BOOK OF ABSTRACTS

15 -18 OCTOBER 2006
SPIŠSKÁ NOVÁ VES
SLOVAKIA

Edited by Jana Kubová and Ingrid Hagarová

Printed by Roko a.s.

ISBN 80-223-2244-X

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Preface

It is a great privilege and pleasure for me to welcome all of you to the XVIII Slovak Spectroscopic Conference which is held in Spišská Nová Ves – a gate to Slovak Paradise. Since its founding in 1970, this event continues its tradition of biennial meetings. The first meetings were quite small. The participants were mostly Slovak and Czech specialists of the spectroscopic community who have focused mostly on atomic emission spectrochemistry. Later the atomic absorption spectrometry was also included. As the time was passing by, our small gatherings grew in size and their scope became what it is today. Since about 1990, the number of international participants started to increase and these events were successfully established as a forum for presentation and discussion of new developments in all branches of analytical spectroscopy.

The main goal of our Conference is to bring together experts from universities, academia, official centres, various laboratories and industry on a worldwide scale, to summarize the current progress in different areas of spectroscopy and to stimulate contacts and mutual exchange of experience and ideas. The emphasis is put not only on presentation of the latest scientific achievements, new technologies, and instrumentation but also on the applications and utilization of spectroscopy in different fields of practical life. The Conference also provides a possibility to get acquainted with new instrumental techniques, spectroscopy equipment, laboratory materials and instruments, reference materials, science literature, etc. which are exhibited by several distribution companies.

This year Conference offers a 3 days scientific program that consists of 11 invited lectures, about 50 oral presentations, 46 poster displays, and 20 commercial presentations. The main Conference topics comprise Theory, Techniques and Trends in Environmental, Geological, Biochemical, Food and Industrial Analysis by spectroscopy methods, Speciation analysis, Sample preparation and pretreatment, Chemometrics, Metrology and Quality Assurance.

I hope that our Conference will provide a great opportunity for developing new cooperative projects, new personal collaborations or exchanges, and many fruitful ideas for the advance of spectroscopy.

I wish all of you a very enjoyable stay here in Spišská Nová Ves and I hope that despite of rather busy schedule you will be able to visit some of cultural, historical, and natural monuments for which the Spiš region is unusually rich. At the same time I am convinced that you will feel the hospitality, willingness, and warmth of Slovak people.

With my best regards

Jana Kubová
chair of the organizing committee

Sunday, October 15, 2006

17.00-22.00 Registration

17.00-22.00 Installation of posters

19.00-22.00 Welcome party

Monday, October 16, 2006

08.30-22.00 Registration

09.00-09.30 Opening ceremony

Chairperson: J. Kubová

09.30-10.00 **E. Plško** Resolution as a general metrological parameter of spectrochemical results

10.00-10.30 **M. Matherny** Validation of the spectroscopic tandem method on the base of information theory

10.30-11.00 Coffee break

Chairperson: B. Dočekal

11.00-11.30 **J. Dědina** New way of hydride trapping for atomic absorption spectrometry: in quartz tube atomizers!

11.30-11.50 **J. Kratzer** A challenging approach to trace analysis: AsH_3 trapping at quartz surface for HG-AAS

11.50-12.10 **P. Krejčí** Trapping of hydride forming elements on a molybdenum-foil strip

12.10-12.20 **J. Murgaš** Centralchem - experience and flexibility

12.20-14.00 Lunch

Chairperon: J. Dědina

14.00-14.30 **B. Dočekal** Direct solid sampling electrothermal atomic absorption spectrometry

14.30-14.50 **I. Loskotová** Determination of trace elements in steels by GFAAS

14.50-15.10 **H.-M. Kuss** New T-shaped graphite furnace for AAS used for trace element analysis in highly concentrated material

15.10-15.30 **L. Husáková** Direct determination of selenium in urine by D2-GFAAS method

15.30-16.00 Coffee break

Chairperson: H.-M. Kuss

16.00-16.20 **G. M. Hermann** Characterization of an electrothermal vaporization (ETV) device with axially focusing convection upstream zone

16.20-16.40 **A. Manová** On-line electrochemical preconcentration of trace metals for GFAAS

16.40-17.00 **M. Knápek** Determination of metals by atomic absorption spectrometry after electrodeposition

17.00-17.20 **M. Konečná** Determination of gold by electrothermal atomic absorption spectrometry after electrochemical preconcentration

17.20-17.30 **K. Olša** The contrAA 700 - high-resolution continuum source AAS

19.30- 22.00 Poster session with Tokay wine tasting

Tuesday, October 17, 2006

08.30-18.00 Registration

Session A

Chairperson: H. Dočekalová

08.30-09.00 **K. Pyrzyńska** Solid phase extraction sample processing with AAS detection

09.00-09.20 **M. Fišera** Application of atomic spectrometry methods and ICP-MS as tools for speciation of selected elements

09.20-09.40 **M. Žemberyová** The role and the application of AAS techniques in speciation analysis of the elements in environmental samples

09.40-10.00 **P. Matúš** State of the art in determination, fractionation and speciation analysis of aluminium in environmental samples by spectrochemical analytical methods

10.00-10.10 **R. Varga** The selected products of Merck for inorganic instrumental analysis

Session B

Chairperson: B. Vlčková

08.30-09.00 **J. Sitek** Mössbauer spectroscopy and its applications

09.00-09.20 **R. Zbořil** Iron oxide nano-particles from the solid-state syntheses: reaction mechanism, structural and magnetic properties by view of Mössbauer spectroscopy

09.20-09.40 **M. Miglierini** Mössbauer, X-ray diffraction, and infrared study of iron(II) octacyanomolybdate(IV)

09.40-10.00 **M. Seberíni** Surface analysis by CEMS - an overview of the method

10.00-10.20 **M. Mašláň** Magnetically modified bentonite as a possible contrast agent in MRI of gastrointestinal tract

10.20-10.50 Coffee break

Session A

Chairperson: M. Fišera

10.50-11.10 **H. Dočekalová** Determination of labile metal species in nature aquatic systems by gel techniques and atomic spectrometry methods

11.10-11.30 **V. Vojteková** Fast monitoring of the element mobility changes in environmental pollution

11.30-11.50 **O. Mestek** Speciation of elements in cereals and pseudo-cereals flours

11.50-12.10 **R. Koplík** Changes of element speciation in cereal flakes caused by simulated gastrointestinal digestion

12.10-12.30 **J. Polák** Trace elements distribution and species fractionation in *Brassica napus* plant

Session B

Chairperson: V. Kanický

10.50-11.10 **S. Ružičková** Calibration process at the optimization of the novel spectrometric tandem technique

11.10-11.30 **A. Majchrák** Determination of some elements in samples of emissions trapped on filters by energy dispersive X-ray fluorescence spectrometry

11.30-11.50 **A. Shearman** The application of AFS to the determination of Hg and Se in environmental samples

11.50-12.10 **U. Oppermann** Quality control of biodiesel using a simultaneous ICP spectrometer

12.10-12.30 **E. Reszke** Selected applications of MW energy in laboratory

12.30-14.00 Lunch

Session A

Chairperson: D. Günther

14.00-14.30 **G. Heltai** Coupling of microwave induced plasma atomic emission spectrometry with HPLC separations for speciation analysis

14.30-14.50 **K. Flórián** DC-ARC-OES vs. ETV-ICP-OES in solid sampling atomic spectrometry: competitive or complementary methods?

14.50-15.10 **J. Hassler** Round robin test of metallic impurities in silicon carbide via DC-Arc-OES – Result and interpretation

15.10-15.30 **A. Krejčová** ICP OES analysis of impurities in pure hydroxides and salts

15.30-15.50 **E. Svätý** On-line analysis of cleanness characteristics and inclusion composition by OES Spark-DAT in Trinec steel works

Session B

Chairperson: M. Miglierini

14.00-14.30 **B. Vlčková** Surface-enhanced Raman spectroscopy on single molecule level: perspectives of analytical applications

14.30-14.50 **J. Sedlmeier** Via reflex Raman microscope and combined spectroscopy techniques

14.50-15.10 **J. Andertová** Development of infrared spetroscopy for study of ceramic materials ageing

15.10-15.30 **J. Škrlíková** Determination of some organic compounds in the form of ion-associates with polymethine dyes

15.30-15.50 **M. Pavlovič** Trends in ion-beam based spectroscopic techniques

15.50-16.20 Coffee break

Session A

Chairperson: K. Flórián

16.20-16.50 **D. Günther** Plasma-induced matrix effects in laser ablation inductively coupled plasma mass spectrometry

16.50-17.10 **V. Kanický** Laser-assisted plasma spectrometry of solid samples

17.10-17.30 **A. Hrdlička** Characterization of in-depth analysis of ceramic tiles by acoustic emission at laser-induced breakdown spectroscopy (LIBS)

17.30-17.40 **V. Helán** Laboratory instruments and equipment as a supplement or substitution for spectrometric methods

Session B

Chairperson: D. Mackových

16.30-16.50 **J. Čáslavský** Electrospray ionization – ion trap mass spectrometry of carboranes

16.50-17.10 **L. Vavrušová** Determination of selected metals in urine by inductively coupled plasma orthogonal time-of-flight mass spectrometry

17.10-17.30 **T. Gál** Study of alloy-clusters with the use of mass spectrometer

17.30-17.40 **Z. Červenák** Applied biosystems/MDS sciex LC/MS/MS technologies for small molecules analysis

17.40-17.50 **J. Hrouzek** Agilent 7500 ICP-MS

20.00-24.00 Conference dinner with prizes giving

Wednesday, October 18, 2006

Chairperson: K. Danzer

09.00-09.30 **T. Czocher** Accreditation of testing and medicine laboratories – the most frequent drawbacks of quality management systems and good professional laboratory practice

09.30-09.50 **P. Lučivjanský** Certified reference materials as a tool for quality assurance of environmental measurements

09.50-10.10 **V. Sychra** Matrix environmental certified reference materials: production and certification of a candidate CRM CZ 7006 „PCDD, PCDF and toxic PCB in a sewage sludge“

10.10-10.20 **M. Fuchsberger** Significant trifles

10.20-10.50 Coffee break

Chairperson: T. Czocher

10.50-11.20 **K. Danzer** Metrology in analytical chemistry – pros and cons

11.20-11.40 **L. Dempírová** Control charts in quality assurance

11.40-12.00 **D. Remeteiová** Uncertainties sources in the fractionation analysis of the gravitation dust sediment

12.00-12.30 Closing ceremony

12.30-14.00 Lunch

14.30-19.00 Organ concert and museum tour of quaint furniture and keyboard musical instruments exhibition (Renaissance-Rococo manor-house and summer resort Dardanely in Markušovce)

Thursday, October 19, 2006

09.00 Excursion 1, Historical monuments of Spišská Kapitula, Spiš Castle and Žehra (included in the List of the World Heritage of UNESCO)

09.00 Excursion 2, Historical town of Levoča

09.00 Excursion 3, The National Park of the Slovak Paradise

POSTER SESSION

19.30- 22.00 Monday, October 16, 2006

Chairpersons: K. Pyrzyńska, G. Heltai, E. Plško, M. Matherny

P-1 **A. A. Asweisi** Development of graphite furnace for atomic absorption spectrometry

P-2 **N. R. Bader** Determination of zinc, copper, cadmium and nickel by flame atomic absorption spectrometry after preconcentration using silica gel coated with Schiff's bases

P-3 **Y. Bazel'** New spectrophotometric method for determination of gold

P-4 **D. Borošová** Estimating uncertainty and quality of lead determination in blood in the occupation exposure

P-5 **M. Bujdoš** Influencing of cadmium translocation in *Matricaria recutita*, var. Lutea by the presence of selenium

P-6 **M. Bujdoš** Vapor generation of cadmium for its determination using atomic absorption spectrometry – recent developments

P-7 **F. Čacho** Determination of arsenic and antimony by on-line electrochemical preconcentration/GFAAS

P-8 **B. Dočekal** Electric focusing preconcentration devices for element in-time monitoring of airborne particles by atomic emission spectroscopy

P-9 **B. Dočekal** Determination of trace impurities in titanium dioxide by direct solid sampling ETAAS

P-10 **R. El-Kailany** Identification and comparison of coal samples by GC-mass spectrometry

P-11 **K. Elsherif** Simultaneous determination of trace elements using multielement graphite furnace atomic absorption spectrometer (SIMAA 6000)

P-12 **I. Hagarová** Determination of beryllium in natural waters by electrothermal atomic absorption spectrometry

P-13 **I. Hagarová** Comparison of various reaction media for the determination of arsenite in the presence of arsenate by HGAAS

P-14 **G. M. Hermann** Condensation in an axially focusing convection (AFC) ETV-upstream – a new model

P-15 **M. Holá** Laser ablation of powdered materials: pellet preparation techniques for LA-ICP-OES/MS

P-16 **I. Chovancová** Heavy metals in contaminated soils

P-17 **M. Kališ** Determination of thallium in fungal biomass by ETAAS

P-18 **L. Kašparová** Determination of lead in blood by electrothermal atomic absorption spectrometry -long-term participation in external quality control for lead in blood

P-19 **M. Kopecká** Inhomogeneity of geological sample quantified by X-ray spectrometry and atomic absorption spectrometry. Comparison of the results

P-20 **M. Koreňovská** Effect of gamma irradiation on trichromatic values of some spices

P-21 **M. Koreňovská** Application of elemental analysis on tracing the geographical origin of food

P-22 **V. Korunová** Study of selenium hydride trapping in filter furnace atomizer for atomic absorption spectrometry

P-23 **J. Laštincová** Calculation of combined uncertainty for measurement of pressure CO_2 in sparking wine by afrometer

P-24 **I. M. Maga** Study of the spectroscopic characteristics and chromatographic determination of hydrophilic organic compounds in derivates on the basis of the reactions of diazolinking

P-25 **V. Machovič** Raman microspectroscopy and microstructural study of ITZ in concretes reinforced by PET fibres

P-26 **P. Matúš** Fractionation of aluminium by coupled separation and spectrometry detection techniques

P-27 **J. Medveď** Application of a modified BCR sequential extraction scheme for the ETAAS determination of thallium in soils

P-28 **J. Mihalčová** Study of properties change of turbine oils after heat stress

P-29 **F. Novák** Quantitative ^{31}P NMR spectroscopy of soil and peat humic acids

P-30 **U. Oppermann** The determination of hazardous substances according to the electrical and electronic equipment Act (WEEE & ROHS)

P-31 **V. Orescanin** Determination of lanthanides in environmental samples by source excited EDXRF method

P-32 **Z. Poulová** Optimization of conditions of sample preparation for the determination of metals in sludges and soils

P-33 **S. Rapi** Analysis of metal content and speciation of foodstuffs

P-34 **R. Rusnák** Evaluation of the availability of the FAAS method for determination of Cd, Cu, Pb, and Zn in the extracts of fractionation analysis of the gravitation dust sediment

P-35 **A. Shearman** Inter-laboratory comparison tests - the evaluation of analytical techniques applied to the elemental analysis of water matrices

P-36 **L. Strnad** Quantitative determination of platinum group elements in ombrotrophic peat profile using improved nickel-sulphide fire-assay with ICP-MS

P-37 **M. Svoboda** Hydride generation for arsenic speciation analysis by atomic absorption spectrometry

P-38 **J. Száková** The effect of ameliorative materials addition on the distribution of As, Cd, Pb, and Zn among main soil fractions determined by sequential extraction procedure

P-39 **J. Száková** Mobility of important toxic analytes in urban dust and simulated air filters determined by sequential extraction and GFAAS/ICP-AES methods

P-40 **K. Szováti** Plant uptake of pesticides

P-41 **O. Šebek** Multielement analysis of the air-pollution-control (APC) residues from a secondary lead smelter - comparison of the decomposition methods

P-42 **D. Virág** Study of photodecomposition products and kinetics of distinctive pesticides

P-43 **D. Virág** GC-MS investigation of interaction of pesticides with soil with regard to plant uptake

P-44 **V. Vojteková** Evaluation of the mobility of Fe and Mn in individual parts of environment

P-45 **M. Žemberyová** Determination of vanadium after fractionation of soils and sludges by electrothermal atomic absorption spectrometry

P-46 **M. Žemberyová** Fractionation of molybdenum in soils and sludges and the determination by electrothermal atomic absorption spectrometry

ACCREDITATION OF TESTING AND MEDICAL LABORATORIES. THE MOST FREQUENT SHORTCOMINGS IN THE LABORATORY MANAGEMENT SYSTEMS

Tibor Czocher

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Nowadays, testing and medical laboratories of which results are used for decisions in so important areas as human health, environment and economy, have to work under suitable management system. Very important role in increasing of customer confidence and satisfaction with the results of testing and measurement is played by accreditation which is the process in which competent body (accreditation authority) assess and formally confirm that subject is competent perform specific activity, e.g. testing or measurement in the specific area. Accreditation is voluntary and it serves mainly for non-regulated area but its importance grows in the regulated area as well in the connection with authorization and notification. It is generally known that requirements for such system for laboratories are given in the standard ISO/IEC 17025: 2005 "General requirement for the competence of testing and calibration laboratories". To be successful in the process of accreditation laboratory has to fulfill not only requirements of the standard ISO/IEC 17025: 2005 but fulfill specific sector requirements, too. For medical laboratories were published standards ISO 15189: 2003 "Medical laboratories - Particular requirements for quality and competence" and ISO 15195: 2003 "Laboratory medicine - Requirements for reference measurement laboratories". Every laboratory has to decide for the most suitable process for realization of quality requirements in such a way which is suitable for its practice, forms customer confidence and constitute balance between costs for implementation, maintaining and improving management system and benefit from this system. The most frequent problems arise in the following management and technical requirements of standard ISO/IEC 17025: 2005: 4.1 Organization, 4.3 Document control, 4.6 Purchasing services and supplies, 4.9 Control of nonconforming work, 4.12 Preventive action, 4.13 Control of records, 4.14 Internal audits, 5.4 Testing and calibration methods and method validation, 5.5 Equipment, 5.6 Traceability, 5.9 Assuring the quality of test and calibration results and further in the so called good laboratory practice in the meaning of good professional practice, personnel skills and laboratory equipment.

