DR. Sensitivity and selectivity for the determination of oxygen, nitrogen and hydrogen were checked by scanning intensity versus time and wavelength at the respective wavelengths of 777 nm, 174 nm and 486 nm respectively on the gases produced by CGHE from blank and analyte. Calibration samples for analyte masses of oxygen, nitrogen and hydrogen between 5 µg and 50 µg were prepared in tin capsules from Fe<sub>2</sub>O<sub>3</sub>, Si<sub>3</sub>N<sub>4</sub> and TiH<sub>2</sub>. The response of the combination was well linear for hydrogen and oxygen with limits of determination of about 0,2 µg and 0,02 µg respectively. In these experiments nitrogen did not show a fully linear response and a limit of determination of 2 µg. Especially for low concentrations the combination of CGHE and MIP looks promising.

**MoPo31. EFFECT OF DIFFERENT COMPOUNDS ON THE SIGNAL OF ELEMENTS IN ICP-MS ANALYSIS**

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A flame atomic absorption spectrometer (FAAS), a graphite furnace atomic absorption spectrometer (GF-AAS), an inductively coupled plasma optical emission spectrometer (ICP-OES) and an inductively coupled plasma mass spectrometer (ICP-MS) are applied for analysis of elements in different samples (plant, soil, food raw material and food, feed, organic fertiliser, irrigation- and soil-water, sewage, sewage sludge) in our laboratory. Nowadays there is very important to analyse growingly smaller concentrations of elements. From the above analytical instruments the inductively coupled plasma mass spectrometer is capable of analysing the smallest concentration of elements. The applied X7 type (Thermo Elemental, Winsford, UK) ICP-MS instrument has Collision Cell Technology (CCT) also. Using CCT working method certain elements have better detection limits with 1-3 magnitudes comparing to a normal ICP-MS analytical method. The CCT has better detection limits mainly for analysis of arsenic, selenium, germanium, vanadium and chromium. Beside these the collision cell can be applied for the analysis of silicon, sulphur, zinc, copper, iron, calcium, magnesium and potassium in smaller concentrations also.

Analysing the above types of samples a new interfering effect emerged in ICP-MS, 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 ICP-MS equipment was used to analyse the effects of different compounds containing various carbon content as sample matrix.

The effect of different type of compounds furthermore the effect of various quantity of carbon content were applied. As the ICP-MS instrument is capable of analysing many elements virtually in parallel way (in a multielemental analytical method) so 16 different 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 examined the effect of different water-soluble compounds on changes of intensity of the above 16 elements. The same amount of carbon content was used in the case of each water-soluble chemical. The carbon content (the concentration of applied compounds) was also changed.

Finally we tried to improve or advise a method which can eliminate the effect of the above interference, so we can decrease the extent of error in the analysis of the above elements (mainly selenium and arsenic).

The 2 % carbon content resulted approximately 4 times higher measured concentration of selenium and approximately 7 times higher measured concentration of arsenic. This means 400-700 % error in the analysis of selenium and arsenic.

#### **Acknowledgements**

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#### **MoPo32. APPLICATION OF DRC FOR SPECTRAL INTERFERENCES ELIMINATION IN ICP-MS DETERMINATION OF Fe AND Ca IN Ni-Mo/Al<sub>2</sub>O<sub>3</sub> CATALYSTS**

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Iron and copper are poisons to Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts used in hydroprocessing of heavy petroleum products and their content in the catalyst is an important factor influencing technological decisions. The main components of catalysts are: heavy petroleum oil, Al, V, Ni, Mo, S (up to 40, 33, 16, 4, 11, 8%, respectively). Fe and Ca, as well as Na, Cl, Zn, Si, Ti, P, As, Cu and Co belong to minor or trace catalysts components.

Systematic studies lead to the choice of the following procedure for total decomposition of this difficult material: extraction with toluene in Soxhlet apparatus, ashing at 500°C in Pt crucibles in muffle furnace, evaporation with HClO<sub>4</sub>+HF, evaporation with H<sub>3</sub>BO<sub>3</sub>, and, dissolution of residue with HCl.

Determination of Fe and Ca in catalysts is a very rare analytical task. There are not any CRMs, interlaboratory comparisons or proficiency testing in this field. To confirm reliability of results different analytical techniques, among others ICP-MS, have been chosen for metals determination in the obtained catalysts solutions.

Although ICP-MS is a sensitive technique, dilution of minor components in the final catalyst solution limited the choice of isotopes to these with higher abundance. However, spectral interferences in determination of <sup>56</sup>Fe, <sup>54</sup>Fe and <sup>40</sup>Ca isotopes, caused,

respectively, by  $^{40}\text{Ar}^{16}\text{O}^+$ ,  $^{40}\text{Ar}^{14}\text{N}^+$  and  $^{40}\text{Ar}^+$  ions are very strong. Also trials of  $^{57}\text{Fe}$ ,  $^{42}\text{Ca}$  and  $^{44}\text{Ca}$  isotopes determination led to too high results. Finally, DRC with ammonia as reaction gas has been used. Careful optimization of ammonia flow rate, and RPq parameter enabled to find proper analysis conditions. The chosen isotopes were  $^{56}\text{Fe}$  and  $^{42}\text{Ca}$ . The accuracy of ICP-MS analysis was evaluated by comparison with the results obtained by previously developed ICP-OES and FAAS methods. Also recovery of Fe and Ca, spiked with original catalysts before samples decomposition, was satisfactory. Elimination of spectral interferences in determination of Fe and Ca enables to use ICP-MS as the additional techniques of catalysts analysis, which is important in this difficult case of quality control.

It is interesting that trials of  $^{40}\text{Ca}$  isotope use for Ca determination were not successful. The optimization of ammonia flow rate led to excellent reduction of interferences for Ca standard solution, however, it was impossible to reach similar effect for much complicated catalyst solution.

### **MoPo33.** OPTIMISED SAMPLE INTRODUCTION FOR CE-ICP-MS COUPLING

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Due to the small sample flow rate from the capillary electrophoresis (CE) the uptake of the sample introduction system has to be filled up by an extra electrolyte. With most of the standard sample introduction systems only 1-10% of the sample uptake are converted into a stable aerosol introduced into the plasma. This causes a loss in sensitivity that reduces the analytical performance of this technique.

By a carefully selected combination of low consumption nebuliser and spray chamber the fraction of introduced sample can be increased. By heating the spray chamber and the transfer line to the torch the degree of introduction can be increased up to 100%. So the performance of the coupling of CE to ICP-MS can be enhanced dramatically.

The signal to noise ration in dependence of the temperature of the spray chamber and the transfer line was investigated, and also the short and long term stability of the system.

Advantages and disadvantages of this system have been evaluated and some applications with lowered limits of detection will be presented.

### **MoPo34.** MODELING THE INFLUENCE OF FIRST IONIZATION ENERGIES OF ADDED EASILY IONIZED ELEMENTS ON ANALYTE EMISSION INTENSITIES IN ARGON ARC PLASMA

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In direct current argon arc plasma the enhancement of analyte emission intensity in the presence of easily ionized elements (EIE) is a well known fact. In this work the influence

of EIE with different ionization energies was modeled taking into account their contribution to radial distribution of electron density and further on radial electric field. The force that this field acts on partly ionized analyte is oriented from arc core to its periphery. The result of this field influence is that partial pressure of analyte will be different depending on actual radial position, i.e. it will cause a demixing effect. The presence of analyte atoms in hotter plasma zones, and so analyte emission intensity, will depend on the ionization energy and concentration of added EIE. The aim of this work was to compare the enhancement obtained for same analyte with addition of EIE with different ionization energies in same molar concentrations. The calculated and experimentally obtained enhancements show a similar dependence on EIE first ionization energy: the enhancement is greater for EIE with lower ionization energies.

