

E23 ELEMENTAL ANALYSIS OF SOLID SAMPLES BY TOF-ICP-MS. János Fucskó, Rudolf Weck, Lloyd Allen, and S. Georgitis, LECO Corp., 3000 Lakeview Ave., St. Joseph, MI 49085

Multielement solid material analysis is still a major challenge in analytical chemistry. Samples are typically not homogeneous and homogenization could cause contamination and it is often difficult to ensure the appropriate and statistically correct sample and particle size. Analysis of distribution of contamination would require exact sampling and true multielement analysis of very small sample amounts. Laser ablation combined with TOF-ICP-MS appears to be an excellent selection for many solid material analysis problems. Laser ablation can not only introduce sample from a 10 µm sample area, but it also can provide sampling from different depths and different surface areas. Coupled with a very fast multielement detection system, the TOF-ICP-MS, distribution of different elements can be studied in wide variety samples. In fact, full spectrum analysis can be performed from nanogram amounts of materials with the possibility of isotope ratio measurement in the 0.1-1% precision range. Ceramic, metallic, plastic and geological materials were analyzed using LA-TOF-ICP-MS and heterogeneity of these samples were studied. For microvolume samples, especially for spatial distribution analysis TOF-ICP-MS is a perfect ion signal detection technique for most solid sample introduction techniques.

E24 POTENTIAL PROMISES AND ANALYTICAL REALITY: PRACTICAL EXPERIENCES OF LA-ICP-MS APPLIED TO POLYMER ANALYSIS. Andrew M. Dobney, Huub Klinkenberg, Chris de Koster, DSM Research, MD 6160 Geleen, The Netherlands; A. Mank, Philips CFT, Prof. Holstlaan 4 (WB71), 5656 AA Eindhoven, The Netherlands

Whilst the potential of LA-ICP-MS for direct analysis of solids has long been apparent the analytical reality is that calibration is problematic which translates into less accurate measurements than for samples introduced into an ICP-MS in liquid form. The potential of using PVC doped with known concentrations of elements as a matrix matched standard has been demonstrated [1]. However, different polymer types do not respond identically to the same laser ablation conditions (e.g., ablated masses differ, the extent of melting differs) which means that no one polymer standard is a suitable external standard for all polymers. Unfortunately, polymer standards are not readily commercially available. This has led recently to several groups devising calibration strategies that employ liquid standards [2, 3]. DSM is fortunate to have prepared over many years a range of polymer samples for use as in-house reference materials. This collection of solid standards provides a splendid opportunity to assess the reality of using LA-ICP-MS to determine elemental concentrations in polymers. Various polymers have been studied, including polycarbonate, polyamides and EPDM. Time resolved ion currents (without any form of processing) for line and grid ablation are presented pictorially to show the actual raw signals for the different polymers and to indicate the effect of changing various laser parameters. Problems in using this raw data to construct calibration curves are discussed. Results for bulk analyses based on external standard calibrations are discussed and compared with those achieved by

semiquantitative analyses (with and without normalization to known internal standard concentrations). The conclusions reached refer to the state of the practice of LA-ICP-MS for polymer analysis.

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- [3] Günther, D., Frischknecht, R., Müschenborn, H.-J. and Heinrich, C. A., *Fres. J. Anal. Chem.*, **359**, 1997, 390.

E25 SPATIALLY RESOLVED ANALYSIS OF GREEN PLANT TISSUE BY LA-ICP-MS. Erwin Hoffmann, Christian Luedke, and H. Stepanowitz, Inst. f. Spektroskopie u. angewandte Spektroskopie, Laboratorium f. spektrosk. Methoden der Umweltanalytik, D-12484 Berlin, Germany