METROLOGY IN ANALYTICAL CHEMISTRY – PROS AND CONS

Klaus Danzer

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In the context of quality assurance in Analytical Chemistry, the validation of analytical procedures is of crucial importance. Validation is quantified by figures of merit characterizing measurements and measuring results as well as analytical procedures and samples. The performance parameters, needed in validation, are summarized in the following table.

Performance characteristics for		
Analytical results	Analytical procedures	Samples
Accuracy, trueness (precision)		Homogeneity Sample amount Analyte amount
Extended uncertainty	Measurement uncertainty	
	Selectivity, specificity	
	Linear (dynamic) range	
Limit of decision, detection and quantitation		
Traceability	Robustness, ruggedness	

The relevant performance characteristics have been developed and derived both inside and outside of Analytical Chemistry. Metrology has proved to be a helpful tool in establishing quality norms and standards. Metrology, being the science of measurement, includes all aspects both theoretical and practical with reference to measurements, whatever their uncertainty, and in whatever fields of science or technology they occur [1]. Therefore, Analytical Chemistry as the science of chemical measurement is concerned, too.

However, problems still exist which concern harmonization, use, and meaning of fundamental terms. It is desirable that the verbal meaning of characteristics is consistent with their quantitation.

A critical survey will be given on the most important analytical performance characteristics, their definition, quantitation and use.

Reference

[1] DIN/ISO (1994) *Internationales Wörterbuch der Metrologie / International Vocabulary of Basis and General Terms in Metrology*. Beuth Verlag, Berlin, Wien, Zürich

NEW WAY OF HYDRIDE TRAPPING FOR ATOMIC ABSORPTION SPECTROMETRY: IN QUARTZ TUBE ATOMIZERS!

Jiří Dědina, Jan Kratzer

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In atomizer trapping, especially in-situ trapping in commercial graphite tubes, is due to its simplicity the most convenient way of hydride collection. However, there is another promising approach to in-atomizer trapping - to collect hydride at the quartz surface. A successful trapping of plumbane, stibine and Cd in a quartz tube was announced recently.

The aim of this presentation is to discuss all relevant aspects (trapping efficiency and interferences, atomization efficiency and interferences, peak area characteristic mass, detection limit, user friendliness, investment and operation costs) of various approaches to in-atomizer trapping of hydrides. A particular emphasis will be put on new ways of the trapping in quartz atomizers - feasibility of this approach for in-atomizer collection of stibine, arsine and bismuthine will be assessed.

Our the most recent findings on the influence of atomizer design and other experimental parameters on the efficiency of trapping, volatilization and atomization of hydrides in several types of quartz tube atomizers, including various designs of multiple microflame quartz tube atomizer (multiatomizer) and conventional externally heated quartz tube atomizers, will be discussed. Conclusions on the mechanism of hydride trapping and of analyte transfer will be presented. Also the perspectives of in-situ trapping of other hydrides in quartz atomizers will be outlined.

Acknowledgement: Financial support from the Grant Agency of the ASCR (Project No. A400310507) is gratefully acknowledged.

DIRECT SOLID SAMPLING ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

Bohumil Dočekal

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ET AAS plays a decisive role in the analysis of modern HiTech materials for microelectronics and high performance ceramics, in the determination of technologically important trace and ultra-trace elements, which considerably influence the properties of final products. Conventional wet analytical procedures, involving preparation of sample, are typically characterized by an enhanced risk of contamination or by dissolution difficulties due to chemical resistance of most ceramic-based samples. Slurry sampling or true direct solid sampling is very powerful technique to overcome time consuming and troublesome sample preparation procedures. Some aspects of solid sampling should be taken into account in the development of novel direct analytical methods, especially, enhanced refractory matrix interference, spectral interference, lack of appropriate standards and reference materials, and non-homogeneity of the sample. The convenient instrumentation should be also designed and optimized for the application of these techniques.

Usefulness of the solid sampling technique (reduction of time of the analysis, elimination of labor-intensive routines and an extreme chemical treatment, improvement of the detection power by several orders of magnitude down to the *ppb*-level) is demonstrated by some examples of using slurry sampling in the analysis of powdered ceramic materials (oxide and non-oxide refractory compounds) and true solid sampling in the analysis of refractory metals and their compounds for microelectronic applications.

Acknowledgement: This work was performed and supported within the Institutional research plan AV0 Z40310501.

PLASMA-INDUCED MATRIX EFFECTS IN LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

D. Günther, J. Koch, J. Pisonero, M. Wälle, I. Kroslakova, H.-R. Kuhn, B. Hattendorf, Z. Wang

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Different laser based techniques are available for elemental analysis and their potential have been described in detail. Searching for applicability of different laser based techniques for quantitative analysis without matrix-matched calibration standards, laser ablation-inductively coupled plasma mass spectrometry has become the most suitable laser based technique for direct analyses of major, minor and trace elements and isotope ratio determinations. Due to a separated sampling and ionization process, the potential of non-matrix matched calibration for quantification of a variety of solids (geology, biology, material science) has been demonstrated. Unfortunately, only a selected number of elements can be quantified accurately. Therefore, many types of lasers and laser parameter have been introduced and studied. Unfortunately, most of these improvements have not helped to overcome the major limitations. Therefore, this presentation will focus on ICP-induced effects when introducing laser generated aerosols.

Studies on aerosol generation, aerosol transport and vaporization, atomization and ionization within the ICP demonstrated that the particle size distribution and the composition of the laser generated aerosols have a major impact on their excitation within the ICP and therefore on the quantification capabilities. An optimization procedure using the most common laser wavelengths will be presented and it will be shown that the ICP operating conditions are significantly dependent on the type of aerosol introduced.

Furthermore, elemental fractionation in LA-ICP-MS was studied in detail. Various mass fractions of a single glass matrix were generated using a 193 nm laser and were introduced into an ICP. A double ablation set up and an aerosol dilution set up were used to change the mass introduced into the ICP. It will be shown that the mass load of the ICP influences the ion response significantly and leads to plasma-induced matrix effects. Especially high volatile elements with a high 1st ionization potential undergo a signal depression when the mass load is changed. Quantification of these effects led to deviations of up to 30 % (Zn, Cd), which are independent of the ablation process. In contrast to previously reported laser induced elemental fractionation it will be shown that ion generation for different types of elements occur at different positions within the plasma, which finally leads to a different ion sampling efficiency through the interface.

Since the matrix effects are based on the amount of material entering the plasma, aerosol manipulation might be a strategy to overcome some of the limitations. A Venturi-based ablation cell has been constructed, which extracts the aerosol in a directed gas stream out of the ablation cell. The working principle and some figures of merit achievable using this new aerosol sampling technique will be discussed.

Finally, femtosecond laser ablation has been strongly promoted to be the “super star” solution to overcome the drawbacks of LA-ICP-MS. Preliminary ablation studies and inter-matrix calibrations will be shown to demonstrate that the fundamental understanding gained by fs laser ablation will have an impact on the performance of ns laser.

COUPLING OF MICROWAVE INDUCED PLASMA ATOMIC EMISSION SPECTROMETRY WITH HPLC SEPARATION FOR SPECIATION ANALYSIS

György Heltai, Márk Horváth

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Microwave induced plasma (MIP) atomic emission spectrometry (AES) has special advantages as element specific detection method related to inductively coupled plasma (ICP) spectrometry. The MIPs are very attractive in excitation, particularly in the case of nonmetals, they can be operated at low power (50 – 300 W) with a moderate noble gas consumption. Coupling of MIP – AES with HPLC separations, however is not free from difficulties due to the low mass flow loading capacity of MIP sources and their matrix sensitivities. Fitting an HPLC eluent flow to a MIP loading capacity requires application of high performance nebulization methods equipped with effective desolvation techniques. Present paper gives a survey of recent development of MIP – torches and related sample introduction techniques. As an example optimization of Cr(III) / Cr(VI) speciation analysis will be discussed. In this case a low power helium MIP was coupled to ion – pair forming HPLC separation by means of hydraulic high pressure nebulization (HHPN) – radiative heating desolvation (RHD) interface. In this system the organic reagents and eluents, and easily ionisable elements cause different MIP – AES signal depression in the case Cr(III) or Cr(VI) analyte.

These effects proved not to negligible when ICP – AES detection was applied with the same interface. In general it can be concluded that HPLC coupling with plasma atomic emission element specific detection techniques requires species selective calibration.

VALIDATION OF THE SPECTROSCOPIC TANDEM METHOD ON THE BASE OF INFORMATION THEORY

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The tandem methods, whereas they are latter version of the spectroscopic techniques, need a complex optimization because of finding of their acquisition in term of figures of merit. It is propper to use the determination of information theory parameters for verification of complex experimental optimization. The experimental optimization is partially based on the one-dimensional exploratory analysis but mainly on the complex analytical calibration [1, 2]. By this manner will be obtained input data for calculation of the information theory parameters which represent atomic specifical parameters: information content I(p, po) and information effectivity E(p, po). From these two parameters will be received final figures of merit by the summation for all element specifical values of information contents: measure of information content MI(p, po) and measure of information effectivity ME(p, po) [3].

Calculation of these parameters needs knowledge of limited values of method c(X)max, c(X)min, where X means current element or concentration range Δc(X). Next, it is necessary to define (absolute) standard deviation s(X) and experimentally defined limit of detection value (LOD) c(X)L. It is valid to calculate these parameters throught the QC.ExpertTM statistical software [1]. Another calculation is needed to focus to the determination of information effectivity. It needs specification of values number of partial effectivity coefficients e(Xi) as well as final effectivity coefficients E(X). In some specific cases it is valid to realize relevance and redundancy correction as well as accuracy and recovery correction [3]. In the given case the new tandem method of the powder sample evaporation was tested. Evaporation is overshoots in the separated cell for aerosol production. Created sample aerosol is transported by the carrier Ar gas into the Marinković plasma source where the atoms of the evaporated sample are excitated [4,5]. Current intensity of 20 A and 42 s exposition time were used as an optimal values.

In the all cases was confirmed linear model of the calibration lines. Determination coefficient in the range of $R \in \langle 96, 98 \rangle$ % ensured that all used concentrations took part in the calibration process. Valuation results with using of synthetic oxide mixtures with AgCl additive confirmed considerably higher agreement of experimental data with data of analytical order [6] than at the comparison of theoretical values and values obtained by analysis of certified standards.

Acknowledgement: This work was supported by the grant project 1/3149/06 and APVV 20-009404 project.

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RESOLUTION AS A GENERAL METROLOGICAL PARAMETER OF SPECTROCHEMICAL RESULTS

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The performance of spectrochemical procedures is usually characterized by several metrologic and economic parameters. In the lecture an attempt to find out that resolution can be considered as a common general basis for metrologic parameters is presented.

Detection power of an analytical procedure represents de facto resolution between the smallest content of the analyte present in the sample and the analytical response corresponding to the blank. In the case of precision, we have again in principle to do with determination of resolution between two close contents.

What concerns accuracy of spectrochemical results it represents the resolution between the obtained and the true (certified) value of content. The presence and the value of the corresponding systematic error follows in a considerable extent from present non-spectral and spectral interferences. The last ones depend on the self width of spectral lines in question, as well as on the resolving power of the used spectral apparatus. It means that the resolving power plays a basic and general role also in the case of accuracy.

In the following part of the lecture the corpuscular approach to the resolving power of dispersive spectral instruments will therefore be dealt with. The significance of action quantification (Planck's constant) is disacussed and its till now not considered important consequence that electromagnetic radiation can be emitted and propagated only as integer vibrations i.e. in integer multiles of full wavelengths which cannot be further divided in smaller parts is explained. This corpuscular approach confirms the Rayleight's condition for resolution introduced on the basis of wavelength character of radiation and enables the presented simple calculation of the known formulas for theoretical resolving power of a prism and of a diffraction grating.

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SOLID PHASE EXTRACTION SAMPLE PROCESSING WITH AAS DETECTION

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Despite its single-element capabilities, atomic absorption spectrometry (AAS) is a powerful tool to monitor many elements in different kind of samples. However, there are some drawback In environmental and biological samples, complex matrix cannot be directly processed as they pose severe matrix interferences. These interferences very often cannot be minimized even by existing efficient background correction devices. Successful matrix separation combined with an enrichment step can be achieved by coprecipitation, generation of volatile compounds, solvent and solid phase extraction techniques. Among them column separation and preconcentration systems are the most often used.

The separation/preconcentration procedures with sorption on a solid phase could be executed in off- or on-line mode. Application of off-line approach is adequate when higher preconcentration factors are needed. However, these procedures require a great amounts of reagent and samples. When on-line systems are considered, the main advantage is the possibility of automation which increases precision and accuracy. Further, it reduces the risks of sample contamination.

This lecture aims to provide an account of the state-of-art of solid phase extraction sample processing before the determination step by AAS. Different solid sorbents will be described and presented with selected application for the environmental monitoring of elements. Advantages, limitations and potentials of on-line sample pretreatment will be also discussed.

MÖSSBAUER SPECTROSCOPY AND ITS APPLICATIONS

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During the last 45 years, Mössbauer Spectroscopy has become standard and a very sensitive analytical method. More than 85 % of all experiments were carried out on iron containing materials. It proved to be a suitable tool for such studies because the measured spectral para-meters are very sensitive to changes in the vicinity of the ^{57}Fe probe nucleus. This technique provides a wide variety of information about structural and physical behaviour of the Fe-con-taining materials.

In the past, Mössbauer Spectroscopy, apart from other scientific branches, was widely used in chemistry, physical metallurgy, mineralogy and magnetic measurements. Through further development of measuring techniques, the analytical potential of this method increased immensely for practically all materials containing iron. Since recently, the method has often been used in a combination with other spectroscopic analytical methods.

SURFACE-ENHANCED RAMAN SPECTROSCOPY ON SINGLE MOLECULE LEVEL: PERSPECTIVES OF ANALYTICAL APPLICATIONS

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Recent challenging development in SERS and SERRS spectroscopy is associated with the discovery of its single molecule sensitivity [1]. Achievement of single molecule level of SERS (Surface-Enhanced Resonance Raman Scattering) and/or SERRS (Surface-Enhanced Resonance Raman Scattering) spectral detection is conditioned by localization of detected molecules into strong nanoscale-localized optical fields (dubbed hot spots [2]). Recent theoretical treatments predict SERS enhancement factors as high as 1 x 10^{15} for chromophoric molecules (in particular rhodamine 6G) located in the hot spot amidst two Ag nanoparticles of a suitable size [3] . Owing to a combination of single molecule sensitivity with the fingerprint selectivity inherent to methods of vibrational spectroscopy, single molecule SERS spectroscopy offers unprecedented possibilities of analytical applications. On the other hand, one of the most challenging questions is whether the perspectives of single molecule detection are open to all kinds of molecular species as the prospective analytes. A possible limitation in a widespread use of single molecule SERS could stem from surface-enhanced and/or surface-induced photochemical processes which may obstruct a reliable analyte detection on a single molecule level. In addition to that, several important questions, such as the origin of the SERS signal fluctuations, remain to be answered. The highlights and possible limitations of single molecule SERS will be discussed on the basis of the results recently obtained in our laboratories in comparison to those recently published by other research groups. We will compare several strategies by which dimers and small aggregates of silver (Ag) nanoparticles are assembled and by which molecules are localized into hot spots created by an external laser excitation in the interstices between the nanoparticles. One of our recently elaborated approaches is based on an idea that molecules linking together two or more Ag nanoparticles will be automatically located in hot spots. Dimers and small aggregates of Ag nanoparticles linked together by several types of bifunctional linkers have been assembled on chemically functionalized supporting surfaces suitable for combined TEM-SERS micro-Raman studies. Temporally fluctuating SERS signals of linker molecules measured from a selected single nanoobject are interpreted in terms of molecular dynamics of a single or a very few molecules. Finally, several prospective pathways towards decreasing the risks of thermal and/or photochemical decomposition of molecules localized in strong optical fields in the course of single molecule SERS experiment will be outlined.

Acknowledgement: Financial support by the 203/04/0688 (GACR), 1P05ME790 (MSMT of CR) and the OISE-0406665 (NSF) grants is gratefully acknowledged.

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DEVELOPMENT OF INFRARED SPECTROSCOPY FOR STUDY OF CERAMIC MATERIALS AGEING

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The work deals with study of ageing and degradation of ceramic materials, e.g. study of earthenware irreversible moisture expansion.