**MoPo35. MULTI-ELEMENT ICP-OES DETERMINATION IN ATMOSPHERIC PARTICULATE MATTER (PM10 AND PM2.5) AFTER CHELATING SOLVENTS BASED PRESSURISED LIQUID EXTRACTION**

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The close association between atmospheric particulate matter concentration and public health has been recently proved in epidemiological studies. Thus, the characterisation of atmospheric aerosol composition is mandatory. Trace metals are a part of the atmospheric pollutants and their determination in the total suspended particles (TSP) as well as in the inhalable fraction (PM10 and PM2.5) offers useful information when evaluating the interaction between air pollutants and public health. The sample pre-treatment is one of the more time consuming stages in a chemical analysis, mainly when analysing solid matrices. This is quite important for atmospheric particulate matter since the large acid digestion pre-treatments recommended to extract trace and major elements. Although Pressurised Liquid Extraction (PLE) has been designed and mainly used for organic compounds extraction, this technique has been recently applied for extracting organometallic species and even total metals. PLE offers a high rate of automation together with the minimal manipulation of the extracts and short times to complete the extraction. Therefore the aim of the current work has been the study of the feasibility of PLE for total metal extraction from atmospheric particulate matter. Aqueous solutions prepared from different chelating reagents such as ethylenediaminetetra-acetic acid (EDTA), 2,2-azobis-(2-methylpropionamide) dihydrochloride, chloramine-T, o-phenanthroline, 1,1-trifluoro-2,4-pentadione, diphenylcarbazone, 8-hydroxyquinoline and imidazole were tested as extracting pressurised solvents. The target elements (Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Na, Pb, Sr, V and Zn) were directly measured by inductively coupled plasma – optical emission spectrometry (ICP-OES) under

standard plasma conditions (1300 W and 1.5, 0.5 and 0.8 l min<sup>-1</sup> for plasma gas flow, auxiliary gas flow and nebulizer gas flow, respectively) and using a GemCone nebulizer – cyclonic spray chamber. Ten circular portion of 3.14 cm<sup>2</sup> were cut from the PM10 and PM2.5 filters and then they were mixed with 1.50 g of diatomaceous earth (dispersing agent) and placed into 11 ml stainless steel extraction cells. Good metals recoveries have been reached when using EDTA as an extracting solvent. The operating extraction conditions such as extraction temperature, pressure and static steps were fully optimised. This study has been supported by Ministerio de Ciencia y Tecnología, project REN 2003-08603-C04-01.

**MoPo36.** CHEMOMETRIC STUDY OF RAFT MUSSELS FROM RÍA DE AROUSA ESTUARY ACCORDING WITH TRACE METALS CONTENT AFTER ICP–OES DETERMINATION

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The Ría de Arousa estuary, comprising around 200 km<sup>2</sup>, is the largest of the eighteen Galician Rías. It is located in north–western Spain and its socioeconomic importance is based on aquaculture, mainly mussel production (around the 70 % of the Spanish mussel production). Since the great importance of this natural ecosystem, there are many projects to evaluate and guarantee the quality of the seawater and the harvested mussels.

In the current work, raft mussels (*Mytilus galloprovincialis*) specimens were collected in February and July 2002 and February and July 2003 at sixteen sampling sites along the Ría de Arousa estuary. This implied two sampling cruises before *Prestige* oil spillage and other two sampling cruises after the *Prestige* accident. After raft mussel collection, the byssus and shell were removed and from each site a composite sample of about 50 mussels was prepared by pooling together specimens of different size, with shell lengths ranging from 3 to 7 cm. Then, the soft tissues were homogenized and lyophilized. Finally, dried mussel samples were subjected to an optimized microwave assisted acid digestion procedure and the different acid digests were analyzed for the target elements (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, V and Zn) by inductively coupled plasma – optical emission spectrometry (ICP–OES). ICP–OES measurements were made under standard plasma conditions. All determinations were carried out by using the standard addition technique and the recommended wavelengths emission lines.

A chemometric study (principal components analysis, PCA, and cluster analysis, CA) was performed using trace metals concentrations as discriminating factors. The half–range central value transformation was used as data pre–treatment to homogenise the data sets. Results have shown a natural grouping of mussel samples collected along the right part of the estuary before the *Prestige* oil spillage. Since water circulation in Ría de Arousa estuary takes place in two layers with a surface outgoing current (left part of the estuary) and a deeper inflowing current (right part of the estuary), the discrimination of these mussel samples could be attributed to the lixiviates from the *Prestige* oil spillage. These results also agree with a slight increase on Cr, Ni and V concentrations in rafts mussels from sites located at the outer–right part of the estuary. Cr, Ni and mainly V have

been reported as key trace elements after oil spillage episodes. Other findings such as season variations were also observed after the application of the unsupervised pattern recognition techniques.

**MoPo37. METHOD DEVELOPMENTS TO PERFORM METAL DETERMINATION USING HYDRIDE GENERATION-ICP-OES**

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Chemical vapour generation can be used as an appropriate way of introducing metallic solutions in spectroscopic instruments, increasing the sensitivity of determinations. Thus, hydride generation can be used for simultaneous determination of silver, gold, cadmium, copper, nickel and zinc using Inductively Coupled Plasma Optical Emission Spectrometry, with good reproducibility and sensitivity. 2.24% sodium tetrahydroborate was used as reducing agent and hydrides were produced from a 0.43 M nitrid acid matrix. 8-hydroxiquinoline ( $38 \mu\text{g L}^{-1}$ ) and cobalt ( $1 \mu\text{g L}^{-1}$ ) were added to all the samples in order to increase the efficiency of the reaction. A home-made glass gas-liquid separator was the preferred option and an Ar flow rate  $0.74 \text{ L min}^{-1}$  was used to transport hydrides to plasma torch.

Peaks for tin, iron, molybdenum and chromium can be observed in the optimised conditions and so, analytical characteristics for these elements were determined. A comparison was carried out between direct introduction of hydrides in the plasma and the work with the Cyclonic spray chamber and the Gem Cone nebuliser (Perkin Elmer).

The main drawback of metal hydride generation methods are interferences, mainly from copper and nickel. Therefore, several reagents (thiourea, potassium iodide, EDTA, L-cistein, tartaric acid, ascorbic acid ... ) were tested in order to diminish interferences in the hydride generation step of the method and to increase sensitivity, as well.

**MoPo38. UV VAPOUR GENERATION AS INTRODUCTION TECHNIQUE FOR ICP-OES**

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UV vapour generation is an interesting method to introduce metallic solutions in spectroscopic instruments, avoiding associated problems to hydride generation such as overpressure or contamination with reagents.

During this work an UV reactor consisting in a PTFE reaction tube and a mercury lamp was coupled to a gas liquid separator and to the Inductively Coupled Plasma Optical Emission Spectrometer. Vapours were generated from an acetic acid matrix. Metallic and hydride forming elements were studied but peaks were obtained for mercury, selenium

and arsenic. The influence of parameters affecting determination was examined: acid concentration, type of gas liquid separator (PTFE membrane or glass home made separator), sample and waste flows, sample irradiation time, argon flow to transport vapours to the plasma, signal acquisition (measure mode (peak or area) and number and duration of replicates).

Several compounds were added in order to increase sensitivity and improve performance of the system: citric acid, ascorbic acid, oxalic acid, EDTA, APDC, 8-hydroxyquinoline, formic acid,... The type of additive influenced reaction rates and the amount of observed signals. Best results were obtained with EDTA (selenium and mercury) and formic acid (arsenic, selenium).

Analytical characteristics in optimum conditions were determined and possibility of simultaneous determination of studied elements was evaluated.

### **MoPo39. COMPUTER SIMULATIONS OF DIELECTRIC BARRIER DISCHARGES USED FOR ANALYTICAL SPECTROMETRY**

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A dielectric barrier discharge (DBD) is a plasma, created in a small gap between two electrodes. One or both of the electrodes is covered with a dielectric layer. An alternating polarity high voltage waveform, with typical frequency in the kHz range, is applied between the two electrodes. In recent years, DBDs are gaining increasing interest in the field of analytical spectrometry, as powerful microchip sources with excellent dissociation capability for molecular species, hence for the analysis of, for instance, halogenated hydrocarbons.

In this contribution, we present the results of a numerical model, applied to a DBD, in order to improve its analytical capabilities. The model is based on the fluid approach, and consists of a set of continuity and transport equations (for every species taken into account), coupled to the Poisson equation for a self-consistent calculation of the electric field distribution in the plasma. Special attention is paid to the boundary conditions, applied at the dielectric barriers. The model is applied to a helium DBD, and the species taken into account, are electrons, He<sup>+</sup> and He<sub>2</sub><sup>+</sup> ions, He ground state atoms, He atoms in metastable levels (He<sup>m</sup>) and He<sub>2</sub> dimers.

Typical calculation results include the potential (and electric field) distribution inside the plasma, the density profiles of the different species, information about important production and loss mechanisms of the different species, as well as the time-evolution of all these quantities. The electrical current waveform as a function of time, which can be calculated from the microscopic fluxes of the charged species, can be compared with experimental data, to check the validity of the model results.