The results of basic investigations for the spatially resolved analysis of green plant material by LA-ICP-MS will be described. Our instrument contains a Nd:YAG laser with the basic wavelength of 1064 nm. Additionally we installed a device with frequency doubling crystals which allows the generation of second (532 nm), third (355 nm) and fourth (266 nm) harmonics. The depth and the orifice of the crater, the shape of the crater rim and the amount of vaporized sample mass were studied with respect to the four wavelengths and the pulse energy for various types of samples. The reproducibility of the analytical signals and the limits of detection have been also investigated for the same parameters. We used self-made pellets of dried and pressed cellulose doped with multielement solutions as calibration standards. A comparison of analytical results obtained by laser-ICP-MS with those measured by solution-ICP-MS after digestion of the plant materials showed that the calibration method provides sufficient accuracy. The results agreed within a confidence interval of 95%. It will be demonstrated that the utility of the analytical technique developed for green plant materials of environmental significance by its application on two different types of samples: the determination of element distributions in leaves of oaks and pine needles. Ten elements were determined simultaneously in each sample. The relative standard deviations were smaller than 8%. The results of the spatially resolved element determinations in oak leaves will be compared with the results obtained by spatially resolved determinations of the photosynthetic effectiveness.

E26 ANALYSIS OF GLASS REFERENCE MATERIALS BY UV-LASER ABLATION HIGH RESOLUTION ICP-MS (LA-HR-ICP-MS). Jorge Eduardo de Souza Sarkis, Elisa Kayo, Shibuya, Helio, and A. Furusawa, Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Grupo de Caracterização Isotópica Supervisão de de Caracterização de Materiais, MEQ Travessa R, 400, Cidade Universitária, São Paulo, SP CEP 05508-900, Brazil

During the last decade the laser ablation system coupled to an ICP-MS has appeared as a very powerful analytical tool for solid samples analysis. In this work we shall present the results obtained during the analysis of some standard reference materials (NIST 611, NIST 612, NIST 614, NIST 616) by using a UV laser ablation system (LUV266, Gen 3, Merchantek) coupled to a high resolution inductively coupled plasma mass

spectrometer (Element, Finnigan MAT). The main figures of merits of the system will also be presented (*i.e.*, repeatability, the reproducibility, accuracy and detection limits). Quantitative analysis of the main certified elements as well as the lead isotope ratios will be shown. In order to improve the stability of the signals, aluminum was used as internal standard.

E27 VALIDATION OF TRACE ELEMENT SIGNATURES IN FISH OTOLITHS BY LASER ABLATION MICROPROBE (LAMP)-ICP-MS. Simon Chenery, Geoff Nowell, Jennifer Cook, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK; David Milton, S. Blaber, CSIRO, Marine Laboratories, PO Box 120, Cleveland, Queensland 4163, Australia

The authors have been investigating the application of Laser Ablation MicroProbe (LAMP)-ICP-MS to the determination of trace elements across fish otoliths (earbones), from a number of species living in different environments, particularly tropical shads that move between freshwater and seawater. The methodology used in these studies will be described, indicating elemental detection limits and the routine accuracy and precision obtained. Modifications to the ICP-MS instrumentation, such as a high sensitivity interface and cool plasma option, has given rise to improvements in sensitivity and a reduction in polyatomic interferences for many elements; direct comparisons with routine analytical conditions will be made. The interpretation of trace element (Sr, Cu and Pb) distributions in otoliths has been validated by growing fish, in tanks, in water of known chemical compositions. From these data, distribution coefficients and rate of uptake have been determined. Perhaps the most exciting step forward has been the development of magnetic-sector/multi-collector ICP-MS which has allowed us to determine precise isotopic ratios for elements with natural variations such as Sr. Isotopic data which correlate with the elemental signatures will be presented.

E28 DETERMINATION OF ELEMENTAL DISTRIBUTIONS IN SOFT TISSUE MATERIALS BY LASER ABLATION ICP-MS OF SAMPLES FROZEN WITH LIQUID NITROGEN. P. Ek, Laboratory of Analytical Chemistry, Åbo Akademi University, FIN-20500 Åbo, Finland

Laser ablation is a sample introduction technique for direct analysis of solid materials. It is normally used in combination with an inductively coupled plasma mass spectrometer for multi-elemental analysis of for example environmental materials. In this work the use of the laser ablation technique has been applied to samples of soft tissue materials. In order to obtain a reproducible results from the ablated target surface, it have to be "solidified" in some way. Therefore freezing of the sample by liquid nitrogen is used to transform the soft tissue material into solid form.