It was studied influence of raw materials constitutions on tendency of ceramic earthenware undergo to volume changes in consequence of hydrothermal exposition. Values of irreversible moisture expansion were determined in step with conditions of standard tests (volume changes of samples) and supplemented using infrared spectroscopy in order to detection of physical-chemical and chemical changes (bond changes) of earthenware potsherds after standardized hydrothermal exposition.

Confirmation of relative changes of OH-group's content after hydrothermal exposition corresponds with negative volume changes detected on ceramic materials.

ELECTROSPRAY IONIZATION – ION TRAP MASS SPECTROMETRY OF CARBORANES

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Boron belongs to few elements which are able to form binary hydrides – boranes - composed from more than two atoms of the element. Borane architecture is based on cluster structures characterized by three dimensional skeletons with triangular facets. These compounds have found their use in several special fields. Apart from already abandoned high energy rocket fuel development in 1950's and 1960's, other more promising application have been designed ranging from Boron Neutron Capture Therapy, radionuclide extraction, high temperature polymers, solid electrolytes, catalysts etc.

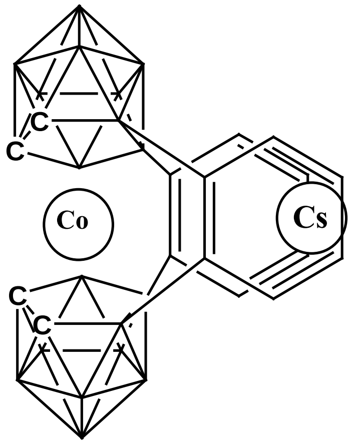

Fig. 1: Structure of metalla-carborane

Substitution of one or several boron atoms in the skeleton by carbon gives carboranes (or carbaboranes) belonging to the group of heteroboranes. Boron cluster compound and especially carboranes represent distinctive covalent species with unique molecular architecture, nonconventional cluster bonding and unusual chemistry. The specific properties of the electron-deficient carborane system were the reason for the appearance of a large number of theoretical and experimental papers.

In the present study we focused on identification and determination of newly synthesized compounds of carborane type. Electrospray ionization and spherical trap mass spectrometry were employed for this purpose. Due to isotopic distribution of boron ^{10}B and ^{11}B (19.78:80.22) complex multiplets were observed in the mass spectra of carboranes; their elemental composition could be assessed by the comparison of the experimental and modeled distribution of the carborane ions. The interpretation of these complex multiplets was often complicated by hydrogen looses.

Tandem mass spectrometry in spherical ion trap proved is usefulness in structural elucidation of analyzed compounds; fragmentation of monoisotopically isolated parent compound showed neutral loses which were used for the proposed structure confirmation. In case of metallacarboranes their reluctance against fragmentation in the presence of Cs^+ ions made this process sometimes difficult.

Acknowledgement: This study was supported by the grant No. A400310613 from the Grant Agency of the Academy of Sciences of the Czech Republic.

APPLIED BIOSYSTEMS/MDS SCIEX LC/MS/MS TECHNOLOGIES FOR SMALL MOLECULES ANALYSIS

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Mass spectrometry is a critical and core enabling technology for the life science and analytical industry. From basic research to drug discovery and development, clinical, forensic, food and environmental analysis, mass spectrometry-based methods play a key role because of their sensitivity, robustness and reliability. As a one of main players in mass spectrometry, Applied Biosystems/MDS SCIEX is dedicated for more then 20 years to develop the unparalleled performance solutions in order to deliver the most powerful systems available to scientific and industry customers.

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- Hybrid linear ion trap performance delivers structural identification or confirmation (MS2, MS3, enhanced resolution, high sensitivity—full scan)
- Analyst® software provides innovative qualitative analysis tools, including spectrum library and fragment interpretation

CONTROL CHARTS IN QUALITY ASSURANCE

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Quality assurance of analytical methods requires the values of precision and trueness to be monitored simultaneously. The requirement on monitoring results from the Gauss equation because random variable probability of occurrence is a function of two variables, μ and σ ($y = \frac{\exp\left\{-(x-\mu)^2/2\sigma^2\right\}}{\sigma\sqrt{2\pi}}$). For method control purposes, certified reference materials suit best. When analyzed, both characteristics are identified quickly and easily. It is presumed that the results have Gaussian distribution.

Control charts are commonly used in accredited laboratories. By constructing these charts, we check statistic regulation of the data scatter. If shifts in control sample data occur in the frame of statistic rules, the scatter is random, only. At this point, analytical method reached the state of competence for performing routine operations. It is believed that the method development has come to an end and further method improvement will not bring any new knowledge.

Chemical metrology is known by certain speciality. The personnel do not compare the result of analytical procedure with firmly adjusted specifications. They will not simply discard the result on the basis of single static control mechanism. The detection of nonconforming result may be difficult. Efforts to disclose faults rather aim at error prevention. Two-three control samples, covering method concentration range, are analyzed instead. The fact that the results scatter is regulated by chance only is evidenced from control samples charts. The conclusion about statistic regulation is extended then to all samples of the tested analytical method. The role of control charts in laboratory routine is considerable for error prevention.

Three examples of stable method condition will be shown. The determination of Al in CRM BCR 609 by ETAAS, the determination of SO_4^{2-} in water by HPLC and the determination of Hg in granite by AMA 254 will be discussed. $R-$charts and $\overline{X}$-charts are constructed for 40-50 points with subgroup size $n = 2$. Regulation limits are defined as 3s.

The capability of analytical method is expressed by capability index

$$PCI = \frac{tolerance}{method\ \mathrm{var}iance\ range} = \frac{tolerance}{6\sigma}$$

where tolerance for given analyte is taken from established practice (e.g. ± 20%), σ is the mean subgroup variability derived from the control charts. For comparison, tolerances are replaced by expanded uncertainties, but with coverage factor of 3. The capability indexes of methods tested are compared for routine tolerances and for ranges given by laboratory uncertainties.

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DETERMINATION OF LABILE METAL SPECIES IN NATURE AQUATIC SYSTEMS BY GEL TECHNIQUES AND ATOMIC SPECTROMETRY METHODS

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Reliable measurement of trace species in environmental systems is essential for studies of pollution, trace element cycling, phytoavailability of nutrients and toxic species, for study of processes taking place in sediments and soils, but is difficult, partly because the distribution of chemical species often changes during sampling and storage. DET diffusive equilibrium in thin-films technique and DGT, diffusive gradients in thin-films technique, invented by Davison in 1991 [1,2], overcomes these problems. These techniques provide an *in situ* means of quantitatively measuring labile species in aqueous systems. DET technique relies a similar equilibration principle as peepers, but rather than confining the solution to compartments, it uses a thin film of hydrogel for equilibration with solutes in waters. Using the DGT technique trace metals are measured easily by accumulation them on a selective binding resin after passage through a well-defined diffusive gel layer. The diffusive gel layer used in this work has an open structure that allows free diffusion of inorganic labile species and some metal organic complexes. Gel techniques can be used to distinguish between small and large species, which we have ascribed to inorganic and organic species present in aquatic systems. The discrimination of measured species by DGT is also kinetically based according to similar principles to those of anodic stripping voltammetry. When used in solution, it measures those species that can dissociate within the time it takes for ions to be transported through the diffusion layer (typically minutes). When DGT is applied to sediments and soils, it also measures labile species, but interpretation of measured results needs more other information about this system [3]. The simple plastic assembly can be deployed *in situ* in rivers, lakes, and oceans, sediments or soils and effluents where it automatically separates metal ions from solution. Metals are subsequently analyzed conveniently in the laboratory, by direct measurement of the concentration in gel/resin layer with the techniques capable of analyzing solids, such as XRF or PIXE [1]. Alternatively, metal ions in resin layer can be eluted using a known volume of acid solution. ET AAS or ICP AES are used for the determination of the concentration of ions in the acid eluent. The ICP MS is very useful due to its detection power in this instance.DET and DGT techniques were tested in model solutions and artificial sediment [4]. The results obtained by DET and DGT techniques applied in real rivers, sediments and soils and the comparison with results obtained by biomonitoring using aquatic moss *Frontinalis Antipyretica* are presented [5,6,7,8].

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APPLICATION OF ATOMIC SPECTROMETRY METHODS AND ICP-MS AS TOOLS FOR SPECIATION OF SELECTED ELEMENTS

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Concerning ion exchangers used for ICP-AES detection, organically bonded selenium and tin weren't sorbed and eluted when batching already. Using off-line coupling of liquid chromatography and ETA-AAS, all forms were separated on the appropriate column but from practical point of view the method is more difficult and time-consuming than e.g. HPLC-(UV)-HG-AFS which is being thoroughly tested in our laboratory. The use of suitable sample introduction system is necessary for on-line hyphenation of CZE and ICP-AES. At first we used micro concentric nebulizer MCN-100, model M-2 and than we used the direct injection high efficiency nebulizer (DIHEN) and ICP-MS. We intend to apply the developed methods to real samples of food supplements.

Although selenium ranks among essential elements, the range between concentrations with favourable and toxic effects on the human organism is relatively narrow. Toxic doses are only hundred times higher than those required for physiological functions. This dual effect has been recognized for many naturally occurring chemicals. The Czech Republic belongs to the zone with deficiency of selenium and that is why this study was aimed on monitoring the amount and forms of selenium just in food supplements.

The research deals with determination of particular forms of selenium in food supplements. Separation of the species was performed by liquid chromatographic techniques coupled with atomic spectrometry.

Chromatographic separation of inorganic forms of selenium was achieved using ion exchange columns coupled with low-pressure pump and on-line detection by ICP-AES. High performance liquid chromatography was used for separation of organic species of selenium with detection by ETA-AAS and HG-AFS and ICP-MS.

The common procedures used for the speciation of selenium in yeast, plants and vegetables have been hot water extraction, enzymatic hydrolysis, buffers, water-methanol and HCl extraction. In this study, protease XIV, Subtilisin A and Protease from Bacillus licheniformis (13, 1 units/mg) were used for enzymatic extraction to cleave peptide bonds in proteins. The speciation of selenite, selenate, selenoethionine, selenocysteine and selenomethionine was satisfactory when using the combination HPLC-Heating-UV-HG-AFS. This method is relatively free of interferences, involving low cost and maintenance.

DC-ARC-OES VS. ETV-ICP-OES IN SOLID SAMPLING ATOMIC SPECTROMETRY: COMPETITIVE OR COMPLEMENTARY METHODS?

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During the history of the spectroscopy various electric discharges (DC- and AC- arcs, low-middle- and high-voltage sparks, but also low pressure discharges as GD-OES) have been used as excitation sources. In this time, the analysis of the solid samples of geological and similar origin played the leading role. The introduction of new plasma sources, first of all the most successful of them – the ICP, have led mostly to the use of the solution methods in the daily practice and the old fashioned solid sampling methods lost their importance.

Some years later the increased use of advanced ceramic materials (e.g. SiC, Si_3N_4, B_4C, etc.) in industrial area, where engines, turbines, heat-transfer units could be mentioned at first, recalled the interest in direct methods of analysis. The strength of the mentioned materials at high temperatures, as well as their chemical resistance and hardness are of main importance. On the other hand, these characteristics could be degraded very quickly by some impurities as Ca, Al, Fe, etc. Therefore suitable analytical methods should be used in all production steps [1]. As the methods of the atomic spectroscopy played an important role in this area also in the past, at the beginning modernized applications of the solution methods using decomposition of samples as F-AAS, GF-AAS and also ICP-OES were used. Later, the well known disadvantages of the digestion methods (environmental and contamination risks, time consuming, etc.) led back the attention to the direct solid sampling methods of analysis.

In spite of the fact, that the ETV-ICP-OES methods are the most used solid-sampling techniques, they are going to be developed in mentioned field of analysis. Besides them also other solid sampling techniques are used, like slurry nebulization, direct sample insertion, spark and laser ablation. As the use of ETV-technique is limited by the maximum achievable temperature about 2900°C, the evaporation of the carbide-forming elements could not be complete. Therefore the use of the special working atmospheres or additives was needed. On the other hand, the temperature of DC-arc excitation about 4000 °C fulfils the requirements on the total evaporation also of the refractory elements. The new technologies, namely the use of a modern, programmable and computer-controlled DC-arc has therefore turned back the interest of the spectrochemists to this old instrumentation. Besides the high excitation temperature also other advantages as high stability and reproducibility of the excitation should be mentioned. As an interesting aspect of the DC-arc-applications should be not forgotten, some tandem techniques were applied in solid sampling of the discussed materials. Preuss [2] has described the first combination of "ETV" with DC-arc. Besides this also the combination of the DC-arc - Marinković plasma source should be mentioned, where the arc serves as evaporation source and the Marinković plasma as an excitation source [3]. A review [4] about arc and spark optical emission spectroscopy includes also other recent applications.

Some typical results and comparisons of both (ETV-ICP-OES vs. DC-ARC-OES) spectrochemical techniques used in discussed area will be presented in the lecture.

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SIGNIFICANT TRIFLES

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At present, we are confronted with a wide offer of various goods. It concerns both, personal as well as professional needs.

This fact seems to be positive, but there are certain problems that come along with it. Many commodities, such as laboratory instruments, different aids or diagnostics differ often in details only.

But exactly these „trifles“ can, in some sense, become a significant contribution, improvement of the quality of work, decrease of some hazard etc, or on the other hand can cause various problems, or lower quality.

Therefore it is necessary to pay adequate attention to these details, when selecting the laboratory equipment.

In this lecture we would like to call attention to such „trifles“ in case of liquid handling tools of the company BIOHIT (Finland) and pH – meters of the company SENTRON (Netherlands) which are represented by company ECOMED – as their exclusive representative for Slovak Republic - for more then 13 years.

We assume that just these two groups of commodities from our offer are indicated by several “significant trifles”, meaning a big contribution and progress for a high a quality and progressive laboratory work.

STUDY OF ALLOY-CLUSTERS WITH THE USE OF MASS SPECTROMETER

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During our work we were looking for the possibilities of the analysis of alloy build-up mechanisms. We have analysed polyatomic particles, cluster existence, relative frequency and stability that have arisen in plasma from two metal atoms. All these have been made with the respect of current laboratory and measuring facilites.

The clusterchemical studies that started more than two decades ago with arising elan have important aims. One of these aims is to make connection among material study researches both in atomic-molecular size and macroscopic size ones, too.

The first part of our pilot studies was oriented on vacuum discharge plasma with huge energy. In such plasma we wanted to detect two-atomic clusters of different metals, in other words: to identify with precise mass measuring and to determine their relative frequency.

Clusters were prepared in vacuum discharge plasma with huge energy on a photoplate after their rectification and dividing on the base of mass. The evaluation of these mass spectrums was made by comparator-denzitometer. Identification of some M2 dimers was made by precise mass measuring and by determination of isotope proportions on one hand and the determination of their relative frequency was made by denzitometering on the other hand.

Our pilot analysis from the point of view of further study possibilities had positive result. We have determined two-atomic clusters of alkali metals, A and B metals, transitional metals, half-metals, no-metals and their relative frequency. We have stated that in case of two-atomic metal clusters we can count just with weak bindings and that is why that occasionally just with a small frequency. The demonstration was successful in case of each element included in the analysis. The identification could be done by precise mass measuring with the use of given experimenting possibilities.

We have rectified clusters of 22 elements and it succeeded firstly that we could cover practically the whole periodic table and could serve tentative material to understand the first step of metal cluster formation.

Because of this we have made up the formating frequency data in case of identified two-atomic clusters. Their comparison may serve information about factors that influence the dimer formation.

ROUND ROBIN TEST OF METALLIC IMPURITIES IN SILICON CARBIDE VIA DC-ARC-OES - RESULTS AND INTERPRETATION

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DC-Arc, one of the oldest excitation sources in spectroscopy was definitely established as a method for quantification of trace elements 70 years ago by Gerlach and Schweizer and became the most common spectroscopic method worldwide within the following decades. During the 60th and 70th more and more substituted by other methods (AAS, ICP-OES,…) it was nearly disrupted in the western hemisphere in the 80th.

Because of its interesting advantages – but also because of new technologies like CID-sensors with gating and time resolved data acquisition, fibre optics, high-power semiconductors and microcomputers that were existing meanwhile this sleeping method was awakened again since the mid 90th. Based on these and other modern technologies a commercial state-of-the-art equipment is available on the market for some years now.

Very soon there was an increasing interest especially using ceramic samples, oxides, silicates and carbides. Because of these demands a DIN norm project was established for OES analysis of ceramic materials with DC-Arc as excitation source. For collecting the necessary statistical data including the validation of the method a round robin test was initiated. For this exercise 6 well analyzed SiC materials were chosen which were treated by the same procedure in each participating laboratory: Each material was analysed 6 times and 3 materials were evaluated on their trace concentrations against the respective 5 others. The results for Al, B, Ca, Cu, Fe, Ni, Mg, Ti, V, Zr are shown and discussed in this report. Also included in this report are the first test-results of a magnetic field DC-Arc-source.

Due to the high number of 14 participating labs from 4 European countries using OES-spectrometers from 4 manufacturers the information output was much higher than expected – and the exercise became one of the biggest DC-Arc round robin tests ever that has been performed during the last decades.

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LABORATORY INTRUMENTS AND EQUIPMENT AS A SUPPLEMENT OR SUBSTITUTION FOR SPECTROMETRIC METHODS

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Sample taking and sample preparation is an important part of the analysis. Choice of proper material and construction of samplers must be done according to physical, chemical, mechanical and microbiological properties of the sample, kind of sampling, situation at sampling and the properties of sampled unit. Sometimes special preparation like crushing and milling of obtained sample is necessary.