We have applied the model to a range of operating conditions (gas pressure, applied voltage and frequency), to investigate under which conditions the DBD gives rise to a stable plasma, and whether different processes play a role in sustaining the plasma.

**MoPo40.** THE INFLUENCE OF SMALL ADDITION OF MOLECULAR GASES ON ANALYTE RADIAL DISTRIBUTION OF EMISSION AND ABSORPTION IN ARGON DC ARC PLASMA

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The object of this work was U-shaped direct current argon arc operating at atmospheric pressure, with continual water aerosol supply. Main argon stream was doped with controlled low flow of molecular gases: oxygen, nitrogen, hydrogen and acetylene. The addition of molecular gases is expected to influence both the fundamental and bulk properties of the plasma and also the energy transport through the discharge. For instance, it changes the thermal conduction of argon plasma causing the changes in distribution of electron number density and temperature. Oxygen and acetylene also changes the oxydo-reduction properties of the plasma which is important for analytes that forms refractory oxides. Radial distribution of analyte emission and absorption were monitored by moving the arc column perpendicularly to the optical axis of the monochromator. The obtained results have shown that addition of small amounts of molecular gases causes displacement of emission and absorption to the arc periphery. Also, it was shown that molecular gas depresses the influence that easily ionized elements (EIE) have on analyte emission. These results are important in analytical applications of this plasma source.

**MoPo41.** THE INFLUENCE OF NITROGEN, EITHER ADDED AS PLASMA GAS OR PRESENT AS ANALYTE, IN GLOW DISCHARGE-OPTICAL EMISSION SPECTROMETRY

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Quality control requirements of advanced materials in the industrial field (hard coatings, nanomaterials, etc) have motivated the development of analytical techniques with high capabilities. In this line, the radiofrequency glow discharge coupled to optical emission spectrometry (rf-GD-OES) is very useful for both homogenous and in depth profile analysis of conductive, semiconducting or insulating materials, and among its properties it is included accuracy and rapidity.

One topic of particular interest is the effect of elements such as oxygen, nitrogen or hydrogen. Traces of these elements may come from the sample itself (e.g. nitride layers of elements of the IV-VI groups), or as molecular gases either from contamination in the source or even externally added on purpose, affecting the analytical quantification procedures.

Considering the advantages that arise from the industrial application of materials like nitrides (mechanical resistance), it becomes interesting to investigate the effect of nitrogen in rf-GD-OES. In this communication, the effect of nitrogen (either externally added with the plasma gas or from the sample) in different matrices has been investigated. In order to discard spectral interferences, it was analysed the spectra in the

surroundings of the selected atomic line for each analyte. Also, the potential influence exercised by the nature of the nitride coatings or by the added molecular gas on the analytical characteristics of the rf-GD has been studied in terms of analytical performance characteristics and examples of successful quantitative analysis of samples of technological interest will be shown.

**MoPo42.** ANALYSIS OF HIGH PURITY METALS AND BEYOND USING GLOW DISCHARGE MASS SPECTROMETRY

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Glow discharge mass spectrometry (GD-MS) has been established as the high performance tool for the analysis of high purity metals in the solid state down to single digit parts per trillion (ppt) levels. Thermo Electron Corporation introduced a new GD-MS in 2005, the *Finnigan ELEMENT GD*. The instrument enables the highest mass accuracy and stability, allowing sharp determination of the mass of interest – this directly translates into short analysis times and high sample throughput.

Special emphasis was taken on the development of the glow discharge source in the ELEMENT GD. To fully use the scan speed of the mass analyser, a so-called fast flow GD source was implemented. This is a high power source (similar to a ‘Grimm type source’) that typically uses currents between 40 and 60mA, voltages between 600V and 1000V, and Argon flows of around 400ml/min. The combination of high power with high Argon flow results in high sputter rates and sensitivity. As a consequence, lowest detection limits are achieved within a time frame of several samples per hour.

The measurement of high purity metals such as 5N and 6N qualities will be demonstrated. However, GD-MS is a powerful tool for the analysis of solar cell silicon. The presentation will demonstrate the capabilities for this type of application. Furthermore performance characteristics for depth profiling down to the nm dimension will be shown.

**MoPo43.** ANALYSIS OF LIGHT ELEMENTS BY GLOW DISCHARGE OPTICAL EMISSION SPECTROMETRY -

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The Glow Discharge Optical Emission Spectroscopy (GD-OES) is well known as a fast and reliable depth profiling technique with multi element capability. The possibility to get information on the concentration and depth distribution of light elements, like H, C, N and O is of special interest, because there are only few analytical methods, which are able to analyze these elements.

Because light elements are present in many types of new materials, like glass, ceramics, hard coatings etc., their reliable and quantitative measurement by GD-OES becomes more and more essential. Therefore, the different problems linked to this kind of analysis need special attention in research and development.

Firstly, these elements are present as contaminations of the glow discharge source and sample and influence the properties of the plasma. Thus, especially the analysis of thin films at the surface is complicated or impossible. The thinner the layers under examination are, the more this effect is disturbing.

Because of the venting of the glow source before each measurement contaminations of films of water and hydrocarbons cannot be prevented totally. Accurate results of light element concentration can be only achieved, when these contaminations are reduced. The decrease of sample contamination for analysis of thin layers is more important, than the reduction of contaminations in the gas in principle for the analysis of bulk materials. Different procedures for the reduction of contaminations of source and sample were applied and will be compared.

Secondly, there is a lack of standard material for calibration and the possibility of a matrix independent calibration for the light elements is still an open question. Therefore, at IFW new materials for the calibration of H was tested. Calibration curves for O, C and N are presented too.

**MoPo44.** AN EFFECTIVE RESISTANCE APPROACH FOR MEASURING THE PLASMA POWER IN RF-GLOW DISCHARGES USED FOR GDOES.

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In this work, a novel method to calculate the plasma power in rf-GD-OES is presented. The method is based on an effective resistance located in the inductive coil of the impedance matching. The correction method is experimentally evaluated and compared to the method based on an integral plasma power calculation. The generator power was measured for a large range of dc-bias voltages at constant pressure (800 Pa). The forward power delivered by the rf-generator has been varied from 10 W to 90W during the experiment. For each setting the difference in generator power was related to the difference in the square of a current probe signal. The results confirm the assumption of a single effective resistance.

The power loss in the rf-supply circuit can be estimated from the current through the inductive coil of the impedance matching system. The effective resistance approach has been validated through two independent experiments. Compared to existing methods the new approach has the advantage of being easily implemented in existing instruments. As the correction method is independent of the sample size and nature blind power measurements prior to each analysis are not required. The correction method is compared to other correction methods described in the literature.

**MoPo45. DETERMINATION OF BROMINE IN FLAME RETARDANT COATINGS BY RADIOFREQUENCY GLOW DISCHARGE - OPTICAL EMISSION SPECTROMETRY**

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There is an increasing concern over the toxicity and environmental distribution of a number of classes of brominated compounds employed as flame retardants. Flame retardants are used in coatings on electric wires, plastic housings, printed circuit board of electronic equipment, textiles and other materials to prevent fires [1].

Radiofrequency glow discharge plasma spectrometry coupled to optical emission spectrometry (rf-GD-OES) is regarded nowadays as a powerful tool for the rapid control of manufactured materials (conductors and insulators) and coatings [2]. In this communication, the feasibility of using rf-GD-OES as a rapid and simple tool to analyze bromine-containing flame-retardants polymeric layers deposited onto glass matrices was investigated. The polymeric layer was prepared by mixing appropriate amounts of tetrabromobisphenol A, bisphenol A, phloroglucinol and diphenylmethane-4,4'-diisocyanate in tetrahydrofurane. Blanks (without tetrabromobisphenol A) were also prepared

Detection of bromine was performed both in the visible at 470.48 nm and in the near-infrared at 827.24 nm, using a charge-coupled device. Discharge parameters affecting the emission intensity of bromine (pressure and power) were investigated comparing argon and helium as plasma gas and the analytical performance characteristics were evaluated.

Finally, applicability of the method for the quantitative analysis of bromine in samples of technological interest was successfully carried out using for the calibration polymers synthesized in our laboratory with different concentrations of the analyte.