A special sample ablation cell was constructed to keep the sample in solid form during the entire experiment by freezing the bottom of the cell with liquid nitrogen. The laser beam, generated from a CETAC LSX-200 laser ablation instrument is focused on the frozen sample and the vaporised material is conveyed into an Elan 6000 ICP-MS instrument. This analysis technique makes it possible to study trace elemental distribution in the micro-structure of soft target materials by moving the laser beam in a two dimensional pattern on the

sample surface with a profiling speed of a few mm/sec.

One of the main features of this method is that the distribution pattern of different elements in the tissue, can be determined in the horizontal plane and it allows the gathered data to be plotted as a topographic image. The developed technique could have a great potential in biological and medical research for monitoring of the elemental distribution in different body tissues at the micro scale level.

E29 DETERMINATION OF TRACE ELEMENTS IN ZEOLITES BY LASER ABLATION ICP-MS. C. Pickhardt, J.S. Becker, H.J. Dietze, Zentralabteilung für Chemische Analysen, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany; I.B. Brenner, Environmental Analysis Laboratory, Engineering Science Faculty, Ben Gurion University of the Negev, Beersheva, Israel; W. McGregor, Steelhead Specialty Minerals, Rocke Pointe Corporate Center, 1212 North Washington

Laser ablation ICP-MS (LA-ICP-MS) is widely accepted as a rapid and sensitive technique for local and bulk trace and ultra-trace elemental analysis of conducting, semiconducting and nonconducting solid materials [1]. Due to its direct solid sample analysis capability, LA-ICP-MS is applied for the analysis of geological materials [2]. Included in these materials are a wide range of natural zeolite minerals, which are used in toxic and radwaste clean-up procedures [3]. In the present investigation we evaluated an LA-ICP-MS system for the determination of trace and minor elements in zeolites using a Nd:YAG laser (wavelength: 266 nm, 10 Hz, 5 ns). The laser ablation system was coupled to a quadrupole ICP-MS [4]. Several zeolite samples from Steelhead Specialty Minerals (TSM 150, TSM 180, TSM 300) and several geological standard reference materials (NIM-G granite, NIM-L Iujavrite, NIM-S syenite) were fused with a lithium borate mixture (90% $\text{Li}_2\text{B}_4\text{O}_7$, 10% LiBO_2) at 1050°C in a Pt-Au crucible to eliminate mineralogical properties and to chemically homogenize the sample. For quantitative determination, two different approaches were used (calibration curves, correction of measured values by relative sensitivity coefficients). The values obtained for SRMs are compared to the recommended values from the literature.

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E30 APPLICATION OF LASER ABLATION ICP-MS FOR THE ANALYSIS OF HIGH-PURITY GRAPHITE. C. Pickhardt, J.S. Becker, *Central Department of Analytical Chemistry, Research Centre Jülich, D-52425 Jülich, Germany; K.G. Heumann, Institute of Inorganic and Analytical Chemistry, University of Mainz, D-55099 Mainz, Germany; H.-J. Dietze*

Laser ablation ICP-MS has become established as a very efficient and sensitive technique for the analysis of solids. On the other hand, this method has not yet gained acceptance for

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C1 THE POSSIBILITIES FOR AFS IN SPECIATION ANALYSIS. F. Pete, University of Horticulture and Food Industry Department of Chemistry and Biochemistry, Villanyi ut 35-41, 1114 Budapest, Hungary