Systems for high pressure mineralization in focused microwave field are useful tools for preparation of samples before spectrometric analysis. Main advantages of this system are extremely high weights of samples, short time of decomposition, water cooling immediately after decomposition and possibility of combination of pressure and atmospheric systems.

In many cases, however, spectrometric methods can be replaced with modern electroanalytical methods, which have advantages not only in low costs of instrumentation and low operating expenses. Stripping chronopotentiometry, e.g., enables the determination of all toxicologically interesting elements and also anions and some organic compounds already at concentration levels about 0.1 μg/L. Main advantages of used analytical system are: automatic analysis including the calibration, high sample throughput, some applications in the calibrationless mode, large dynamic concentration range, no need of technical gases for sample deairation. The system is variable, the hardware and software enables the use of other modes such as direct coulometry, voltammetry, potentiometry, conductometry as well as other electrode systems.

Stripping chronopotentiometry with microwave enhanced sample preparation is a suitable analytical method for determination of trace elements in various matrices. Low cost of analysers and low running costs make it possible to built analysis of trace elements in laboratories which were not able to afford purchasing of much more expensive equipment for spectrometric methods like ETA AAS or ICP. Broadening of progressive electroanalytical methods could lead to better environmental and hygienic control of water, soil, plant and animal materials, food and beverages and clinical samples as well as to a better control of industrial processes.

DEVICE WITH AXIALLY FOCUSING CONVECTION UPSTREAM ZONE

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In this paper we present experimental results with a new upstream ETV device with an Axially Focusing Convection (AFC) upstream that achieves analyte condensation apart from colder walls. The hot gas flow released from the outlet hole in the center of the tube containing the analyte vapor and already condensed carbon particles forms a laminar flow centered on the axis of the vertical AFC tube. The upstream is shielded against emission of incandescent light from the graphite tube walls and is surrounded with several cooling argon flows in order to increase temperature gradients right above the tube outlet and facilitate vapor condensation.

Detailed measurements are shown with the new system with and without different sample/carrier modifiers. For optimization, the temperature course above the outlet has been measured with a fast thermocouple. Particles were collected with thermophoresis on different substrates beginning at 2.5 mm above the tube outlet hole and also inside the furnace for analyzing the sizes of condensed particles with SEM and TEM.

Analyte transport efficiencies were directly measured with quantitative electrostatic precipitation of the transported aerosol onto secondary platforms and analysis via atomic spectrometry. The effect of K and Pd as matrix/carrier modifier has been investigated as well as of gaseous modifier cyclohexane. The latter stabilizes the carbon presence that varies with the tube aging.

Directly determined analyte transport efficiencies are 70-80% for medium volatile elements (Fe, Ni). Increase in the number carbon-containing compounds during the vaporization step makes the analyte transport more efficient.

Measurements with modifiers show a positive effect of potassium and palladium modifiers as well as of gaseous carbon hydrates, especially on the transport efficiency of volatile elements. Thus, sample analytes are transported to an analytical instrument with more equal ratios (60-70% for Ag, Cu, Mn, Pb; 70-80% for Fe, Ni).

It is shown with the micrographs of particles deposited on substrates via thermophoresis that carbon particles are already present inside the furnace and in the released gas flow. These particles are crucial for the analyte condensation process at the carriers.

The measured results are compared with calculations on the bases of a simple model that is presented in another paper (poster) on this conference. It allows the calculation of analyte losses in different parts of the ETV and tubing system, and of analyte transport efficiencies for medium and high volatile analytes, with and without matrix/carrier modifiers, such potassium and palladium.

CHARACTERIZATION OF IN-DEPTH ANALYSIS OF CERAMIC TILES BY ACOUSTIC EMISSION AT LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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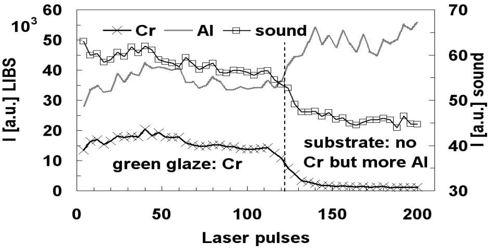
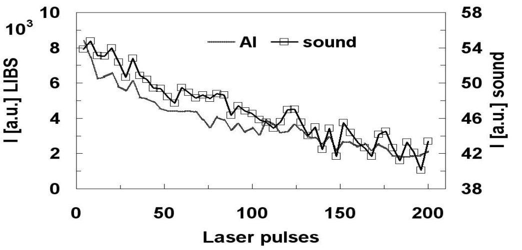
In order to correct for signal changes an internal standard element is frequently used at laser ablation (LA)-based techniques. The spatial distribution of this element must be well-known, thus limiting the use of LA. Acoustic emission accompanying LA has been already studied on ceramic [1], metallic [2] or glass [3] samples. This work is aimed to substitute an internal standard element with an acoustic signal accompanying the ablation process at LIBS as well as to characterize the transition area glaze-substrate of ceramic tiles.

Experimental: Q-switched Nd:YAG laser Quantel Brilliant 1064 nm with a Gaussian beam profile, Horiba JY ICCD detector implemented into a Triax 320 monochromator, impact pulse energy 45 mJ, single-lens focusing behind the sample surface, single-spot ablation, sound recording with a small air microphone and a piezoelectric contact probe DAKEL.

Acquired optical emission signals correlate with those of sound under appropriate conditions. The acoustic emission provides very similar results regardless of the chosen frequency interval or used sample fixation system. Optical emission depth profiles show on a decrease of the ablation signal when the laser drills throughout the glaze into the ceramic body. This can be successfully compensated with sound intensity signals (left Fig.). Moreover, shot-to-shot fluctuations of the optical emission signal are distinguished from those arisen from a real grain structure. A LIBS signal decrease during LA of a ceramic body can be corrected too (right Fig.). The relation between the sound intensity and the optical signal is not fully linear and hence a more sophisticated approach is required for better results.





Acknowledgement: The authors acknowledge the Ministry of Education, Youth and Sports of the Czech Republic for research project MSM0021622411.

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AGILENT 7500 ICP-MS

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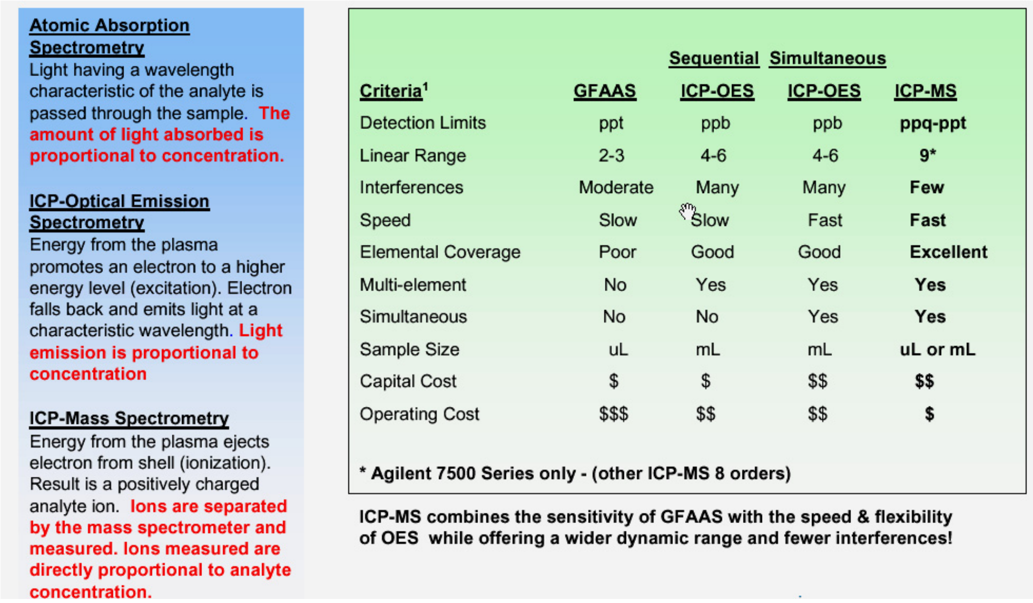
Well established technique of ICP MS is compared to other inorganic analysis approaches as GF-AAS, ICP-OES sequential and ICP-OES simultaneous.

Flexibility regarding sample introduction possibilities and ease of sample handling is discussed along with connection to external devices as laser ablation, gas chromatograph, liquid chromatograph, capillary electrophoresis and surface metal extraction.

Examples of different analyses are shown e.g. high matrix sample – sea water, silicon wafer surface characterization in semiconductor analysis and drinking water analysis. Efficiency of polyatomic background reduction via octopole reaction system is also presented.

Economic factors of running ICP-MS instrument such as sample throughput, versatility, instrument up time and reliability are also important while considering this technique.

Finally application fields of inorganic analysis performed via ICP-MS and statistics which industries the users are comming from is presented.



Atomic Absorption Spectrometry
Light having a wavelength characteristic of the analyte is passed through the sample. **The amount of light absorbed is proportional to concentration.**

ICP-Optical Emission Spectrometry
Energy from the plasma promotes an electron to a higher energy level (excitation). Electron falls back and emits light at a characteristic wavelength. **Light emission is proportional to concentration**

ICP-Mass Spectrometry
Energy from the plasma ejects electron from shell (ionization). Result is a positively charged analyte ion. **Ions are separated by the mass spectrometer and measured. Ions measured are directly proportional to analyte concentration.**

		Sequential	Simultaneous	
Criteria[1]	**GFAAS**	**ICP-OES**	**ICP-OES**	**ICP-MS**
Detection Limits	ppt	ppb	ppb	**ppq-ppt**
Linear Range	2-3	4-6	4-6	**9***
Interferences	Moderate	Many	Many	**Few**
Speed	Slow	Slow	Fast	**Fast**
Elemental Coverage	Poor	Good	Good	**Excellent**
Multi-element	No	Yes	Yes	**Yes**
Simultaneous	No	No	Yes	**Yes**
Sample Size	uL	mL	mL	**uL or mL**
Capital Cost	$	$	$$	**$$**
Operating Cost	$$$	$$	$$	**$**

*** Agilent 7500 Series only - (other ICP-MS 8 orders)**

ICP-MS combines the sensitivity of GFAAS with the speed & flexibility of OES while offering a wider dynamic range and fewer interferences!

DIRECT DETERMINATION OF SELENIUM IN URINE BY D2-GFAAS

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Direct measurement of selenium in urine by graphite furnace atomic absorption spectrometry with deuterium background correction (D_2-GFAAS) is affected to severe matrix and spectral interferences. In order to remove this negative interference effect, various chemical modifiers were tested. The detail study concerning the pyrolysis and atomization temperatures, background profiles, characteristic masses, detection limits, accuracy and recoveries was performed for all modifiers tested. The effect of entire matrix was studied using calibration and standard additions slopes. The proposed procedure involves the use of Pd+Ag as a modifier. Using this modifier the best analytical recoveries, close to 100 %, were obtained. Characteristic mass 18 pg and limit of detection with a 10-μl aliquot of sample (using peak height measurement) 2.9 $\mu g\ l^{-1}$ were achieved. Typical relative standard deviation values (n = 3) were bellow 3 %. Good agreement between experimental and reference values was observed in the analysis of certified reference materials using the recommended chemical modifier and simple calibration method.

Acknowledgement: The study was developed owing to financial support of the Ministry of Education, Youth and Sports of Czech Republic (project No. 0021627502).

LASER ASSISTED PLASMA SPECTROMETRY OF SOLID SAMPLES

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Utilization of laser beam interaction with solids is being studied for purpose of chemical analysis during four decades. A group of analytical techniques called Laser Assisted Plasma Spectroscopy – LAPS uses appropriately focused beam of pulsed laser to release material from a sample surface layer in thickness from units to hundreds of micrometers (laser ablation - LA), which is accompanied by formation of a microplasma. Laser-induced aerosol is then introduced by means of a carrier gas flow into an inductively coupled plasma source (ICP), where the particles are vaporized, ionized and excited. Analytical signal is represented by photons and ions that are detected by techniques of optical emission or mass spectrometry (LA-ICP-OES, LA-ICP-MS). Laser- produced microplasma serves as a reservoir of excited atoms and ions of a sample and ambient atmosphere. Optical emission of this microplasma represents signal for Laser Induced Breakdown Spectroscopy (LIBS).

At the laser pulse duration in the orders from nanoseconds to femtoseconds and irradiated areas with diameters from units to hundreds of micrometers the laser power density reaches values from units to tens of GW/cm^2. At these conditions the composition of ablated material approaches stoichiometry of original intact sample, which is beneficial for quantitative analysis. The technique of LA is being employed for a relatively long time in physical and technical branches for deposition of thin layers or machining of complex structures and thus represents routine technological procedures. However, in chemical analysis the laser ablation-based procedures belong so far to those methods that head in development towards the parameters of quantitative analysis. While LA-ICP-OES does not attain values of detection limits that are appropriate for trace analysis and rather can be employed for determination of contents on levels from 0.0X % to XX % with RSD of precision about 5 %, LA-ICP-MS is suitable for trace analysis and, if simultaneous mass spectrometers are applied, also for isotope ratio determination. The technique of LIBS can not compete with LA-ICP-MS as far as limits of detection and linear range of calibration are concerned, however, it represents the alternative of less expensive and compact device that can be adapted for field applications, in situ measurements and measurements of distant and difficultly accessible samples.

Important common merit of LAPS techniques consists in features of local analysis, microanalysis, a possibility of analysis both electrically conductive and non-conductive materials without any surface treatment. Scanning with laser beam can be used for elemental chemical mapping of surfaces and interfaces on sections as well as for depth profiles acquisition. Important role consists also in capability of conducting bulk analysis of chemically resistant materials.

In this contribution, capabilities of LAPS techniques will be demonstrated with examples of bulk analysis of steels, slags, tungsten carbides, soils, acquisition of depth profiles of some metal or ceramic coatings and chemical mapping of sections of glazed ceramics and some metal/solidified salt melt interfaces. Problems of powdered sample preparation for LAPS analysis will be discussed.

Acknowledgement: The Ministry of Education, Youth and Sports of the Czech Republic is acknowledged for support of the projects MSM0021622411 and MSM0021622412.

DETERMINATION OF CADMIUM BY ATOMIC ABSORPTION SPECTROMETRY AFTER ELECTRODEPOSITION

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For the atomic absorption spectrometry determination of traces of metals in samples with high concentration of salts a separation step is usually needed for the elimination of chemical and spectral interferences. Moreover, many elements occur in low concentrations in the environment. Electrochemical deposition serves as one of many techniques for preconcentration and separation of analyte from the matrix. During electrolysis the analyte is accumulated onto the surface of the electrode. After the electrolysis the deposit is dissoluted and subsequently injected into the atomizer as solution. In connection with atomic absorption spectrometry used electrodes can be manufactured from different materials, such as high melting metals, graphite or mercury.

In this work preconcentration and separation of cadmium in the flow mode was studied. The various electrode materials and designs of electrochemical cell were investigated. Conditions for the electrodeposition, such as pH of solution, the deposition potential, current and concentration of electrolyte were optimized. Electrodeposition with injection of dissolved deposit into electrothermal atomizer was applied for the determination of cadmium in samples of water.

Acknowledgement: This work was supported by project MSM 0021622412 of Ministry of Education, Youth and Sports of the Czech Republic.

DETERMINATION OF GOLD BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY AFTER ELECTROCHEMICAL PRECONCENTRATION

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The low concentrations of gold in environmental and biological samples require high sensitive techniques for its determination. Electrothermal atomic absorption spectrometry (ET AAS) in connection with electrochemical deposition is suitable because the analyte is separated from the interfering matrix and preconcentrated in one step. For the electrodeposition procedure the graphite tube and the graphite ridge probe can be applied like working electrodes in the arrangement of a flow-through cell and a stationary cell, respectively.

With regard to relative volatility of gold chemical modification is recommended in order to increase the maximum pyrolysis temperature and minimize interferences. Noble metals in the form of their salts are frequently used chemical modifiers. Another possibility is electrolysis of the noble metals on the surface of graphite atomizer. In this case the noble metal is deposited in its elemental form. The part of electrodeposited metal could penetrate into the subsurface layers and remains there for the atomizer lifetime. Then the noble metal serves as the permanent modifier.

Different modifications of the tube and the probe surface by electrochemically predeposited noble metals were studied. On the modified surfaces gold was electrodeposited and determined by ET AAS. The conditions of electrodeposition of both – noble metal and gold were optimized and gold was determined in natural samples.

Acknowledgement: This work was supported by project MSM 0021622412 of Ministry of Education, Youth and Sports of the Czech Republic.

CHANGES OF ELEMENT SPECIATION IN CEREAL FLAKES CAUSED BY SIMULATED GASTROINTESTINAL DIGESTION

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Element speciation analysis of biological matrices can be efficiently accomplished by liquid chromatography with element specific detection. Size exclusion chromatography – inductively coupled plasma mass spectrometry (SEC/ICP-MS) had been successfully used for element species fractionation of various food samples such as legumes [1-2] or cereals [3]. The main reason why trace element speciation in food is investigated consists in the influence of chemical status of the element on its bioavailability or toxicity. The original chemical species of elements present in food raw materials are somewhat changed by food processing, e.g. thermal treatment of food causes denaturation of metalloproteins or other metallobiomolecules resulting in drop of elements solubility [4]. This is accompanied in part by release of metal ions from some organic chelates. Nevertheless, the most significant chemical changes of metal-binding compounds take place during digestion of food in gastrointestinal system just before absorption.