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**MoPo46. DETERMINATION OF IMPURITIES ON THE SURFACE AND IN THE SUB-SURFACE OF SILICA AND KDP OPTICS BY ICP AND GD ANALYTICAL TECHNIQUES**

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Lifetime of fused silica and KDP optics used in high power laser facilities such as Megajoule laser (LMJ) or National Ignition Facility (NIF) is the subject of extensive studies to reduce maintenance operations and costs. In the case of fused silica, damage initiators can be subsurface cracks or nano-absorbing centers ; for KDP single crystals, initiators are bulk defects of unknown origin (impurities ?). In this context, detection of

impurities on the surface and in the subsurface of silica samples, and in the volume of KDP ones, is of great interest.

For fused silica samples of 100 mm diameter, it was possible to characterize the surface after cycles of washing with concentrated HNO<sub>3</sub>. Then, each sample was etched in a mixture of concentrated HNO<sub>3</sub> and HF (90 %vol/10 %vol) for one micron steps digestion. Suitable depth profiles were thus obtained for the concentrations of the main impurities which may be incorporated during grinding and polishing processes (Ce, La, Zr, Hf, Al, Fe, Cu). Results show a good correlation between cerium content in the interface and damage density at 14 J/cm<sup>2</sup> for samples with high cerium concentrations. Complementary tests will be run soon on full scale optics (400 mm x 400 mm).

In the case of KDP samples of 100 mm diameter, small volumes were sampled with a devoted cell of 2 mm inner diameter. These volumes were deposited on porous graphite electrodes which were analyzed with GD-MS spectrometers (a home made device and a VG 9000 one). Detection limits of 10 to 30 ng/g were obtained for the controlled elements, as well as depth profiles (up to 500 microns) of impurities concentrations. GD-MS results were compared with ICP-AES, ICP-MS, HR-ICP-MS ones.

#### **MoPo47. CLUSTERS IN TIME-OF-FLIGHT MASS SPECTROMETRY WITH PULSED GLOW DISCHARGE IN COMBINED HOLLOW CATHODE.**

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Clusters in glow discharge as clusters in ICP MS can appreciably worsen the analytical parameters of a spectrometer. High resolution mass spectrometry almost free from appropriate interference, but for others spectrometers this problem exists. Therefore decreasing of intensities of clusters components can improve detection limits for some elements.

A novel time-of-flight mass-spectrometer (TOF MS) with pulsed glow discharge in combined hollow cathode was used in experiments. Argon is usually used as the plasma gas, various plasma gases and their mixtures and modification have been investigated. Different types of clusters were investigated in the experiment:

- sample elements (M) with hydroxyl ion ( $\text{MOH}^+$ ,  $\text{MOH}_2^+$ ,  $\text{M}(\text{OH}_2)_2^+$ );
- clusters  $\text{M}\text{Ar}^+$ ;  $\text{M}\text{M}\text{Ar}^+$  and  $\text{M}\text{N}\text{Ar}^+$ , where N – element of cathode wall.

The intensities of the clusters components as function of pulse duration, current, pressure, concentration of hydrogen in discharge gas were measured in the experiments. Processes of clusters formation in discharge and optimization plasma gases are discussed in the presentation

#### **MoPo48. MICROSECOND GRIMM-TYPE PULSED GLOW DISCHARGE AS IONS SOURCE FOR MASS-SPECTROMETRY**

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Microsecond DC-Pulsed Glow Discharge (PGD) source of ions for mass-spectrometry is not enough investigated yet. To demonstrate its possibilities in comparison with DC GD for mass-spectrometry an experimental setup based on a quadrupol mass-spectrometer "TS-Sola" was created. The instrument is equipped with a commercially used Grimm-type source. Application of pulsed supply mode to the source and optimization of PGD parameters (pulses duration, frequency, amplitude and gas pressure) causes improvement of detection limits of the system in 15-125 times for miscellaneous elements. To study processes of the sample conversions in PGD both experimental and theoretical investigations were carried out. The experimental investigation was performed by measurement of dynamics of different ions extracted from the discharge to mass-analyzer. At that a special new method to measure intensity of ions in a quadrupol mass-spectrometer with satisfactory time resolution (10  $\mu$ s) was developed. To study the PGD processes theoretically a new model for Microsecond PGD in Grimm-type source simulation was developed. Results of the model are compared with measured dynamics of different ions. The comparison shows that probably there is an additional ionization source behind a sampler orifice.

**MoPo49.** TRACE ELEMENTS ANALYSIS IN LAVA FROM ETNA BY GDMS

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Petrological monitoring of volcanic activity based on major/ trace elements and isotopes ratios is generally carried out using the bulk rock composition of lava samples. GDMS has been exploited for the determination of major and trace analysis in lava samples collected from Mont Etna. Uranium, Thorium and REE are investigated. Lava samples and certified reference soils dried and homogenised, were mixed with tantalum and indium high purity powder in different ratio and pressed into pellets. Interferences arising from both the lava matrix and the host conductive matrix on the sensitivity of methods is discussed. Results from different measurements of reference materials and from lava samples are presented and the applied methods compared in terms of their detection limits, accuracy and precision.

**MoPo50.** MICROSECOND PULSED GLOW DISCHARGE TIME-OF-FLIGHT MASS SPECTROMETRY FOR THE ANALYSIS OF THIN LAYERS ON SOLID SAMPLES

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Glow discharge (GD) devices are very useful as sources of ionization in the mass spectrometric determination of trace elements. The GDs used in such instruments can be either continuous discharges (direct current or radiofrequency GD) or pulsed GDs. This last type of discharge presents some advantages such as enhanced excitation/ionization yield and lower thermal effects on the sample.

The time-of-flight mass spectrometer TOF(MS) is particularly suited for pulsed sources, due to the time-dependent nature of the ion signals and the use of temporal gating techniques. The pulsed mode allows temporal decoupling of the two types of discharge species: gaseous components and sputtered cathode material. Moreover, since the sputtering process can be controlled changing the duty cycle of the pulsed signal, the pulsed GD-TOF(MS) allows the analysis of very thin layers.

In the present work, the coupling of a home-made microsecond pulsed glow discharge source to a TOF(MS) has been evaluated for the analysis of homogeneous and layered samples. The temporal separation between the discharge gas species and the sputtered sample ions has been studied by using a certified homogeneous copper-zinc sample. Sputtering rates, crater shapes and sensitivities have been evaluated analysing homogeneous certified materials with different matrixes (Cu-Zn, Al and steel). Finally, the in-depth profile of tinplate has been carried out at different pulse frequencies and pulse widths in order to study the duty cycle influence on the resulting profiles.

#### **MoPo51. EXPLOSIVE DETECTION BY GLOW DISCHARGE MASS SPECTROMETRY (GD-MS)**

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Detection and identification of explosive compounds are necessary given the current state of world affairs. Identification and quantification can be quite challenging as explosives are present at trace quantities in the atmosphere. In order to achieve specific, sensitive, and accurate detection of explosive compounds, techniques employing mass spectrometry detection are required. Presented here is the direct introduction of explosive compounds and surrogates into a GD-MS ionization source through a particle beam (PB) momentum separator. Vacuum action through a narrow stainless steel tube allows the introduction of discrete samples of latent explosives in powdered form as well as airborne vapors and particles. Explosive-containing particles then pass through the momentum separator and are flash-vaporized into the gas phase through impact with a heated source block. The resultant gas-phase species are ionized and specifically detected by MS. This facilitates screening of powdered explosives and airborne explosive vapors by GD-MS. The multitude of sampling capabilities of the PB-GD apparatus holds promise for application in continuous monitoring and discrete particle sampling.

**MoPo52.** LIQUID CHROMATOGRAPHY-PARTICLE BEAM/MASS SPECTROMETRY (LC-PB/MS) ANALYSIS OF NUTRACEUTICALS USING ELECTRON IMPACT AND GLOW DISCHARGE IONIZATION SOURCES

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Nutraceuticals are biologically active components derived from functional foods (e.g. wine, green tea, and fruits). The active components of such products often contain beneficial medicinal properties, and are commonly used as nutritional supplements. Presented here is a liquid chromatography-particle beam/mass spectrometry method (LC-PB/MS) with interchangeable electron impact and glow discharge ionization sources for the analysis of ephedra and echinacea extracts.

The separation of the components in ephedra and echinacea was accomplished by reversed phase chromatography with analysis times of less than 25 and 45 minutes, respectively. The eluting analytes are introduced into the particle beam interface to undergo nebulization and desolvation. Subsequently, the dry analyte particles experience vaporization and ionization in the ion source. The glow discharge ion source provides EI-like molecular fragmentation of each eluting compound, allowing mass spectra comparison between both sources. In both examples, the main components are characterized and quantified, with detection limits on the single nanogram level.