For speciation analysis, the most commonly used instrumentation set-up is the hyphenation of HPLC-ICP-MS through a derivatization unit. The main advantages of this set-up are high sensitivity, easy connection and the possibility of isotope ratio determination. The drawback of the ICP-MS instrumentation is its high cost, which hampers its wide-spread use. Compared to the ICP-MS system, flame AFS with optical detection is a cheap and easy to use system with high selectivity, easy connection and, in most cases, high enough sensitivity. In the last few years, in our laboratory, several analytical systems were developed where the main part of the hyphenation is an HPLC and an AFS. For derivatization, different analytical possibilities were compared-ultrasonic nebulization, hydride generation, high pressure nebulization and the combination of these. These systems were used for the speciation of arsenic (As III, As V, MMA, DMA, AsBe, AsCo) and selenium species (Se IV, Se VI, SeMe, SeEt, SeCy) from different environmental, biological and food samples. The sensitivity and selectivity of the system were controlled by GC-MS and HPLC-MS combinations. The character of the AFS signal was investigated in a wide concentration range and the phenomenon of self-absorption was detected at high As concentrations. Presently we are developing a system for simultaneous multielement speciation where, instead of AFS, an ICP-AES is used with a CID detector, which is suitable for simultaneous background correction. The possibilities of a GC-AFS hyphenation with a home made fiber optics AFS detector is being investigated for arsenic speciation.

C2 QUANTITATIVE AND QUALITATIVE SPECIATION USING LOW PRESSURE PLASMAS. E. Hywel Evans, Gavin O. Connor, and B. Rosencranz, University of Plymouth, Department of Environmental Sciences, Drake Circus, Plymouth, PL4 8AA, UK

In the field of elemental speciation the next major requirement is for an analytical method which is both qualitative and quantitative in nature, and is also highly sensitive. No single instrument will accomplish this task, with quantitation usually undertaken using element selective detection, and identification relying on chromatographic separation and co-injection of standards, or a separate analysis with another technique. Low pressure plasma ionisation sources for mass spectrometry may go some way towards addressing this need. Such sources have been used extensively in the authors laboratory for a variety of applications. The development of a low pressure MIP and ICP ionisation sources, and their applica-

tion, will be described. Applications will include the headspace analysis of volatile organic compounds, and the determination of organo-lead and organo-mercury compounds in environmental samples. Problems and benefits associated with this type of analysis will be discussed with reference to fundamental studies of the plasma and ionisation mechanisms.

C3 COUPLING CE WITH ICP SPECTROMETRY: DEVELOPMENT AND TECHNICAL DETAILS OF A NEW INTERFACE. Dirk Schaumlöffel and A. Prange, GKSS Research Centre, Institute of Physical and Chemical Analysis, Max-Planck-Straße, D-21502 Geesthacht, Germany

This poster illustrates the development and construction of a new, efficient interface for CE-ICP-MS coupling. The interface is based on a modified microconcentric nebuliser (MCN 100) from CETAC, which permits a low flow rate of about 5 µL/min in the free aspiration mode. The main requirements on the interface are that it should provide the electrical connection for stable electrophoretic separations, adapt the flow rate of the electro-osmotic flow (EOF) inside the CE-capillary to the flow rate of the nebuliser for efficient transport of the analytes into the plasma, and, prevent the nebuliser from exerting a suction effect on the CE-capillary. The solutions to these problems, in particular the prevention of the suction effect, which is potentially a very serious problem because it could disturb the high resolving power of the capillary electrophoresis, will be presented. This special interface construction enables the use of short CE capillaries, down to 30 cm, thus allowing short analysis times down to 80 seconds. Furthermore, the optimisation of the flow rate of the nebuliser for an efficient analyte transport will be described and the use of a guard-electrode at the ICP torch in order to enhance sensitivity will be discussed.

C4 QUANTITATIVE ELEMENTAL SPECIATION AT TRACE LEVELS USING CAPILLARY ELECTROPHORESIS COUPLED WITH HIGH-RESOLUTION ICP-MS. Andreas Prange and D. Schaumlöffel, GKSS Research Centre, Institute of Physical and Chemical Analysis, Max-Planck-Straße, D-21502, Geesthacht, Germany

The coupling of capillary electrophoresis (CE) with high sensitivity ICP-sector field-MS is a topical research theme in analytical chemistry for the determination of metal species. The present paper describes the development and the analytical characterization of a new on-line coupled CE/ICP-MS system. It allows multielement/multicompound analysis at trace levels and reproducible separations with excellent peak shapes and short analysis times by using a new, efficient interface which provides stable electrophoretic conditions. The coupled system consists of a Hewlett Packard Capillary Electrophoresis HP 3D, with fused silica capillaries of lengths between 30 and 60 cm and an inner diameter of 75 µm, a