To investigate element speciation in digested food samples the enzyme digestion using pig's pepsin and pancreatin was performed. The flakes samples were firstly hydrolysed by pepsin in 0.02M HCl for 12 hours and then by pancreatin at pH=7.5 (adjusted by ammonium carbonate and ammonia) for 12 hours. The temperature was maintained at 37°C. After cooling and centrifugation the digest was analysed by SEC/ICP-MS using Superdex 75 column (300×10 mm) and 0.02M Tris-HCl buffer solution (pH=7.5) as a mobile phase. Elan 6000 ICP-mass spectrometer (Perkin-Elmer) was used for element-specific detection.

Great deal of elements from cereal flakes is solubilised by enzyme hydrolysis, e.g. in case of rye flakes the rates of solubilised P, Mn, Fe, Co, Cu, Zn, Mo, Cd and Pb are 83, 77, 51, 80, 29, 46, 63, 76 and 94 %, respectively. Soluble portions of most elements in original flakes (ascertained by pH 7.5 Tris-HCl buffer extraction) are lower. Phosphorus and molybdenum recoveries of SEC analysis of the digest approach to 100 %, while those of iron and copper amount to 60-80 % and that of zinc varies from 10 to 40 %. The non-recovered portion of the element is represented by ionic species or labile complexes. Proportions among individual element species fractions are changed as a result of enzyme digestion, e.g. 4 kDa fraction of phosphorus compounds and high molecular mass fraction of copper compounds increase owing to release of originally less soluble species. While no iron is recovered in SEC analysis of flakes extract the majority of iron in the digest is bound to medium molecular mass (4-5 kDa) fraction. Low molecular mass (<2 kDa) fractions of copper and zinc partially persist in the digest.

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A CHALLENGING APPROACH TO TRACE ANALYSIS: AsH_3 TRAPPING AT QUARTZ SURFACE FOR HG-AAS

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Due to their toxicity, hydride forming elements must be monitored in the environment even at ultratrace levels. Thus, analyte must be preconcentrated prior to detection. Until recently, the most popular approach to analyte preconcentration was *in-situ* trapping in commercial graphite furnaces.

However, quartz surface was found to be a promising material for hydride preconcentration recently. Quartz preconcentration devices can be simply interfaced to quartz atomizers (QTA) that are predominantly used for hydride atomization. Moreover, under certain circumstances, hydride preconcentration could be done directly in the atomizer using a very simple and cheap apparatus arrangement. Lossless *in-situ* trapping of Sb[1] and Bi[2] hydrides in commercial QTA was announced last year. This novel approach enables to decrease the detection limit down to low $pg.ml^{-1}$ levels.

The aim of the present work was to extend our previous investigations to arsine trapping in a quartz trap because arsenic is one of the most toxicologically important elements. Also speciation analysis calls for ultrasensitive arsenic detection.

In principle, analyte hydride is collected at the quartz surface using O_2 excess over H_2 in the carrier gas (ca 15 $ml.min^{-1}$ H_2 formed in hydride generator decreases trappig efficiency). Subsequently, trapped analyte is re-volatilized by H_2 excess over O_2.

Optimization of the fundamental experimental parameters is presented. Arsine is efficiently trapped within ambient temperature and 650 °C using 15 $ml.min^{-1}$ O_2 to eliminate H_2 formed in hydride generator. Optimum volatilization temperature ranges between 650–800 °C. Optimum H_2 flow for volatilization was found to be 100 $ml.min^{-1}$. Hydrogen radicals are required to atomize trapped As species. Therefore, volatilized As species are able to be atomized only in a special type of quartz atomizer - in the multiatomizer[3], not in the plain QTA.

Furthermore, other analytical aspects as trapping efficiency or possibility of *in-situ* trapping of arsine in the quartz multiatomizer are discussed.

Acknowledgment: Financial support from Grant Agency of the ASCR (Project No. A400310507), Institute of Analytical Chemistry AS CR (No. Z40310501), the Grant Agency of Charles University (Project No. GAUK 306/2006/B-CH/PrF) and FRVS (Project No. 1011/2006/G6) is gratefully acknowledged.

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TRAPPING OF HYDRIDE FORMING ELEMENTS ON A MOLYBDENUM-FOIL STRIP

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Trapping behaviour of As, Bi, Sb and Se hydrides on the bare and modified molybdenum surface were investigated in a prototype of miniature electrothermal trapping/vaporization (ETV) device. It is based on a strip of the molybdenum foil and combined with miniature hydrogen diffusion flame for specific analyte detection in atomic absorption spectrometry system. Influence of trapping temperature, modification of the foil surface with noble metals – Ir, Pt and Rh, distance between the orifice of the injection capillary and the strip, argon carrier gas flow rate and composition of the gaseous phase (argon-hydrogen-oxygen) was investigated. Analytical figures of merit (LOD, LOQ) were assessed. Maximum trapping efficiency of Bi, Sb and As, Se was found on a bare molybdenum surface at temperatures of 550ºC, 750°C and 1200°C respectively. In contrary to As and Se, modification of the surface reduces trapping efficiency of Bi and Sb at higher amounts of modifiers (>30 μg) tested. Presence or absence of hydrogen in the gaseous phase during collection step does not play significant role in trapping Sb and Bi. Efficient trapping of As and Se is achieved only in hydrogen-rich atmosphere (>40 ml min^{-1} H_2). Some mutual interference effects of co-generated hydride forming elements were also studied and discussed.

Acknowledgement: This work was supported by The Grant Agency of the Czech Republic (Project No. 203/06/1441) and by Ministry of Education, Youth and Sports of the CZ (FRVS 1054/2006).

ICP OES ANALYSIS OF IMPURITIES IN PURE HYDROXIDES AND SALTS

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An effective, rapid and simple analytical method for the determination of Na, K, Ca, Mg, Ag, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, V and Zn at $mg.kg^{-1}$ levels in pure and ultra-pure NaOH, KOH, NaCl and KCl using the optical emission spectrometry was developed. The optimisation of operation condition was performed with real sample of ultra-pure hydroxides and salts. The results of determination with multi-elemental water standards were compared with the internal standardisation and the standard addition methods and the maximal allowable content of above mentioned elements in pure chemicals. The method was shown to be very sensitive with limits of detection: Na 0.902, K 2.96, Ca 0.0636, Mg 0.0257, Ag 0.326, Al 0.427, B 0.127, Ba 0.0153, Cd 0.0232, Co 0.0562, Cr 0.0412, Cu 0.0632, Fe 0.0600, Li 0.0169, Mn 0.0347, Mo 0.189, Ni 0.0549, Pb 0.389, Sr 0.0299, V 0.0651 and Zn 0.0428 (all in $mg.kg^{-1}$). The method exhibited satisfactory precision (relative standard deviation 4 – 11%), high analytical recoveries, linear responses of least 4 orders of magnitude accuracy and low contamination susceptibility.

Acknowledgement: Financial support from the Ministry of Education, Youth and Sports of the Czech Republic within project MSM 0021627502 used in this work is greatly appreciated.

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NEW T-SHAPED GRAPHITE FURNACE FOR AAS USED FOR TRACE ELEMENT ANALYSIS IN HIGHLY CONCENTRATED MATERIAL

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Graphite Furnace AAS is a powerful tool for trace element analysis in various kinds of materials. Despite of the fact that several background correction systems are available the efficiency of background correction is depending on the system itself, the kind of matrix compounds, and the concentration of the matrix. In many cases a complete correction of the background is not possible. Increasing amount of background signal can cause dramatic change of the analyte signal with the fact that in many cases the chap of the analyte signal cannot be used for quantitative analysis. This is e.g. the fact for the analysis of not diluted urine. This drawback reduces the application of GF-AAS for trace element analysis in complex matrix.

If we could separate the analyte from the background signal we would expect minimized influence of background signal on analyte signal. The classical setup of GF-AAS does not provide us with the possibility to separate both signals. A previous work with two-step atomizer by Grinshtein offers the first possibility of separation [1]. We developed consequently the idea of two-step system into the direction of best separation of the two signals. Finally we found the solution in a dynamic flow system with AAS detector. We designed a new T-shaped graphite furnace with one power supply system for heating of the furnace. The sample solution is introduced into one arm of the furnace. The evaporated compounds and particles are transported by an Argon gas stream perpendicular through the other graphite tube of the T-shaped furnace. Within the sampling arm different types of materials being introduced and used as chromatographic column for separation of analyte and matrix gas volume. Perpendicular to the gas stream the radiation beam from e.g. hollow cathode lamp of an AAS-system interacts with atoms in the small measurement zone.

Results of the new T-shaped graphite furnace with AAS-detection show e.g. complete separation of analyte and matrix signals of undiluted urine sample. This system offers advanced possibilities in the determination of trace elements in samples with high amount of matrix. The T-shaped furnace is designed in such a way that it fits directly in normal classical graphite furnace system commercially available.

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DETERMINATION OF TRACE ELEMENTS IN STEELS BY GF AAS

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The monitoring of low concentration of trace elements in special high-grade steels and cast steels is very important from the metallurgical point of view. The demands for the precise determination of As, Sn, Sb, Bi, Cd and Pb in steels in the concentration levels of 10^{-4} – 10^{-3} % are raising recently, so the procedure of the determination of these elements by atomic absorption spectroscopy with electrothermal atomization was elaborated and applied in the chemical laboratories department of Trinecke zelezarny.

The samples in form of steel chips were mineralised in hydrochloric and nitric acid in the high-pressure microwave digestion system. The µg/l concentration level was obtained by digestion of 1g of sample into 100ml volume and ten-fold dilution before the measurement.

Mixed chemical modifier Pd–$Mg(NO_3)_2$ was used for the thermal stabilization of cadmium and lead, whilst only $Mg(NO_3)_2$ was used for stabilization of tin. Antimony, bismuth and arsenic were stabilized by Ni. The correct sample injection and the drying step were set up using GFTV technique.

The analytical ranges 1–50 µg/g and 1-100 µg/g in solid samples were studied for these elements with exception of cadmium, which was measured in the range 1 – 10 µg/g in solid sample.

The validation of analytical method was done by analysing certified reference materials: GBW 01360, GBW 01362, NIST 362, GBW 01619, GBW 01620, ČKD 228, IMŽ 1.7/4, IMŽ 1.21/1, EuroNo.289-1, EuroNo.097-1 and also by taking part in CNAL Proficiency Testing Program T0127 Determination of impurity elements in pure iron.

The GF AAS technique is very sensitive and precise method for analyses of trace elements in steels. Limits of detection are suitable for the metallurgical requirements for these determinations. The Zeeman background correction eliminates spectral interferences due to iron matrix without necessity to use any other additional separation technique.

CERTIFIED REFERENCE MATERIALS AS A TOOL FOR QUALITY ASSURANCE OF ENVIRONMENTAL MEASUREMENTS

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The importance and role of matrix reference materials in analytical geochemistry is well established. Certified reference materials enable laboratories to assure quality of the environmental measurements, and reliable and comparable results to be obtained. The Geoanalytical Laboratories has undertaken a "Programme of Metrology Development in Slovak Republic" and research projects "Reference Laboratory of Ministry of Environment of Slovak Republic for Geology and Analyses of Geological Material and Rock Environment"to develop a series environmental and geological reference materials.

Since 1998 have been prepared and certified five reference materials: natural zeolite CRM – Z1, natural bentonite CRM – B1, black coal fly ash CRM – EVO1, city waste incineration ash CRM – SKO1 and contaminated soil CRM – KZ1. Raw candidate reference materials were collected from twenty-five to one hundred-fifty kilograms. The natural zeolite was sampled in the deposit Majerovce situated close to the city Vranov nad Topľov, natural bentonite in exploited deposit Stará Kremnička- Jelšový potok, contaminated soil in locality Zlata Idka close to the city Košice, black coal fly ash was collected from power plant Vojany and city waste incineration ash from incinerator Košice.

Typical procedures for processing of all reference materials were drying, crushing, grinding, and quartering RMs into final amount of twenty-five kg RM, sieving, testing of grine size and bottling. The homogeneity test of all five candidate reference materials was performed prior to the certification on series of ten to twenty units (bottles) randomly selected from batch of five-hundred bottles that have been packed in their final form. The stability testing was performed when homogeneity of candidate reference material has been demonstrated by X – ray fluorescence spectrometry.

The interlaboratory comparative tests and one-stage nested design according ISO Guide 35 was used for the certification of reference materials. From twenty-three to thirty-seven laboratories from seven to thirteen countries took part in the certification of chemical composition of candidate RMs. All participants had experience in the analysis of similar types of samples and were requested to carry out three independent analyses. The certified values were calculated as the arithmetic mean of laboratory means after excluding of outlying values. The expanded uncertainty was evaluated according to, requirements of Guide to the Expression of Uncertainty in Measurement, ISO 1993.

It was confirmed that the most frequent analytical methods applied in laboratories for determination of major (silicate) components of RMs were inductively coupled plasma atomic emission spectrometry and X – ray fluorescence with material melted and for quantification of contents of trace components were used inductively coupled plasma mass spectrometry and X – ray fluorescence with material pressed.

There were estimated 27 certified and 33 non-certified compounds in natural zeolite CRM – Z1, 43 certified and 23 non-certified compounds in natural bentonite CRM – B1, 27 certified and 33 non-certified compounds in contaminated soil CRM – KZ1, 34 certified and 35 non-certified compounds in black coal fly ash CRM – EVO1 and 31 certified and 40 non-certified compounds in city waste incineration ash CRM – SKO1.

DETERMINATION OF SOME ELEMENTS IN SAMPLES OF EMISSIONS TRAPEED ON FILTERS BY ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

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Big emphasis is layed for improvement of environment in nowadays . Atomic absorption (AAS), atomic emission (AES) and X-ray fluorescence spectrometry (XRF) are high-speed and accurate techniques for determination of elements in emissions. Producers of emissions of solid contaminate elements have responsibilities to monitor amount of these harmful elements. For this purpose are using bleeding facilities where samples of emissions are collected on the air filter. Air filter is analysed and amount and concentration of elements are determining.

In Geoanalytical laboratories we used to have for determination of elements in air filters all presented instrumental techniques. For AAS and AES it is necessary to decompose the filter with acids and solution to analyse by these techniques. X-ray fluorescence spectrometry is non-destructive analytical technique what we can use directly without decomposition of sample. Advantage of this method of determination of elements is high-speed, wide concentration range, non-destructive analysis (sample after analysis remains intact and can be analysed by another technique and determined additional elements), high reproducibility and economic aspect of analysis.

In the lecture will be presented development of the method for determination of some elements in samples of emissions trapeed on filters by ED XRF spectrometry and comparison of results with AAS and AES ICP methods.

Method development consist selection of filters, preparation of reference samples- application of certified reference materials on filter, optimalization of working conditions, selection of measuring lines for elements, voltage and current for X-ray lamp, choice suitable evaluation method and preparation of calibration curves for selected elements, validation of method (precision, accuracy, recovery, limit of detection and limit of quantification) and comparison of results for real samples by AAS and AES ICP methods.

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ON-LINE ELECTROCHEMICAL PRECONCENTRATION OF TRACE METALS FOR GF-AAS

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Porous flow-through electrodes have been found to be useful for trace element preconcentration and consequent electrochemical stripping analysis of aquatic samples. The paper presents some original flow-through designs for on-line electrochemical enrichment for atomic absorption spectroscopy based on exhaustive electrochemical deposition in porous electrodes. The cell design plays an important role in the efficiency of the preconcentration procedure. The void volume of the cell should be negligible to minimize dispersion of the analyte after stripping. Since the electrochemical signal does not need to be recorded, a compact two-electrode cell can be used. Various electrode and cell designs will be discussed.

The procedure was optimised and validated for preconcentration and consecutive AAS measurements of trace metals in water samples, such as Mn, Hg, Cr, Zn, Cd, Pb.

If coupling a preconcentration unit to a graphite furnace, there might be some technical problems in on-line transporting the enriched sample to the furnace. The paper presents a simple but reliable pneumatic system enabling the transport of the sample zone to the furnace with high efficiency. The procedure is based on sending the zone of the enriched sample from the cell to a 50 μl sampling loop followed by the transport of the content of the loop to the furnace by air flow. Here, virtually no dispersion of the sample zone occurs. The procedure is demonstrated on the determination of Arsenic traces in water samples. Arsenic is collected from the sample acidified with hydrochloric acid in a gold-coated porous electrode. In the next step the cell is filled with diluted nitric acid and the Arsenic deposit is electrochemically dissolved into it and is transported to the sampling loop. Then, the loop is switched to the airflow carrying the sample zone to the pre-heated furnace.

Acknowledgement: This work was supported by Slovak Grant Agency of Science Vega, project No. 1/2464/05.

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MAGNETICALLY MODIFIED BENTONITE AS A POSSIBLE CONTRAST AGENT IN MRI OF GASTROINTESTINAL TRACT

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The role of magnetic resonance imaging (MRI) as important medical diagnostic method increases at last years. On the one hand, MRI shows a very good sensitivity to tissue differences. On the other hand MRI is an expensive, but risk-free procedure. Partially, the application of MRI in gastrointestinal tract is limited by various problems, including the necessity to use the oral contrast agents for the improvement of the image contrast.