**MoPo53.** INFLUENCE OF HYDROGEN ON THE EMISSION SPECTRA OF SILICON AND GLASS SAMPLES IN AN ARGON RADIOFREQUENCY GLOW DISCHARGE

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Glow discharge (GD) coupled to optical emission spectrometry (OES) is regarded, at present, as a powerful tool for the direct analysis of solid samples. As it is well known, while the direct current (dc)-GD only allows the direct analysis of conductive solids, the radiofrequency (rf) GDs can carry out the direct analysis of conductors, semiconductors and insulators, expanding enormously the field of applications of the GDs.

The presence of hydrogen in the discharge can be due to the presence of this element in the sample or to other causes such as residual air in the chamber, gaseous hydrocarbons coming from the vacuum oil pumps or leakages through the chamber. The presence of hydrogen in an Ar GD affects strongly to the emission spectrum of the sample atoms sputtered and can also supply information about the excitation and ionization mechanisms taking place in the glow discharge plasma.

In this work, the effect of hydrogen on the emission spectra of non conducting samples obtained with an Ar radiofrequency glow discharge has been studied. The experimental set-up consisted in a home-made radiofrequency GD, a 0.5 m Czerny-Turner spectrograph and a CCD as detector. Two non-conducting samples, pure silicon

(99.999%) and a homogeneous glass have been employed. The spectra in the range from 200 nm to 600 nm were obtained at three different mixtures of argon/hydrogen (0%, 0.5%, 1% and 10% H<sub>2</sub> v/v). The most intense atomic and ionic emission lines of the major elements (Si, Na, Ca, Mg) in the samples were measured and the dependence of the emission intensities with the hydrogen concentration studied.

**MoPo54.** THE TIME-OF-FLIGHT MASS SPECTROMETRY WITH PULSED GLOW DISCHARGE IN HOLLOW CATHODE FOR DIELECTRIC SOLID SAMPLES ANALYSIS

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At last time the system with pulsed glow discharge (PGD) in a combined hollow cathode (CHC) and time-of-flight mass-spectrometer (TOFMS) was designed in St.Petersburg State University and was used for metal samples analysis. However the PGD-CHC-TOFMS system allows determining concentration of elements in solid samples and powder samples not only conductive, but dielectric too. The short pulsed discharge allows analyzing the dielectric materials because in this type of discharge the surface charge has not time to arise. Therefore the possibility of the dielectric solid samples analysis with PGD-CHC-TOFMS system was investigated. The results of optimization of some discharge parameters for dielectric samples analysis is presented. The analysis of dielectric samples, such as glass slag (a co-product at lead production) and various glasses, using PGD-CHC-TOFMS system was carried out. The results are discussed in presentation.

**MoPo55.** COMPARISON OF DIFFERENT QUANTIFICATION PROCEDURES IN GLOW DISCHARGE MASS SPECTROMETRY APPLIED TO HIGH-PURITY METALS

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Glow Discharge Mass Spectrometry (GD-MS), with its low limits of determination, is an excellent technique for fast multi-element analysis of solid ultra-high purity metals. A drawback of the method is the lack of suitable calibration procedures for accurate and traceable quantification of low mass fractions with small uncertainties.

The following possibilities of quantification are usually applied in GD-MS: RSF (Relative Sensitivity Factor), Standard RSF and calibration with certified reference materials. But in many cases certified reference materials with very low analyte mass

fractions are lacking and on the other hand the Standard RSF concept often produces only more or less semi-quantitative results.

Therefore another calibration procedure based on wetly doped and pressed powder samples has been developed at BAM for the new GD-MS “Element GD” (Thermo Electron Corporation). Such calibration standards can be prepared very similar to the sample regarding the matrix composition and analyte mass fractions. That minimises errors caused by different compositions of sample and calibration samples. Additionally, this way of sample preparation ensures direct traceability of the measurement results to the International System of Units (SI). In this way GD-MS can be used for the certification of solid reference materials, where usually SI traceability is a prerequisite.

The preparation of calibration samples is described. A comparison of the above mentioned quantification procedures for copper and zinc matrices is presented and the results of measurements of certified reference materials are discussed.

**MoPo56.** ENHANCEMENT OF SIGNAL SENSITIVITY IN GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY BY USE OF THE HOLLOW CATHODE EFFECT FOR THE ANALYSIS OF PURE METALS

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Relatively low analyte line intensities and in some cases rather high background intensities or numerous interferences in glow discharge optical emission spectroscopy (GD-OES) do not allow the analysis of high purity metals. In order to reduce the limits of quantification of GD-OES, the hollow cathode effect was used. For this purpose a 15 mm deep hole was drilled into the samples which were compact specimens of certified reference materials of pure copper and zinc. The investigation was carried out with the GD-OES Leco SDP-750. The optimal parameters for measurements of both types of samples (flat samples and samples with a hole) were established. A signal enhancement caused by the hollow cathode effect was observed for all trace elements. The signals from drilled samples were up to 140 times higher than the signals from flat samples, hence the slopes of the plotted calibration curves were strongly increased. It was also observed, that some analyte signals could be better distinguished from interferences, when drilled samples were measured. Due to these phenomena lower detection limits were achieved. This allows the determination of even those trace elements, which otherwise can not be detected by common GD-OES analysis.

These experiments have shown that by combination of a Grimm type of glow discharge with the hollow cathode effect a significant enhancement of signal sensitivity in GD-OES can be achieved when applied to the analysis of pure metals.

**MoPo57. TARTARIC, CITRIC AND DIPICOLINIC ACID EFFECTS ON ICP-AES EXCITATION CONDITIONS**

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Organic matrix introduction into plasma is challenging analytical problem in inductively coupled plasma atomic emission spectrometry (ICP-AES). Due to their complex nature, these kinds of interferences have not yet been fully explained. Dissolved organic ligands are most common matrices in element separation purposes, especially in hyphenated HPLC and ICP-AES techniques. The effects of solutions of tartaric, citric and dipicolinic acid, usually used as ligands in separation of transition metals by ion chromatography, were studied after introduction into plasma. The changes in intensity of representative Cd, Cu, Li, Mg and Mn emission lines were determined for radial and axial plasma view. Influences of different ligand concentrations on excitation conditions of elements were studied after measurement of emission intensity and determination of signal-to-background ratio and detection limits. The ionic-to-atomic line intensity ratio of selected elements was calculated in order to compare the values obtained for water and solutions with organic acids. The different magnitude of the effects on emission line intensity caused by tartaric, citric and dipicolinic acid introduction into plasma were established.

**MoPo58. DETERMINATION OF MERCURY IN ORGANIC PHASE BY DIRECT INJECTION AND COLD VAPOR GENERATION-INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY**

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A preliminary study to determine mercury by direct injection and cold vapor generation-inductively couple plasma optical emission spectroscopy in organic phase was carried out in this project. In order to generate the cold vapor, a direct hydride nebulizer system elaborated in the Centro de Química Analítica of the Universidad Central de Venezuela was attached to the sample introduction system of the ICP. This nebulizer has three channels, one used to introduce the sample mixed with acetic acid, another to introduce the NaBH<sub>4</sub> (which is prepared in DMF) and the last one for the argon. Two chambers connected in series, a ball type follow by a cyclonic refrigerate at -5 °C were used to increase the quality of the aerosol and avoid overload of the plasma. The operation parameters of the system were evaluated to obtain optimal conditions. The best sensibility was obtained using 30% p/p acetic acid, 1.0% p/v NaBH<sub>4</sub>, 0.4 L/min nebulizer flow, 1.25 mL/min of NaBH<sub>4</sub> flow, 0.5 mL/min of auxiliary gas, 2.0 mL/min rate of sample introduction and 1450 watts of power. Under these conditions a detection limit of

4.15 ng/g was reached. The quantification limit was 8.04 ng/g, and a sensibility of 114.81 ng/g was achieved.

**MoPo59.** ULTRASOUND-ASSISTED ACID LEACHING FOR THE DETERMINATION OF Fe, Ni AND V IN ASPHALTENE SAMPLES USING ICP OES  
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A fast and simple extraction method, previous to ICP OES determination of Fe, Ni and V in asphaltene samples, is proposed. The organic samples (0.5g to 1g) are placed into polypropylene tubes and dispersed in high-purity concentrated nitric acid (10 mL). The mixtures are heated at 85 °C during 30 min and then sonicated during 20 min. The ultrasonic bath used contained 1 L of water and allowed the sonication of up to 8 tubes (placed in vertical position) at a time. The supernatant solution is then directly aspirated into the inductively coupled plasma of an optical emission spectrometer. Quantification of the analytes was made using aqueous standards dissolved in concentrated nitric acid. The method was tested on asphaltene samples separated from NIST 1634 SRM (fuel oil) by a modified IP-143 procedure. For comparison, samples were also analyzed by ICP OES after direct dilution in toluene. Recoveries ranged from 93 to 105 % (n = 3) and the limits of quantification were between 2 and 4 ng g<sup>-1</sup> depending on the analyte. The results showed that only incomplete extraction of the analytes is obtained by the heating step and that sonication is fundamental to achieve quantitative recovery.

**MoPo60.** BETTER CORRECTION FOR STRUCTURED BACKGROUND IN DIFFERENT ICP-OES APPLICATIONS

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Different correction procedures were developed over the last years for a better determination of spectral interferences. Methods like interelement correction, multicomponent analysis, Kalman filtering, and multiple linear regression are well known and widely used. All these methods require measurements of separate standards and spectral interference studies which are usually very time-consuming. When trace elements are present in complex matrices, or strongly structured spectra with changing matrix, like organics, have to be analysed the conventional background corrections are in the most cases of limited use.

Several applications of a spectrum based correction method (pixel-intensity-dilution) will be presented and discussed. The relevant figures of merit will be also presented.

**MoPo61.** DETERMINATION OF TOTAL Cs IN IRRADIATED SALT SAMPLES BY ICP-AES

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The determination of Cs by ICP-AES in irradiated salt samples is complicated by the poor sensitivity of Cs determination by ICP-AES and sample handling considerations. The samples are routinely analyzed via ICP-MS for  $^{133}\text{Cs}$  and  $^{135}\text{Cs}$  and gamma counted for  $^{137}\text{Cs}$ . The sum of the isotopes yields the total Cs in the samples. This presentation will discuss the methods development for a new analytical method to determine total Cs in irradiated salt samples via ICP-AES. The work utilizes an ICP-AES installed in a lead lined glovebox to analyze samples for Cs. Instead of using the 455.28 nm line, which suffers from relatively poor solution detection limits (on the order of tens of part per million), this work utilizes the Cs line at 894.347 nm. The new line yields detection limits less than one part per million. The result of the new method will be compared with the ICP-MS and gamma counting method typically used

**MoPo62. IMPROVED COLLISION/REACTION CELL TECHNOLOGY METHODS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES**

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This presentation describes two approaches for the analysis of environmental samples by ICP-MS utilising latest generation collision/reaction cell technology for the removal of polyatomic interferences arising from gas-based and matrix-based species.

- 1) Reactive collision/reaction cell approaches are often used to remove argon-based polyatomics that hamper selenium measurements. However, when measuring high-matrix environmental samples, incorrect results can be observed, as well as inconsistency between measurements of different isotopes of selenium. This is a sign of the presence of interferences. This work identifies the responsible species as new cell-formed polyatomics and proposes remedies by either reducing the ingress of reactants to the cell, or by blocking the transmission of reaction-products through the mass analyzer. A practical solution involving both methods is proposed and demonstrated, producing accurate results and good isotopic agreement.
- 2) Reactive collision/reaction cell approaches have been shown to be efficient at removing specific interferences, but require prior knowledge of the chemistry between the reagent gas and the interferent and analyte. Such approaches often reduce ICP-MS to a single element technique and increase method development complexity and sample analysis time since multiple gases are often required. Here, we demonstrate a single gas approach for removing multiple interferences typical of environmental analyses.

**MoPo63. UNCERTAINTY CALCULATIONS ASSOCIATED WITH THE CERTIFIED VALUE OF AN ANTIMONY REFERENCE MATERIAL DETERMINED BY ICP USING A THREE POINT CALIBRATION CURVE.**

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Measurements can be made to determine if an instrument is running properly, to assess the value of a product/service, to accept or reject a product, or perhaps to comply with government regulations. To determine the quality of any measurement, a measure of uncertainty must be given along with the value. In other words a measurement where there is no uncertainty listed is of unknown reliability and of limited value.

As a user of analytical instrumentation, it is critical for one to know the accuracy of the calibration standards in use, and the uncertainty associated with the calibration curve itself. Only then can one determine the confidence limit of one's own data.

This presentation will discuss an approach to standardize a method of reporting the certified value of a reference material determined by ICP using a three point calibration curve. A 1000 mg/L Antimony Certified Reference Standard was chosen to demonstrate how the statistical calculation of measurement uncertainty is performed.

**MoPo64. DEVELOPMENT OF NEW DESIGN LOW FLOW PLASMA TORCH FOR ICP-MS**

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Inductively Coupled Plasma (ICP) is one of most powerful and useful emission and ionization source for elemental analysis. Design of ICP torch was almost same design since developed by Greenfield at 1964, which consists of three different sizes of quartz tube (Fassel type torch). This torch design is simple and makes a very powerful plasma. However this torch has the disadvantage that consumption of Ar gas is large ( $20\text{L min}^{-1}$ ) making it expensive to operate. If the cooling gas volume (which is the main Ar flow of about  $14$  to  $18\text{ L min}^{-1}$ ), then the total consumption of Ar gas will be reduced.

The authors have developed a new design of ICP torch for low flow Ar cooling gas which is named "spiral torch". This torch has a modified outer quartz tube design, which increases the turning element and gas speed of the cooling gas (patented by Nippon Telegraph and Telephone (NTT)). The Spiral torch was tested using HP4500 and Thermo PQ-Excel for ICP-MS. In these results we demonstrate that in both instruments it was possible to use at lowest flow rates of cool gas flow (at instrument inter-lock) constantly. Analytical performances (sensitivity and stability) using low Ar flow conditions were almost the same as the normal Fassel torch so there was no reduction in performance.

**MoPo65.      ADVANCES IN THE DETERMINATION OF MERCURY BY THERMAL DECOMPOSITION, AMALGAMATION, AND COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY**

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Many laboratories anticipate increased implementation of the thermal decomposition technique for the determination of mercury<sup>3</sup> in a variety of sample matrices. The method provides rapid analysis with little to no sample pretreatment. In most cases, results can be obtained in less than ten minutes. Moreover, available instrumentation for this technique is remarkably stable and immune from matrix interferences. As a result, a variety of samples can be analyzed for mercury from a single stored calibration curve. In this presentation we will investigate the impact of system characteristics such as moisture control, gas selection, and decomposition temperature on accuracy, sensitivity and stability. Using aqueous calibration standards mercury concentration will be reported for a variety of certified reference materials.

<sup>1</sup> **AN UPDATE OF THE CURRENT STATUS OF THE RCRA METHODS DEVELOPMENT PROGRAM**

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**MoPo66.      A CORRELATION-BASED STRATEGY FOR REDUCING INTERFERENCES IN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY**

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Inductively coupled plasma mass spectrometry (ICPMS) offers low (ppt) limits of detection, a broad linear dynamic range, the potential for multielemental determinations, and the ability to tolerate a wide variety of sample types and matrixes. In spite of the success of ICPMS systems, oxide-based interferences can complicate even the most routine determinations. A number of strategies (selection of an alternative isotope, chromatographic separations, high-resolution mass spectrometry, collision-cell technology, and others) have been developed to overcome problems associated with isobaric interferences. Although each method is successful at reducing or eliminating

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<sup>3</sup> **AN UPDATE OF THE CURRENT STATUS OF THE RCRA METHODS DEVELOPMENT PROGRAM**

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troublesome overlaps, such improvements often come at the cost of analyte sensitivity, operational complexity, or instrumental cost.

In this study, modulation of the central channel gas flow generates unique behavior from analyte and oxide species; behavior which can be mathematically unraveled via correlation calculations. The simple modifications described here reduce a 30-fold error present at  $m/z$  156 due to the interference of  $^{140}\text{Ce}^{16}\text{O}^+$  on  $^{156}\text{Gd}^+$ , without compromising instrumental sensitivity. Additionally, this correlation-based correction strategy can be extended to samples in which multiple analyte-oxide interferences are present. In this work, a time-of-flight mass analyzer permitted *simultaneous* oxide correction at four compromised masses with no loss in analyte sensitivity.