A composite of superparamagnetic iron oxide nanoparticles and mineral matrix, which can be used as an oral contrast agent for MRI of GI tract, has been synthesized. Magnetic modification of natural bentonite is two step process. First step is based on replacing original interlayer cations by iron (II) cations and adsorption of another amount of these cations on the mineral surface. Second step is their conversion to magnetic iron oxide, maghemite or magnetite. Nanoparticles of superparamagnetic magnetite or maghemite guarantee contrast effect and bentonite could act as inert matrix reducing absorption of iron and as an agent improving dispersion of iron oxide particles in whole volume. Both components are non-toxic and low-cost.

A composite of iron oxide nanoparticles and mineral matrix has been studied by XRF analysis, X-ray diffraction, Mössbauer spectroscopy, transmission electron microscopy, nuclear magnetic resonance and magnetic resonance imaging. Magnetite, superparamaagnetic magnetite and interlayer Fe^{2+} have been identified by Mössbauer spectroscopy in the nanocomposite. The correspondence between hyperfine parameters and iron oxide particle size has been confirmed using the transmision electron microscopy. The characteristic relaxation times have been determined for colloid water solutions with various concentration of iron oxide. It is obvious, that iron(III) oxide nanoparticles shortcut the relaxation time, which serves to decreasing the MRI signal.

The optimal concentration of nanocomposite "iron oxide nanoparticles-bentonite", when the MRI signal is fully reduced, has been determined for using this composite as the negative oral contrast agent.

STATE OF THE ART IN DETERMINATION, FRACTIONATION AND SPECIATION ANALYSIS OF ALUMINIUM IN ENVIRONMENTAL SAMPLES BY SPECTROCHEMICAL ANALYTICAL METHODS

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The direct determination of total Al concentration and concentration of various Al fractions and species is a difficult analytical task. A number of different procedures have been developed in order to distinguish between the various Al chemical forms in environmental samples. The separation techniques often employed in the fractionation and speciation analysis of Al can be divided up by their principles, e.g. methods based on size or mass exclusion, kinetic and/or binding strength discrimination, chromatographic and electroseparation techniques and computer simulations. The spectrometry detection techniques coupled with these separation methods played an important role in the fractionation and speciation analysis of Al during the last ten years. Atomic and molecular spectrometry, mass spectrometry and X-ray spectrometry are often used for this purpose. In this research various results are discussed and some general comments and remarks on sample storage and pretreatment, and separation and spectrometry detection methods used for Al prior to its determination, fractionation and speciation analysis are pointed out.

Acknowledgement: The work was supported by Science and Technology Assistance Agency under the contract No. APVT-20-010204 and Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences under the contracts Nos. VEGA 1/2439/05 and VEGA 1/3561/06.

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SPECIATION OF ELEMENTS IN CEREALS AND PSEUDO-CEREALS FLOURS

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Phosphorus, manganese, iron, cobalt, nickel, copper, zinc, and molybdenum species fractions were studied in maize, amaranth and rye flour and the buckwheat semolina. Total and extractable contents of elements were determined by ICP-MS. Extracts of all materials were prepared using 0.02 mol/l Tris-HCl buffer solution (pH=7.5). Extracts were analysed by size exclusion chromatography (SEC) using a Superdex 75 HR 10/30 column on-line coupled to an ICP-MS. The 0.02 mol/l Tris-HCl buffer solution, pH 7.5 served as the mobile phase. The quantification was performed by post-column injection of standards technique. Maize, rye and buckwheat samples exhibited similar pattern of element selective chromatograms: cobalt, copper, nickel, zinc and molybdenum compounds were found in the low molecular weight region (M_r 1–2 kDa). Chromatograms of Co, Mo, Ni and Zn species in amaranth extracts correspond with this pattern too. However, Cu is also bound in a medium-molecular weight fraction (M_r~40 kDa) and in a high-molecular weight one (M_r>150 kDa). Fe extracted from buckwheat and amaranth samples was bound in a high-molecular weight fraction (M_r>150 kDa); in case of maize and rye samples the extractable portion of Fe compounds was very low. The main fraction of phosphorus compounds was found in the approx. 3.5 kDa region, however appreciable amount of phosphorus was found in low-molecular weight region too. The main part of Mn in all extracts is present in a labile complex or an ionic form.

The binding capacity of extracts was tested by spiking with cupric ions; copper was chosen since it forms the most stable complexes. In cases of maize, rye and buckwheat extracts practically all copper was bound to low molecular mass compounds. Chromatographic recovery remained close to 100 % up to Cu^{2+} addition corresponding to approx. 20 multiple of natural copper content. In the case of amaranth extract copper's distribution among proper chromatographic fractions depends on added Cu amount. Up to 5 fold of natural content cupric ions are preferably bound into the high-molecular fraction; after saturation of this fraction the next additions were bound to the low-molecular fraction. The content of Cu in both medium-molecular fractions was only moderately changed.

Fractions rich of trace metals or exhibiting high metal-binding capacity were isolated using preparative-scale SEC and the organic ligands of metals were consequently preconcentrated on Chelex 100 in Cu^{2+} form and eluted by ammonia solution. Low content of sulphur containing amino acids (Cys, Met) and high content of acidic amino acids (Glu, Asp) are typical features of all purified fractions of ligands. No phytochelatins or related peptides were found in MALDI-MS spectra of the isolated low-molecular weight ligands.

MÖSSBAUER, X-RAY DIFFRACTION, AND INFRARED STUDY OF IRON(II) OCTACYANOMOLYBDATE(IV)

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Fe^{II} - octacyanomolybdate (OCM), $Fe_2[Mo(CN)_8] \cdot nH_2O$ was synthesised using different preparation conditions. Low (0.05 mol/dm^3) and high (1 mol/dm^3) concentrations of reactants ($FeSO_4 \cdot 7H_2O$ and $K_4[Mo(CN)_8] \cdot 2H_2O$) were used with the aim to investigate structural arrangements of the resulting OCM. The first apparent difference observed is the colour. Samples prepared by slow diffusion (low concentration) are yellow with a tendency to change their colour to green after being exposed for certain time to normal surrounding atmosphere. High concentration yielded samples which are dark blue in colour.

The compounds crystallize in the tetragonal system. The structure is three-dimensional and highly symmetrical.

We have employed ^{57}Fe transmission Mössbauer spectrometry at room and at liquid nitrogen (77 K) temperature to evaluate positions of Fe ions in the structure. Yellow samples show presence of Fe^{2+} ions only with two nearly equally coordinated tetrahedral sites. The structure seems to be rather unstable and shows deviations from the original arrangement after being exposed to evacuation and/or low temperature. Slight deterioration of the structural arrangement is observed also in green samples. Blue samples prepared from high concentration reactants are the most stable ones. At the same time, they exhibit also trivalent Fe ions in octahedral sites.

Findings from Mössbauer spectroscopy are correlated with the results obtained from X-ray diffraction as well as infrared spectroscopy.

QUALITY CONTROL OF BIODIESEL USING A SIMULTANEOUS ICP SPECTROMETER

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

Biodiesel is a mature fuel with a strictly specified qualitative minimum standard as described in the European standard DIN EN 14214. The major producers and distributors of biodiesel have joined forces in the “Arbeitsgemeinschaft Qualitätsmanagement Biodiesel e. V.” (AGQM – Working Group for Quality Management of Biodiesel). AGQM has set up a controlled quality management system (QM) ensuring a high and long-term unvarying fuel quality. This describes not only the selection of raw material and production processes but also storage and transfer as well as transport of biodiesel.

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

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

TRENDS IN ION-BEAM BASED SPECTROSCOPIC TECHNIQUES

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Ion beams offer several spectroscopic techniques that are commonly called "Ion Beam Analysis" – IBA-techniques. According to the working principle, wide range of beam parameters can be used for IBA and various types of analyses can be performed. A typical example is trace element analysis, determination of concentration depth-profiles, accelerator mass spectrometry (AMS), activation studies and many others. The IBA techniques will be briefly reviewed in the paper with emphasis on the techniques that have been established at the Slovak University of Technology and the techniques that are expected to become available at larger accelerators. Corresponding accelerator and spectroscopic technology will be presented and research possibilities of medically optimised accelerator complexes will be discussed systematically. Examples of activation studies will be given.

Cancer therapy with ion beams was started with accelerators originally designed for physics experiments. It was recognized soon that these machines could not deliver optimal treatments because of their technical limitations with respect to therapy needs. The latest trend is to build multi-species accelerators delivering protons as well as light ions. These accelerators may have free beam-time capacity for non-clinical research too, as proposed for example at MedAustron [1, 2]. Materials science using different ion-beam based spectroscopic methods can be an important part of this research. The machine parameters must be, however, optimised for therapy. That is why, the beams that can be available for non-clinical research are defined by a medically-optimised machine design. It is also investigated in this paper, what beams can be offered by a modern medical accelerator.

Acknowledgement: This work was carried out in the framework of the MedAustron Interreg IIIA Project that is funded by the European Union, Republic of Austria and Country of Lower Austria and GSI-INTAS 03-54-3588 Project that is supported by European Community.

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TRACE ELEMENTS DISTRIBUTION AND SPECIES FRACTIONATION IN *BRASSICA NAPUS* PLANT

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The research was concerned with trace elements status in individual parts of the rape: roots, stalks and leaves, and seeds. Roots are able to accumulate large amounts of various metals (on of the dry weight basis): approx. 2 000 $\mu g \cdot g^{-1}$ Fe; 120 $\mu g \cdot g^{-1}$ Mn; 30 $\mu g \cdot g^{-1}$ Zn; 2-8 $\mu g \cdot g^{-1}$ As, Cr, Ni, Cu and Pb; 0.3-1 $\mu g \cdot g^{-1}$ Co, Mo and Cd and 0.1 $\mu g \cdot g^{-1}$ Ag and Tl. However, the transfer of metals into green tissue is limited. The ratios of element contents in green tissue and roots (on of the dry weight basis) are: 10-30 % for Co, Cr, Fe, Mn, Ni and Pb; 50-100 % for Ag, As, Cd, Cu and Zn > 110 % for Tl and Mo. The transfer of elements into the seeds is even lower except for Cu, Zn, Mo and Tl. The ratios of elements contents in seeds and roots (on of the dry weight basis) are: < 20 % for Ag, Cd, Co, Cr, Fe and Pb; 20-60 % for As, Cu, Mn and Ni; 90 % for Tl and 180-190 % for Mo and Zn. The solubility of Fe, As and Pb compounds in Tris-HCl buffer (pH=7.5) was < 10% of total content (for all three parts of the plant). The solubility of other elements ranged from 10 to 60 %. Extracts of all three parts of the plant were submitted to SEC/ICP-MS analysis. While the majority of Co, Cu, Mo, Mn, Ni and Zn compounds is bound in a low-molecular weight fraction (approx. 1-2 kDa), that of As, Ag, Cr, Tl and Pb is present as metal ions or labile complexes. There is only one exception: Tl in extract of seeds is found in three regions of M_r approx. 80 kDa, 5 kDa and 2 kDa, respectively. The recovery of chromatographic separation of Tl compounds was approx. 100 %. The low-molecular weight peaks of compounds of P and S were poorly separated from those of metals. Subsequently the low-molecular weight fraction of the seeds extract was isolated on preparative-scale SEC and refined by affinity chromatography on Chelex 100 in Cu^{2+} or Tl^{+} form, respectively. Both refined fractions of ligands contain large amount of Cys, Asx, Glx, Gly and S-carboxymethylcysteine. However, no phytochelatins were found in MALDI-MS spectra.

UNCERTAINTIES SOURCES IN THE FRACTIONATION ANALYSIS OF THE GRAVITATION DUST SEDIMENT

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The fractionation analysis is whatever process of classification (isolation and quantification) of element forms from a sample according to their similar physical or chemical properties [1]. One of the methods of the isolation of element forms is the single-step extraction [2]. For the quantification of elements in the extracts is possible to use of some adequate spectral method. These two base parts of fractionation analysis affect of the total uncertainty value of fractionation analysis (the combined standard uncertainty u_C).

This work presents the values of uncertainties native from different operations carried out in process of the fractionation analysis of gravitation dust sediment samples. For the extractions 0.05 mol dm^{-3} Na_2EDTA and 2 mol dm^{-3} HNO_3 were used. For the determination of Cd, Cu, Pb, and Zn in extracts the FAAS method was applied. The standard uncertainty of the type A (u_A, RSD / %) by statistical evaluation 10 repeated measurements of analyte concentrations in one extract was defined. The standard uncertainty of the type B involves uncertainties of dilution (u_{BD}), purity of chemicals (u_{BCH}), preparation of calibration solutions (u_{BC}), weighting of the sample for extraction (u_{BW}), and uncertainty of the extraction (u_{BE}).

The values of uncertainties obtained by evaluation of fractionation analysis by using of 0.05 mol dm^{-3} Na_2EDTA as extracting reagent are summarized in Table 1. The values of the uncertainties (u_A, u_{BE}, u_B, u_C) obtained by application of 2 mol dm^{-3} HNO_3 were lower in comparison with that obtained by application of 0.05 mol dm^{-3} Na_2EDTA, with the exception of Zn.

Tab 1. The uncertainties of fractionation analysis (extracting reagents 0.05 mol dm^{-3} Na_2EDTA)

Element	uncertainties / %						
	u_A	u_{BCH}	u_{BC}	u_{BW}	u_{BE}	u_B	u_C
Cu	1.88	0.062	0.47	0.02	3.19	3.22	3.77
Zn	1.87		0.47		4.71	4.73	4.90
Pb	3.32		0.63		9.57	9.59	10.15
Cd	52.7		0.95		84.4	84.41	99.5

From the results obtained in this work it can be stated that the main source of uncertainties in the fractionation analysis is the extraction process.

Acknowledgement: This research was supported by projects VEGA No. 1/3149/06 and APVV No. 20-0094-04.

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SELECTED APPLICATIONS OF MW ENERGY IN LABORATORY

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Beside the multimode systems based on the use of microwave ovens in analytical laboratories the development of high pressure steel jacketed vessels led to readable improvement of digestion vessel safety and reliability. High pressure modular digestion system Ertec Magnum elaborated by the Author is capable of processing of up to 5 g of organic sample. Each module of PC controlled system has one vessel which is energized from a magnetron with programmed power level and it is equipped with temperature and pressure measuring means. Pressure measurement is very fast: it can stop the delivery of microwave energy one millisecond after the pressure approaches the prescribed limit. Temperature measurements using thermocouples are always retarded nevertheless they may be valuable when a steady state condition is attained. For the new model it is planned to introduce a continuous monitoring of power reflected which would enable the end–point detection in digestion procedure along with protection against the instrument failure when working on dry.

Temperature of digestion and it can be elevated above 260 °C by elevating the operation pressure up to 45 bars using regular acids like for instance HNO_3. In open digestion system which operates at atmospheric pressure one can also reach high temperatures but only with the use of highly boiling acids like for instance sulfuric acid. In that case addition of H_2O_2 as oxidizing agent may be desired. The new open digestion system with 250 mL volume glass vessel is equipped with double temperature measurement. There are two sensors, one at the vessel's bottom and the second one at its throttle. The temperature difference between the sensors enables control of boiling intensity and detection of the boiling temperature which can previously be unknown to the user. There is set of new digestion procedures and one can also use those developed years ago by Prolabo or CEM but as far the open microwave system found its application to carry out microwave-driven organic syntheses.

Despite of wet methods of microwave chemistry research is carried out on application of MW power in excitation of plasma both at atmospheric and reduced pressures. Glow discharge generated within microwave powered Grimm lamp which is to be employed to excite the species of samples in plasma, as ion source for MS or as a generator of dry aerosol for the purposes of emission or absorption spectroscopy.

CALIBRATION PROCESS AT THE OPTIMIZATION OF THE NOVEL SPECTROMETRIC TANDEM TECHNIQUE

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The proposed tandem technique is based on powder sample evaporation in the high-power controlled direct current (DC) arc in the cell for aerosol production and follow transportation of sample aerosol to the Marinković plasma source. From the group of very toxic elements with strong trend of accumulation in the biological systems B, Cr, Mn, Ni, and V elements were determinated. From the group of toxic and delimited toxic elements were Al, Ca, and Mg elements evaluated. In order to find out effeciency of the new tandem method, the exploratory statistical analysis of the one-dimensional input data was performed before calibration process study. Obtained intensity sets were worked and statistically evaluated by the statistical software QC. Expert^{TM} 2.5 [1]. Results confirmed, in most cases (Al, Fe, Mg, Ni, V), normal and homogeneous character of intensities distribution of the chosen spectral lines which were used for optimization of the analytical calibration. The analytical line was designed by least square method by above mentioned software and in accordance with data in literature [2]. At first, the original set of calibrated values of the intensities was worked and then so called „whitewash" set free of leverages and out lyers was defined. After this manner, confidentional limits has narrowed and precision of the calibration has increased [3] whereupon in the other cases the data processing was analogical. Calibration possibilities of the model oxide samples in the graphite matrix of the listed elements without and with spectrochemical additives were studied. AgCl has shown as optimal spectrochemical additive. Importance of concentration range, in term of linearity and precision, by using of synthetic matrix and reference standards was studied too. Values of the limit of determination $c_L \in \langle 0{,}0009; 0{,}001 \rangle$ % and coefficient of determination $R \in \langle 96, 98 \rangle$ % were the most advantageous for the concentration range $\Delta c \in \langle 0.001; 0.04 \rangle$ %. This range seems to be optimal for analytical calibration with synthetic standards. In the case of calibration with SiC standards samples were achieved extremely low sensitivity values of the calibration lines, unfavourable c_L values and R values were low, in the range of 80 – 90 %. These adverse results can be caused by narrow concentration calibration range as well as inadequate grain homogenity of the powder standards. From these reasons, recovery testing was performed for 0.02 % concentration in the $\Delta c \in \langle 0.001, 0.04 \rangle$ % concentration range. There are typical for calibration lines high correlation coefficient values and determination coefficient values too. Results of the agreement test of the tested concentration ($c(X)_0$) and calculated concentration ($c(X)_{calc}$) confirmed a statistical agreement for B, Ca, Fe, Mg, and Ni elements. Disagreement in the case of Al, Cr, and V is probably caused by the above mentioned homogenity of the tested sample.