**MoPo67.** THE ANALYSIS OF RADIOACTIVE PHARMACEUTICAL SAMPLES USING AN ELAN 9000 DRC ADAPTED TO A STANDARD STAINLESS STEEL GLOVE BOX IN COMBINATION WITH A HIGHLY SHIELDED GLOVE BOX.

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The analysis of radioactive pharmaceutical samples with an ICP-MS requires safe equipment to protect the chemist against radiation. To achieve this task a complete sample handling chain has been created. The sample preparation process starts within a hot cell type of laboratory and is continued in a glove box with several layers of shielding in which samples are handled for the final analysis with the ICP-MS.

These samples are then transferred into the final glove box adapted to the ICP-MS.

This poster will give an overview of a very specific technical solution in which the modified ICP-MS has a key function in delivering the final analytical results for each sample.

**MoPo68.** EVALUATION OF INTERFERENCE RETARDING REAGENTS FOR DETERMINATION OF As, Bi, Sb, Se, Sn AND Te IN HIGH ALLOY STEEL AND Ni SUPER ALLOYS USING A MULTIMODE SAMPLE INTRODUCTION SYSTEM (MSIS) AND HYDRIDE GENERATION ICP-AES

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Determination of tramp trace element contaminants (< 10 mg/kg) (As, Bi, Sb, Se, Sn, Te) in chemically resistant high alloy steels and Ni alloys is an important task because they degrade mechanical properties of these materials. Notwithstanding advantages of hydride generation for steel and complex alloy analysis (separation of matrix elements rich in

spectral lines that cause overlap on analyte lines of interest, enhancement of LODs as a result of high transport efficiency), optimum reaction conditions are not easily attained due to chemical interferences on the hydride generation process caused by high concentrations of Ni, Cr, Co, Cu and Mo in the dissolved samples.

In this study we describe the use of a Multimode Sample Introduction System (MSIS) coupled to a simultaneous multielement axially viewed ICP-AES spectrometer (CIROS Vision EOP; Spectro Analytical Instruments, Kleve, Germany). EDTA, tartaric acid, potassium iodide, L-cystein and 1,1,3,3-tetramethyl-2-thiourea were evaluated overcoming matrix induced chemical interferences by means of an experimental design.

Consequently, a procedure was developed for simultaneous determination of As, Bi, Sb, Se, Sn and Te in high alloy steels and Ni super alloys. The proposed procedure was validated using spiked steel solutions and several CRM steel and Ni alloys.

**MoPo69.** EFFECT OF SODIUM, BORON AND HYDROGEN ON THE PLASMA IN HYDRIDE GENERATION INDUCTIVELY COUPLED ATOMIC EMISSION SPECTROMETRY (HG-ICP-AES)

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In hydride generation inductively coupled atomic emission spectrometry (HG-ICP-AES), hydrogen, sodium and boron are introduced in large quantities to the plasma. The presence of large quantities of Na in the plasma is known to decrease plasma robustness, and as a result cause matrix induced reduction of analyte emission intensities. A similar effect by boron can be expected. Hydrogen on the other hand is reported to increase emission intensities of several elements.

In this study we quantified the amount of Na and B delivered to the plasma by hydride generation using a Multimode Sample Introduction System (MSIS), and then systematically studied their effect on hydride and nonhydride forming elements using a mixed hydrogen-argon ICP. Mg II 285/Mg I 280 nm was used as a criterion for plasma robustness together with the determination of  $T_{exc}$  for variable B and Na concentrations and changes in plasma operating such as RF power, and aerosol and sweep gas flow rates using a MSIS and auxiliary pneumatic nebulizer, respectively. The effect of energy potentials of the element and spectral wavelengths were also investigated.

**MoPo70.** ICP-MS WITH ENHANCED TOLERANCE TO MATRIX SAMPLES CONTAINING PERCENTAGE LEVELS OF TOTAL DISSOLVED SOLID

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The determination of trace elements in high matrix samples has often been a difficult application. While ICP-MS has an unsurpassed detection capability for trace metals,

dissolved solid levels must be controlled carefully to minimize deposition of salt or sample matrix on the MS interface. Compared to ICP-OES or other non-MS-based techniques, this has been considered an inherent limitation of ICP-MS. This paper will demonstrate that matrix tolerance of ICP-MS is remarkably improved by simple modification of the sample introduction system. The new technique makes it possible to control sample load on the mass spectrometer and introduce aqueous samples with total dissolved solid (TDS) exceeding 1%. Included in such samples are undiluted seawater (3% TDS) and acid-dissolved copper material (1% TDS), which were successfully analyzed to quantify the trace elements of interest at sub-ppb level or lower. Salt or matrix deposition on the sampling cone and skimmer cone was minimized to achieve stable signals over a 15 hour period of repeated measurements.

**MoPo71. FORENSIC ANALYSIS USING MERCURY CONCENTRATION MEASUREMENTS IN SHOOTING PRODUCTS BY ZEEMAN ATOMIC ABSORPTION SPECTROSCOPY**

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Mercury was used in manufacturing of gun shell cells until 60-70-ties of the last century. Such shells are in wide circulation in criminal circles nowadays. In cooperation with State Forensic Science Bureau it was decided to verify, if mercury concentration measurements can be utilized in forensic investigations. Experiments were performed, using TT pistol, with ammunition manufactured in different years. It was proved that, using Zeeman atomic absorption spectrometer RA-915+, it is possible to detect a presence of mercury in premises, on hands and clothes as well as in gun barrel and used shells. This fact can be used as an argument in criminal cases investigations. Possibility to determine differences between shells of different origin and reproducibility of result between shells of single origin were verified. It was found that there exists a possibility to try to use measurements of mercury concentration changes for determination of shooting time, though improvements in this area are needed, and environmental conditions should be taken into account.

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**MoPo72. ON-LINE ANALYSIS OF Cr(III) AND Cr(VI) BY COUPLING ICP-OES AND A HOLLOW FIBER LIQUID MEMBRANE ANNULAR CONTACTOR**

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A pilot hollow-fiber liquid-membrane contactor has been coupled to ICP-OES for on-line determination of Cr(III) and Cr(VI). The annular geometry of the contactor allows the extraction and stripping processes to be integrated in a single module and the liquid membrane volume to be reduced to a few millilitres. In this contactor, Cr(VI) is

separated from Cr(III) as it is efficiently removed from the inlet water solution by a N-methyl, N-dodecyl-ephedrinium ion organic liquid membrane solution and transported to a HNO<sub>3</sub> aqueous stripping solution. The contactor can be used continuously for several days, while maintaining its efficiency of Cr(VI) removal.

The coupling to ICP-OES was obtained by a switching valve, which alternatively drives to the nebulizer the initial solution containing Cr(III) and Cr(VI) or the solution coming out of the contactor, containing Cr(III) only. Cr(VI) concentration can be then evaluated as the difference between the two measurements.

The work describes the development of the contactor, the optimization of the experimental conditions for Cr(III)/Cr(VI) separation and the coupling to the ICP spectrometer. Reliability of the results has been checked by inter-technique comparison at different concentration levels and in the presence of different Cr(III)/Cr(VI) ratios.

### **MoPo73.** THIN FILMS CHARACTERIZATION USING SEVERAL COMPLEMENTARY SPECTROMETRIC TECHNIQUES

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The surface is the part of the material that interacts with the environment. Surface properties are different from bulk properties. Several phenomena take place at the surface of solids : ageing, wear and tear, corrosion, contaminations, molecular adsorption. The induced changes can alter the properties of the solids themselves. In order to improve these properties, thin layers with different features are often added on top of the materials. A good characterization of surfaces and thin layers is therefore needed to better understand the interactions with the environment.

An analytical approach using complementary techniques such as Ellipsometry, Raman spectroscopy and Glow Discharge Optical Emission Spectrometry (GD-OES) will allow a precise characterization in terms of composition, structure and morphology.

The potential of this multitechnique approach was evaluated on different samples which are of great interest for the industry of semi-conductors, anti-corrosion coatings and organic emitters.

The use of several techniques allowed us to analyse a wider range of samples, obtain more informations on one sample and corroborate the informations obtained.

### **MoPo74.** INVESTIGATION OF DRY PLASMA CONDITIONS IN GC-ICPMS COUPLED SYSTEM

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The combination of capillary GC with ICPMS has become an ideal methodology for speciation analysis for organometallic compounds, such as organotin, because of the high resolution capability of GC and the sensitivity and element specificity of ICPMS. The determination of organotin compounds is complex due to the very low concentration levels (low ppt) they occur in the environment. For this reason, GC-ICPMS provides among others, low detection limit and accurate isotope ratio precision measurement. Although, it has to be taken into account that the above mentioned system needs other approximation. In point of sample introduction procedure there is a great difference of plasma conditions obtained between generally used pneumatic nebulization and sample introduction performed with GC. In the previous case we obtain wet plasma while in latter case we obtain dry plasma conditions. The two methodologies require different optimum of system parameters. One of these is plasma forward power that shows significant change in case of coupled GC-ICPMS system. In this study the robustness of dry plasma was investigated. The effect of impulsed solvent introduction at different plasma conditions, monitoring Xe that was present in the carrier gas, is shown in this poster. During this study we took into account the investigation of sensitivity and repeatability of the system applying tetraethyltin standard solution. Finally, analysis was also performed with GC-FID in order to study the manner of the repeatability of GC-ICPMS system.

**MoPo75. COMPARISON OF DISSOLUTION APPROACHES AND SOLID SAMPLING TECHNIQUES FOR THE DETERMINATION OF SILVER IN POLYMER SAMPLES**

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This work reports on the performance of different procedures and techniques that enable determination of the amount of Ag added as an antimicrobial additive to a large variety of plastics (quality control).

Conventional acid attack and microwave digestion techniques were undertaken to assess the best sample dissolution procedure. The solutions thus obtained were measured by means of ICPMS and F-AAS. Due to the fact that these dissolution procedures are labour-intensive and time-consuming and bring about a risk of analyte losses or incomplete dissolution of the sample, solid sampling analysis was attempted by means of both LA-ICPMS and GF-AAS. In this way, the sensitivity was enhanced, the sample throughput increased and the risk of contamination and analyte losses reduced. LA-ICPMS shows great possibilities, although calibration is still problematic. SS-GF-AAS on the other hand, is a very fast procedure and allows an accurate determination of Ag in all types of polymers investigated. Due to the high Ag content, a 3-field mode Zeeman-

effect background correction system was used to expand the working range to hundreds of nanograms for Ag.

In general terms, all the methods investigated perform in a satisfactory way and are reliable for the determination of Ag in polymers, although they show different strengths and weaknesses.

**MoPo76. EVALUATION OF MASS BIAS AND ITS ASSOCIATED UNCERTAINTY IN QUADRUPOLE, DOUBLE FOCUSING AND MULTICollectOR ICP-MS INSTRUMENTS**

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

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

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

**MoPo77. EVALUATION OF DIFFERENT IONIC IMPRINTED POLYMERS FOR TRACE ELEMENTS SOLID PHASE EXTRACTION FROM SEAWATER FOLLOWED BY ICP-OES DETERMINATION**

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Ionic imprinted polymers (IIPs) are similar than molecular imprinted polymers (MIPs) but they recognize metal ions after imprinting, retaining all virtues of MIPs. A

particularly promising application of IIPs is the use of such polymers for solid phase extraction (SPE) to pre-concentrate trace elements at very low levels or to isolate them from other concomitant ions in complex matrices such as seawater samples.

In the current work, 8-hydroxyquinoline (8-HQ) based IIPs have been synthesised using different templates ( $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ). Two functional monomers were used: 4-vinylpyridine (4-VP) for Al-8-HQ based IIP and 2-(diethylamino) ethyl metacrylate (DEM) for Cu-based IIP and Ni-8-HQ based IIP. The incorporation of 8-HQ in the polymer structure has led to an increase on the imprinting properties of some synthesised polymers when using the precipitation polymerization technique. Around 100 mg of each IIPs were packed in SPE cartridges and seawater samples containing the template elements ( $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ ) and other target ions ( $\text{As}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{V}^{5+}$  and  $\text{Zn}^{2+}$ ) were passed through the IIP cartridges by using a vacuum manifold station. The cartridges were then rinsed with 3.0 ml of an aqueous solution at fixed pH (in function of the pH of the loading solution) and the retained metals were eluted with 3.0 ml of 2.0 M nitric acid.

#### **MoPo78. MULTI-ELEMENT METHOD FOR TRACE ELEMENTS IN EDIBLE OILS BY ICP-MS – REPLACING GF-AAS**

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The presence of metals in vegetable oils can be due to their natural contents in the starting raw materials and the contact/contamination with manufacturing or storage equipment. Heavy and transition metals should not be present for food safety reasons and especially because of their catalytic role in fat oxidation. Maximum permissible concentrations are given by the Codex for lead, copper and arsenic (0.1 mg/kg) and iron (1.5 mg/kg). Checking metal contents in oil samples is therefore very important for the quality and the safety of the products.

Official methods (AOAC) use GF-AAS as analytical technique. This type of analysis is based on direct injection of the oil and demands the presence of the analyst at any time throughout analyses. A more automated system performing simultaneous analyses of several elements would be of great benefit in terms of cost-efficiency. We tried therefore to prepare the oil samples by high pressure ashing and to analyse the digest by ICP-MS for Cd, Cu, Fe, Hg, Mn, Ni, Pb, and Zn. For the determination of Fe and Cu the dynamic reaction cell technique was employed in order to decrease interferences and improve the signal/noise ratio. The main difficulty with this approach was at first sight the possible contamination of the samples and standards through improper handling and high background concentration in used acids. Ultrapure  $\text{HNO}_3$  was therefore employed with certified low background concentrations (ppt levels) of metals. Spiking experiments showed good recovery (90-110%) down to levels of 0.06 mg/kg for all elements and lower for some of them. Results of a small survey on metals in different oil samples are also presented in this poster.

#### **MoPo79.**

## USE OF NORMALIZED PROCEDURES FOR METHOD VALIDATION OF TRACE ELEMENTS IN CCD-BASED ICP-AES

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Method validation remains a key problem in ICP-AES. In order to determine trace elements, validation was conducted with an emphasis on criteria such as linearity of the calibration graph, limits of detection and quantitation, and uncertainty. A series of elements was selected (Co, Cr, Cu, Fe, Ni, Mn and Zn) in the concentration range 0 – 100 µg/L. A HORIBA Jobin Yvon ACTIVA ICP-AES system was used, with two lines per analyte.

In terms of linearity, the  $r$  correlation coefficient was always very close to 1. In contrast, linearity test based on ANOVA, as described in some norms, appeared very severe, and failed for low values of the standard deviation. Actually, ICP-AES seems to provide too low experimental errors for such a test.

Several approaches were used for the determination for limits and quantitation (LOD and LOQ). The method based on the verification of the LOQ with a spiked blank was preferred.

At last, estimation of the uncertainty is certainly the most challenging part. For routine analysis, a global uncertainty *ca* 10% may be accepted, whereas error propagation must be used for a more rigorous estimation.

## **MoPo80.** PULSE SYNCHRONIZED ICP SYSTEM USING DIRECT DROPLET INJECTION NEBULIZER FOR NANO-LITER ANALYSIS

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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. ICP-MS and ICP-AES have high analytical performance for very diluted samples. Recent years, one of the target of the elemental analysis has been shifted to smaller amount of samples such as nano-particles, bio cells, etc. However, the conventional ICP system consumes relatively large volume (~1 mL/min) of sample solutions, so it is not suitable for these targets. In order to reduce consumption of the sample solutions, direct injection systems have been studied. For example, direct injection high efficiency nebulizer (DIHEN) made by Montaser group consume small samples (<85 µL/min) and realize excellent analytical performance.

To realize more efficient sample introduction, we made a new droplet direct injection nebulizer (D-DIN). With D-DIN, aqueous solutions not nebulized but injected one by one with single droplet form through a small injection tip. Therefore, small aqueous droplets can be introduced accurately just onto the axis of the plasma. The

volume of the droplets can be accurately defined by the injection tip hole diameter and the applied back pressure. Therefore, very small and accurate sample introduction can be achieved. At this time, lower limit of the droplet volume for stable injection is 3.9 nL. Furthermore, to achieve better analytical performance, we integrated D-DIN with pulse modulated ICP. Our pulse modulated ICP normally generate moderate power plasma (~1 kW) but when outer trigger applied, generate short time (~1 ms) high power plasma (~3 kW). The average power is not high, so additional cooling system is not necessary. If we synchronize the timing of the droplet arriving to the plasma region and the high power plasma generation, we can get the higher emission intensity for AES or higher ion signal for MS. In this presentation, basic property of D-DIN and the pulse synchronized ICP-AES will be reported.

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