Acknowledgement: This work was supported by the grant project 1/3149/06 and APVV 20-009404 project.

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SURFACE ANALYSIS BY CEMS – AN OVERVIEW OF THE METHOD

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Conversion Electron Mössbauer Spectroscopy (CEMS) is an alternative to the more commonly used transmission or scattering Mössbauer spectroscopy. The same recoil-free nuclear reso-nance is the fundamental principle of the method, however, different product of the resonance is utilized. Instead of 14,4 keV photons (for the case of ^{57}Fe), 7,3 keV conversion electrons are detected. Because of their small penetration depth (up to ~350 nm), only electrons from the surface can escape from the sample; the others are absorbed by the sample material. Thus, we obtain information about the sample surface in this way; the information about the bulk is suppressed.

Apart from this advantage, there are drawbacks, however. It follows from the principle of the measurement alone, that because of absorption of electrons in the bulk, approximately 99 % of resonance events are lost for the measurement. This is why the CEMS method is rather long-lasting as compared with the transmission geometry.

Photoelectrons are another serious drawback. As most of them can not be efficiently separated from the resonance descending conversion electrons, they create noise and increase the non-resonant background of CEMS spectra, thus extending the time of measurement.

Atmospheric corrosion as a surface phenomenon was studied on amorphous and nanocrystal-line samples of FINEMET $Fe_{73,5}Cu_1Nb_3S_{17,5}B_9$ and NANOPERM $Fe_{27,5}Zr_{6,5}B_6$. After exposi-tion up to ten months, γ-FeOOH phase was found to be the main corrosion component. The results obtained from CEMS spectra confirmed the best corrosion resistance for nanocrystalline FINEMET.

Nanocrystalline ribbons of $Fe_{81-x}Co_xNb_7B_{12}$ (x=20÷40) Hitperm alloys were investigated as to their basic magnetic properties as well as to the influence of macroscopic heterogeneity. Different portions of crystalline components were observed on the surface as compared to the bulk, using CEMS and transmission geometry MS measurement, respectively. The heterogeneity is generally more pronounced in Ar annealed samples than in the vacuum-annealed ones.

RENISHAW IN VIA REFLEX RAMAN MICROSCOPE AND COMBINED SPECTROSCOPY TECHNIQUES

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Renishaw manufactures a wide range of spectroscopy products, including Raman microscopes, compact process monitoring spectrometers, structural and chemical analysers for scanning electron microscopes, diode lasers, and state-of-the-art cooled CCD detectors, for end-user and OEM applications. The primary products are the inVia Raman microscopes and the RA series of Raman analysers, which exploit the Raman effect to identify and characterise the chemistry and structure of materials in a non-contacting, non-destructive manner.

InVia Raman microscopes are high sensitivity systems with integrated research grade microscopes, enabling high resolution confocal measurements. InVia Raman microscopes support multiple lasers, with automatic software switching of excitation wavelength.

“Bench top” Raman microscopes have dominated the market for the last ten years. Their ease of use has led to an expansion in the use of the technology over many diverse fields. New demands are now being made to move away from using optical microscopy to visualise samples. This paper illustrates the recent advances in combining other microscopes to identify the sample area of interest. We have worked with other vendors to combine Raman and FT-IR microscopes, Raman microscopy with atomic force and near field scanning microscopy and scanning electron microscopes to provide Raman analysis from inside an SEM.

The SEM structural and chemical analyser (SEM-SCA) combines both SEM and Raman techniques into one system, so that users can take full advantage of the high spatial resolution afforded by the SEM, and the chemical information revealed by Raman. The nature of Raman spectroscopy means that its performance is unaffected by the SEM environment - high vacuum (HV), low vacuum (LV), environmental (ESEM), and high or low (cryogenic) temperatures. The advantages of this method from the microscopy view are that SEM overcomes the limitations of optical microscopy with respect to: (a) depth of field - the SEM retains good depth of field even at high magnifications; (b) contrast - SEM contrast mechanisms can easily distinguish optically identical or similar materials; and (c) spatial resolution - SEM spatial resolution is typically 3-4 orders of magnitude better than optical microscopy.

Raman spectroscopy meets unfulfilled SEM/EDS analytical requirements: (a) EDS yields elemental information only whilst Raman provides structural, chemical, and physical information; and (b) EDS is poor for analysing light elements whilst Raman is sensitive to light element chemistry

The instrument can also perform photoluminescence and cathodoluminescence studies as the SEM-SCA collection optics are fully compatible with both spectroscopies.

Examples are given from various application areas of materials science. The benefits of being able to record Raman, CL and PL data from the same spot from a given sample will be highlighted, as with the benefits of using the combination of EDS with Raman spectroscopy.

THE APPLICATION OF AFS TO THE DETERMINATION OF HG AND SE IN ENVIRONMENTAL SAMPLES

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Atomic fluorescence spectrometry (AFS) is an exceptionally sensitive analytical technique which has found its way to analytical chemists relatively slowly. However, in recent years, an increased interest in this technique has been observed. The capacity of AFS in the determination of Hg and Se in various types of water, water-related and environmental samples is shown, evaluated, discussed and compared with results achieved with atomic absorption spectrometry (AAS).

ON-LINE ANALYSIS OF CLEANNESS CHARACTERISTICS AND INCLUSION COMPOSITION BY OES SPARK-DAT IN TRINEC STEEL WORKS

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In the beginning of 2005 new OES analyser ARL 4460 with Spark-DAT technique was introduced into operation in the BOF steel plant laboratory of Trinec steel works.

Spark – DAT carries out Digital Acquisition and Treatment of every spark signal separately. Considering that a single spark hits a very small area, the resultant light pulses contain information on the local material composition. Therefore it affords a spectacular growth of the analytical information, in improving analytical performance or providing new information like cleanness indices and inclusions determination. Now both digital acquisition and processing algorithms are fully integrated into the instrument software WinOE. It allows the mixture of Spark DAT and conventional acquisition channels in analytical programs. In this way a single analysis can simultaneously give overall concentrations from the conventional analysis as well as information about inclusions or soluble/insoluble distribution from Spark – DAT.

In collaboration with technology and research department the method of on-line analysis of chemical composition of inclusions and cleanness indices on samples taken during steel making process was elaborated. Now after the spectrometric analysis information about total chemical composition as well as information about cleanness indices and chemical composition of some inclusions is sent to the steel plant operator.

This information is very helpful for technologists and now is applied in the following areas:

-monitoring of steel cleaning process during secondary metallurgy treatment
-introducing of the controlled inclusions modification technology (checking of inclusion shape and composition)
-development and improvement of new steel grades with higher added value
-introducing of new steelmaking technology (new additives, shortening of the treatment time) with on-line steel cleanness characteristics assessment

MATRIX ENVIRONMENTAL CERTIFIED REFERENCE MATERIALS: PRODUCTION AND CERTIFICATION OF A CANDIDATE CRM CZ 7006 „PCDD, PCDF AND TOXIC PCB IN A SEWAGE SLUDGE“

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New Trends in the production of matrix certified reference materials are reviewed and discussed. Problems encountered at individual steps of the preparation (sourcing, processing, homogeneity and stability study, certification campaign) of the candidate CRM CZ 7006 („PCDD, PCDF and toxic PCB in a sewage sludge of mixed origin“) are described. Target parameters of the material and parameters of the real product are compared and evaluated.

DETERMINATION OF SOME ORGANIC COMPOUNDS IN THE FORM OF ION-ASSOCIATES WITH POLYMETHINE DYES

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We investigated the conditions for the formation and extraction of ion associates of some organic compounds (nitrophenols, dinitrobenzoic acid, nitrobenzoic acid, phtaleic acid etc.) with polymethine dyes. The method is based on the reaction of organic compounds with above-mentioned dye reagent to form the colored ion associates, which are extracted by liquid solvents. For the formation and extraction of ion associates, it's required to create in aqueous phase the conditions for the domination of components of ion associates: anion of organic compounds and cation of dye. For example, in contradistinction to trinitrophenol, which is extracted by investigated reagent in the wide acidic range pH 3-10, dintrophenol is extracted only from alkaline medium pH 7-10, and mononitrophenol is practically not extracted. Consequently, it is possible to determine both substances in a mixture. The appropriate reaction conditions have been established. The main spectrophotometric characteristics were determined. New, simple, rapid and sensitive spectrophotometric methods have been developed for the determination of nitrophenols, dinitrobenzoic acid, nitrobenzoic acid, phtaleic acid and diclofenac.

DETERMINATION OF SELECTED METALS IN URINE BY INDUCTIVELY COUPLED PLASMA ORTHOGONAL TIME-OF-FLIGHT MASS SPECTROMETRY

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An investigation was carried out to explore the analytical capabilities of a commercial inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometer (Optimass8000 ICP-*oa*-TOFMS, GBC Scientific Equipment Pty Ltd., Australia) for the reliable determination of several metals in human urine. Under an optimum choice of instrumental conditions matrix effects were insignificant at 2 g l^{-1} of NaCl and the determination was free of interferences even for elements, which are known to be difficult to analyze in samples containing chloride matrix using conventional quadrupole (Q-) ICP-MS instruments. In our case there was no observed influence of high chloride concentration on isotope ratio accuracy measurement. The accuracy and precision of the method was evaluated using commercially available reference urine samples and were found to agree within 0-15 % of recommended values. The described method, in which the sample preparation step consisted of a simple 10-fold dilution of the urine sample with water, is thus suitable for the rapid simultaneous determination of metals in urine in a wide range of concentrations.

Acknowledgement: Financial support from the Ministry of Education, Youth and Sports of Czech Republic (project No. 0021627502) is gratefully acknowledged.

FAST MONITORING OF THE ELEMENT MOBILITY CHANGES IN ENVIRONMENTAL POLLUTION

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The mobility of elemental contaminants through the environment is basic information in terms of environmental protection. The evaluation of contaminant mobility in water solutions is realised through the isolation and identification of organic and inorganic elemental species, where it is possible to use complexing agents. For evaluation of the mobility and potential mobility of the elements in other environmental parts (e.g., soils, sediments, sediment dusts, etc.) fractionation analysis is usually used and obviously is realised in the form of sequential extraction. The extraction into a complexing agent could be a solution for the selective separation of elemental species and a simpler alternative for investigating the mobility or potential mobility of elements in the individual segments of the environment. Through single-step extraction into a suitably chosen strong complexing agent, it is theoretically possible to release the total non-residual fraction of the element from the source [1].

This method offers the possibility of combining or partially substituting periodical tests of sedimentary and soil systems by simple and sequential extractions (into suitably selected and tested complexing agents). Single-step extraction into a strong complexing agent could be used as an economical and time saving supplementary test to the sequential extraction procedures recommended and attested by IRMM (Institute for Reference Materials and Measurements). Thus, extraction into a complexing agent could be a rapid means of assessing sources and characterising contamination inputs into the environment (soils, sediments, water solution, biotope); a means of gathering preliminary information about the lithogenic or anthropogenic origin of the pollution; a way of checking the levels and simulation of the input of mobile pollutants in the water biota in a incomparably shorter time and with lower financial costs than an extraction sequence (by using single step extraction into complexing agent) [2, 3, 4].

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IRON OXIDE NANOPARTICLES FROM THE SOLID-STATE SYNTHESES: REACTION MECHANISM, STRUCTURAL AND MAGNETIC PROPERTIES BY VIEW OF MÖSSBAUER SPECTROSCOPY

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The Fe-O based nanoparticles and nanocomposites synthesized by thermally induced solid-state reactions with using of suitable Fe-precursors were found to be very effective in various applications including catalysis, magnetic resonance imaging, drug delivery or water treatment. ^{57}Fe Mössbauer spectroscopy represents a powerful tool in monitoring the reaction mechanism and structural and magnetic properties of the iron oxide nanoparticles [1,2]. The significant contribution of a technique to the solution of the solid-state reaction mechanisms will be demonstrated with the examples of the thermal decomposition of Prussian Blue [3] and the oxidative conversion of iron(II) oxalate [4]. An application of the *in-situ* high temperature Mössbauer analysis allowing to identify the reaction intermediates directly during the thermal process will be shown in the study of the thermal transformation of potassium ferrate(VI) [5]. The structural and magnetic properties of various nanoscopic iron oxides prepared by solid-state route will be presented, including rare nanocrystalline β-nad ε-Fe_2O_3 polymorphs, ultrasmall (1-2 nm) amorphous iron(III) oxide nanoparticles or magnetic nanocomposites of Fe_3O_4 with the biocompatible MgO matrix, which are applicable in medicine for a cancer therapy using hyperthemia or in biomagnetic separation processes [6]. The magnetic regime of iron oxides below the ordering temperature will be discussed with respect to their in-field Mössbauer spectra yielding superior data on the number of iron atoms in the non-equivalent structural positions, a degree of the spin-frustration and the spin canting angle. Moreover, the method, if applied at low temperatures in the sufficiently high external magnetic fields, offers the unique possibility of distinguishing of the isostructural magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) nanoparticles, which is one of the crucial problems of the recent iron oxide research.

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THE ROLE AND THE APPLICATION OF AAS TECHNIQUES IN SPECIATION ANALYSIS OF THE ELEMENTS IN ENVIRONMENTAL SAMPLES

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Speciation analysis of the elements, i.e., the determination of different compounds and/or oxidation states or of the fraction soluble under particular conditions instead of the total content, has found more and more attention over the past decades. The main reason is that the toxicity or bioavailability of an element can be several orders of magnitude different, depending on the chemical forms or the solubility.

Deduced from the number of publications, there is a steadily increasing in speciation analysis over the past years. Atomic absorption spectrometry (AAS) is a comparatively inexpensive, robust analytical technique that is available in most laboratories. It is characterized by a high selectivity and specifity. There is a variety of rather simple procedures available for the rapid determination of a relevant species or group of species, such as hydride-generation AAS under controlled pH conditions or in the presence of a buffer, and on-line solid phase extraction, coupled to graphite furnace AAS.

In the past years HPLC-ICP-MS shows the highest growth rate among the hyphenated techniques used for speciation analysis purposes, but as soon as the laboratories performing routine analysis, forced by legislation or quality control requirements, are involved in speciation analysis, ICP-MS is the most expensive detector for HPLC and other chromatographic systems. It is anticipated that the simple, rapid and inexpensive procedures, based on AAS detection, will be most readily accepted when routine laboratories are involved in speciation analysis.

In the present work will be on some examples demonstrated the possibilities of using AAS techniques in speciation analysis: speciation of inorganic arsenic using simple speciation analysis, by which the differentiation of arsenite and arsenate, can be performed by careful control of reaction conditions in hydride generation atomic absorption detection; speciation of mercury and off-line combination with HPLC technique; speciation of chromium using solid-phase extraction, carried out by Lichrolut cartridges, using strong anionic exchanger (SAX) to separate Cr(VI) and Cr(III) for determination by FAAS; the methods most widely used to study the distribution of the metal in a solid phase, are based on extraction techniques with different chemical extractants, sequential extraction is now a well-established approach for the fractionation of trace metal content in solid samples, mainly soils and sediments.

Acknowledgement: This work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic VEGA/1/2466/05.

P-1

DEVELOPMENT OF GRAPHITE FURNACE FOR ATOMIC ABSORPTION SPECTROMETRY

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A T-shaped graphite furnace has been developed and installed in atomic absorption spectrometer. The oven was made of non pyrocoated graphite material. With this oven structure the sample could be dried, ashed and atomized in the neck of the oven. No interactions between sample and the light from the radiation source occur. The atomized sample was transferred into the measuring zone with the aid of carrier gas. Atomization and transportation of the analyte atoms and the matrix could take place with a very small time difference, which gave the possibility of measuring the analyte signal with a very small matrix interference even in analysing of samples with a very strong interfering matrix such as urine. Non diluted urine sample could be analysed directly with this system without pyrolysis step, which reduce the analysis time compared to normal furnace systems. Peak height is used in this measurement with a good reproducibility and low interference values. Integration of peak area could also be used. Calibration curves were done for some analyte elements in a standard solution, the working range; characteristic mass and RSD % were comparable with the conventional AAS systems. Lower loss of the analyte atoms through the sampling hole is expected because of injecting the sample into the bottom of the oven being about 9 mm far from the sampling hole as compared with the conventional systems.

Analytical results of real samples will also be presented.

P-2

DETERMINATION OF ZINC, COPPER, CADMIUM AND NICKEL BY FLAME ATOMIC ABSORPTION SPECTROMETRY AFTER PRECONCENTRATION USING SILICA GEL COATED WITH SCHIFF'S BASES

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A method for pre concentration of two valent ions in environmentally related elements like Zn(II), Cu(II), Cd(II) and Ni(II) is proposed by using a minicolumn filled with silica gel modified by Schiff's base (N,N'-Bis(salicylidene)ethylenedi-amine or N,N'-Bis(salicylidene)1,3-propylenediamine). The retained analytes on the prepared sorbent were eluted with a small amount of HNO_3. The metal ions in the eluent were determined by flame atomic absorption spectrometer (FAAS). Two Schiff's bases different in structure have been used to compare the effect of the structure on the separation. Different factors, including the pH of the sample solution, the sample volume, and the amount of the Schiff's base were examined to optimize the conditions for the preconcentration of these metal ions in aqueous solutions. The matrix effect of some different compounds has been also studied to know the separation efficiency of the sorbents. The concentration factors were up to 100.

P-3

NEW SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF GOLD

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A new, simple, rapid and sensitive spectrophotometric method has been developed for the determination of gold. The method is based on the reaction of $[AuCl_4]^-$ with cationic dye 2-[2-(4-Dimethylamino-phenyl)-vinyl]-1,3,3-trimethyl-3*H*-indolium (R) to form a coloured ion associate (IA) which is extracted by organic solvents. The acid-base properties and spectrophotometric characteristics of R were investigated. It was shown that the R can exists in 3 forms: single charged R^+ form ($\varepsilon_{537} = 6.6\times10^4$ L mol^{-1} cm^{-1}), protonated double charged RH^{2+} form ($\varepsilon_{382} = 2.6\times10^4$ L mol^{-1} cm^{-1}), and hydrolysed ROH form ($\varepsilon_{290} = 1.9\times10^4$ L mol^{-1} cm^{-1}). The protonation constant, the hydrolysis constant were found to be $pK_{pr} = 1.43$ and $pK_h = 12.20$, respectively. The reactive single charged form exists in over a wide range of pH, and the aqueous solution of dye is intensively coloured and the colour is stable**.**

The best extractants appeared to be the acetic esters and aromatic hydrocarbons with very good extractability of the IA under minimum extraction of the dye simple salt (blank test). The extraction removed 89-98% of the gold in depending on the nature of extractant.

The influence of various factors on the formation and extraction of IA has been studied and the optimal conditions have been found. The optimum condition for gold(III) IA formation and extraction is acidity within the range pH 1.5-5.0, 0.8-1.6×10^{-4} mol dm^{-3} dye. The absorbance of the coloured extracts is stable for a minimum 24 hours. The molar ratio of components in the extracted IA was determined by various spectrophotometric methods. It was found that Au(III) : Cl^- : R^+ molar ratio is 1 : 4 : 1. In the optimum condition of complexation and extraction the main spectrophotometric characteristics of gold(III) IA was determined. The molar absorptivities are $\varepsilon = 6{,}1\text{-}9{,}2\times10^4$ L mol^{-1} cm^{-1}. Influence of diverse ions was investigated. The determination of gold is not hindered even by 1000 fold of Ni, Co, 500 fold of Pb, Zn, 100 fold of Bi, Cu, Cd, Pt, Rh, Ru, 20 fold of Ag. The determination of gold(III) is strongly hindered only by Hg^{2+}. The suggested method can be useful for the pre-concentration of gold. A method was used for the determination of gold in polymetallic ores.

P-4

ESTIMATING UNCERTAINTY AND QUALITY OF LEAD DETERMINATION IN BLOOD IN THE OCCUPATION EXPOSURE

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The determination of lead in blood of workers occupationally exposed in the accumulator production was considered due to the toxicity of lead. In compliance with Slovak regulation limit, the concentration of lead in blood considered to be harmful in occupation exposure is 700 μg/l. The visit of doctor is recommended if concentration of lead in blood exceeds the level 400 μg/l.

The method for the direct determination of lead in whole human blood is presented. A mixed matrix modifier solution containing nitric acid, ammonium dihydrogen phosphate and Triton was used for preparation of venous blood samples. The blood sample with low lead was used for the method of standard additions for calibration. The peak area was applied for evaluation of lead response. The Perkin Elmer 4100 ZL atomic absorption spectrometer with transversely heated graphite furnace atomiser with Zeeman background correction and lead hollow cathode lamp were used for all analyses.

The validation of method was made using series of spiked blood human samples, for evaluation of accuracy and precision. Limit of detection LOD (13 μg/l) and limit of quantification LOQ (38 μg/l) were both calculated by using method of Upper limit approach, newly recommended by IUPAC.

The previous experience and validation data are suggested as sources of performance information. The method recovery, sample recovery, homogeneity, precision and calibration were identified as a reasonable components of uncertainty. All these information were included to estimate measurement uncertainty compliant with standard ISO/IEC 17025 : 2005. The results of measurements using this method have uncertainty (52-23)% in the working range (70 – 700) μg/l.

Two groups of workers were investigated. The statistically significant difference of lead concentration in blood as impact of occupation exposure was found between the unexposed group and workers occupated in the accumulator production.

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INFLUENCING OF CADMIUM TRANSLOCATION IN *MATRICARIA RECUTITA*, VAR. LUTEA BY THE PRESENCE OF SELENIUM

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Chamomile plant species were classified as cadmium hyperaccumulators [1-3], which is important for both chamomile drug as well as use of this medicinal plant in phytotherapy.

Effects of four cadmium compounds $CdSeO_4$, $CdSeO_3$, $Cd(NCSe)_2(nia)_2$ and $Cd(NCS)_2(nia)_2$ applied at concentrations 12, 24 and 60 μmol dm^{-3} on growth, chlorophyll concentration as well as Cd accumulation in roots and shoots of hydroponically cultivated *Matricaria recutita* plants (var. Lutea) were investigated. Cd contents in chamomile plant organs were determined using AAS.

In the applied concentration range (12 - 60 μmol dm^{-3}) the studied compounds affected significantly neither length of roots and shoots nor dry mass of roots and shoots. On the other hand, the accumulated amount of Cd (mg g^{-1} d.m.) in chamomile plant organs was considerably affected by Se speciation. For Cd we estimated bioaccumulation factors (BAF) for roots and shoots, respectively, translocation factors as well as the portion (from total metal amount accumulated by the plant) occurring in the shoots. Bioaccumulation factors (BAF) correspond to C_b/C_w ratio, where C_b was Cd concentration in the biological material expressed as μmol or μg g^{-1} of dry mass and C_w was Cd concentration in external hydroponic solution in μmol or μg dm^{-3}. The translocation factor corresponds to the ratio of accumulated Cd amount in shoots and roots and thus it depends also on the actual dry mass of these plant organs (similarly as the portion from the total accumulated metal amount by the plant occurring in the shoots).

In the investigated concentration range, independently on the applied compound the BAF values determined for Cd accumulation in roots were higher than those determined for Cd accumulation in shoots. The highest BAF values determined for Cd accumulation in shoots were obtained for $CdSeO_4$. The comparison of the effect of $Cd(NCSe)_2(nia)_2$ and $Cd(NCS)_2(nia)_2$ showed that exchange of S for Se in the NCX^- ligand (X = S or Se; nia = nicotinamide) led to decreased translocation of Cd into the shoots. The corresponding BAF values for $Cd(NCSe)_2(nia)_2$ were similar to those of $CdSeO_3$. At the highest applied concentration (60 μmol dm^{-3}) the studied compounds (with the exception of $Cd(NCS)_2(nia)_2$) decreased total leaf chlorophyll content of chamomile plants.

Acknowledgement: This study was supported by the grant VEGA of Ministry of Education of Slovak Republic and Slovak Academy of Science, No. 1/3489/06 and by Science and Technology Assistance Agency under the contract No. APVT-20-42002.

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P-6

VAPOR GENERATION OF CADMIUM FOR ITS DETERMINATION USING ATOMIC ABSORPTION SPECTROMETRY – RECENT DEVELOPMENTS

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Cadmium is a well-known toxic and persistant pollutant, therefore, it is important to be able to accurately determine its content in all components of the environment. Concentrations of cadmium are often determined using atomic absorption spectrometry techniques, especially, electrothermal AAS (ETAAS) and recently VGAAS. The last mentioned technique has low detection limits, rapid analysis times and the ability to utilize simple and inexpensive instrumentation. The most frequently determined elements are hydride-forming elements such as As, Bi, Ge, Hg, In, Pb, Sb, Se, Sn, Te and Tl. Furthermore, in recent years, determination of other elements, e.g., Cd, Ni, Co, Cu, Fe, Ag becomes feasible.

The determination of trace elements at very low concentration levels is an actual analytical problem. Atomic absorption spectrometry (AAS) with different methods of atomization is frequently used for the determination of metals at ppb and sub-ppb concentration levels. The vapor generation (VG) is powerful sample introduction method to AAS. Among various chemical VG systems, volatile hydride generation is the widely used in analytical atomic spectrometry because of its ease of implementation, low reagent cost, high yield and corresponding analytical benefits that accrue when hydride generation (HG) sample introduction is coupled with atomic spectrometric detection. In this brief review a development of new vapor generation techniques for cadmium determination using photochemical vapor generation [1], preconcentration in graphite atomizers [2] and on quartz surfaces [3] are described.

Acknowledgement: The work was supported by Science and Technology Assistance Agency under the contract No. APVT-20-042002.

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P-7

DETERMINATION OF ARSENIC AND ANTIMONY BY ON-LINE ELECTROCHEMICAL PRECONCENTRATION/GFAAS

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The aim of this work was to develop an on-line coupling of electrochemical preconcentration to AAS method and the utilization of the developed system for the determination of ultra-trace amounts of As in water samples. A flow-through electrochemical analyzer EcaFlow (model GLP 150, Istran, Bratislava) was used as the preconcentration unit with a two-electrode cell. The working electrode was an RVC electrode coated with gold. An AAS spectrometer SP9 with graphite furnace atomisator (Pye Unicam) was used to measure the preconcentrated As species. The preconcentration parameters for the electrochemical process were optimized. The deposition runs at a constant current of -2500 μA and the optimum stripping current was found to be 100 μA.

The deposition was made from a hydrochloric acid solution, which was then on-line replaced by a diluted nitric acid facilitating the AAS measurement of Arsenic. The advantage of the used preconcentration system was in an automatic and reliable matrix exchange facility. Optimum electrolyte concentrations were found to be 0.1 mol.dm^{-3} HCl and 2 mol.dm^{-3} HNO_3 for the deposition and stripping/AAS measurement, respectively.

The trueness was determined by means of a certified reference material CRM 12-3-10 (SMÚ) with As content of 21.0 ± 5.0 μg.dm^{-3}. The analysis was performed after a fast and simple selective reduction of As(V) to As(III) by L-cysteine.

Determination of Sb by FTC-GFAAS we develop in this time. Moreover, the determination of Sb by graphite furnace atomic absorption spectrometry was optimised enabling a direct measurement also from hydrochloric acid media. The preconcentration step was optimised and characterised. We are planning to elaborate condition for on-line determination of Sb by FTC-GFAAS.

P-8

ELECTRIC FOCUSING PRECONCENTRATION DEVICES FOR ELEMENT IN-TIME MONITORING OF AIRBORNE PARTICLES BY ATOMIC EMISSION SPECTROSCOPY

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An electric focusing pre-concentration combined with in-time monitoring by atomic emission spectroscopy is the promising way for determination of elemental aerosol particulate composition, and consequently in regulatory, epidemiological and toxicological applications, in detection of primary and secondary aerosol sources. Based on calculations new theoretical models of electric focusing devices were proposed for pre-concentration of aerosol particulate and for specific separation of particle size fractions. One of these perspective designs was optimized for in-line connection to microwave induced argon plasma in order to create stable argon plasma conditions for accommodation of air aerosol pre-concentrate and for excitation of atomic emission radiation achieving very sensitive detection of elemental composition. Preliminary results of experiments with dry aerosols, based on simple inorganic salts and produced artificially in a laboratory made generator, are presented. Technical and analytical figures of merit of the optimized apparatus are also shown.

Acknowledgement: This work was supported by The Grant Agency of the Academy of Sciences of the Czech Republic (Project No. A400310505).

P-9

DETERMINATION OF TRACE IMPURITIES IN TITANIUM DIOXIDE BY DIRECT SOLID SAMPLING ETAAS

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Titanium dioxide plays an important role in food industry (E 171), pharmacy, cosmetics and in other fields of modern technologies. The content of trace toxic impurities such as As, Cd, Cr, Hg, Pb, Sb and Zn is one of the main characteristics of this material, which defines its suitability. Maximum permitted content of these elements at the ppm level and below is required according to various national and international standards. Consequently, determination of these detrimental impurities is of a great importance. Common wet chemical procedures are usually inconvenient, time consuming and suffer from necessity to use concentrated hydrofluoric and/or sulfuric acids for sample dissolution. Furthermore, these acids cause very strong corrosion of the spectrometer and spectral interference, so that the sample solution cannot be directly analyzed without separation of acids. Therefore, direct solid sampling introduction technique is preferred. New method for the direct determination of trace impurities in titanium dioxide solid powders by electrothermal atomic absorption spectrometry was developed when using modern dedicated instrumentation (ANALYTIK Jena Zeenit 60 spectrometer equipped with solid sampling system). Behavior of titanium dioxide matrix in the graphite tube atomizer during the analysis run was investigated. Figures of merit of determination of these detrimental elements are presented. Comparison with results of other analytical methods is provided. Capability of the Zeeman-effect three-field mode compensation system in determination of elements in a wide concentration range is also documented.

Acknowledgement: This work was performed and supported within the Institutional research plan AV0 Z40310501.

P-10

IDENTIFICATION AND COMPARISON OF COAL SAMPLES BY GC-MASS SPECTROMETRY

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Coal is very important for iron steel industry. Because of the fact that coal samples have a very complex structure and contain a huge number of different kinds of organic compounds, a very successful separation tool and a powerful analytical identification method are needed for coal characterization. GC-Mass Spectrometry provides us with relevant analytical data.

Coal samples from different sources were extracted and analysed by GC/MS, several types of organic compounds have been found in the complex coal extracts, the resulting chromatograms differ from each other in retention time, intensities and mass spectra. The resulting GC/MS data can be setup in a data bank. In order to search within this data bank a certain software (MSChromsearch) is needed.

This poster represents how to use this data bank and the software to compare and search within the databank and to reveal the similarities and differences between various coal samples.

P-11

SIMULTANEOUS DETERMINATION OF TRACE ELEMENTS USING MULTIELEMENT GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETER (SIMAA 6000)

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Simultaneous multielement graphite furnace atomic absorption spectrometer (SIMAA 6000) has been used for trace multielement determination for a number of groups of elements. The compromise conditions for each group that has been optimized include, the pyrolysis and the atomization temperature and the use of modifier. These conditions are firstly optimized for each set of elements using standard solutions. The setting of the optimum conditions in the case of single element determinations have been carried out and compared with these of the multielement. The characteristic mass for each element in the simultaneous multielement determinations is comparable to the single mode (± 20%). The optimum conditions for each set will be used to determine these elements simultaneously in real samples.

Announcement: We would like to announce that the project is greatly supported by both German Academic Exchange Service (DAAD) and Slovakian Government.

P-12

DETERMINATION OF BERYLLIUM IN NATURAL WATERS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Although, acute and chronic beryllium poisoning occurs mainly by the inhalation of industrial gases and dust, the determination of trace amounts of beryllium in natural waters is of interest as it can indicate environmental pollution and it could provide some information of the metal uptake through these sources.

Several analytical methods can be used for beryllium determination. Among them, electrothermal atomic absorption spectrometry offers the highest selectivity and sensitivity for its determination.

In this work, the selection of a suitable modifier and the study of the effects of different metals commonly present in natural waters have been made. No interferences in the presence of K, Na, Mg, and Fe were observed. The interferences of Ca have been eliminated by addition of $Mg(NO_3)_2$ as a matrix modifier. The effects of different chloride concentrations on the beryllium determination were also studied in the presence of different modifiers. Decreasing of the beryllium absorption signal in the increasing chloride concentration was observed only in the presence of $Pd(NO_3)_2$ as an analyte modifier.

The results obtained for the determination of beryllium in the certified reference material of drinking water ("Trace Elements in Drinking Water", Charleston, Canada), together with good recovery of the spiked analyte in various types of waters (real drinking waters, mineral waters, waste waters, and also model river water) using $Mg(NO_3)_2$ modification demonstrate the applicability of the procedure to the analysis of real samples. The sensitivity of ETAAS for the determination of beryllium in the presence of $Mg(NO_3)_2$ was enhanced. For the peak area, a 3SD detection limit of 0.065 µg/l, a 10SD quantification limit of 0.217 µg/l, and a characteristic mass of 3.68 pg of Be were obtained. The recovery was 97 – 110 % and RSD was less than 7 %.

Acknowledgement: This work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic VEGA/1/2466/05 and Slovak-German Scientific Project DAAD No.13/2004.

P-13

COMPARISON OF VARIOUS REACTION MEDIA FOR THE DETERMINATION OF ARSENITE IN THE PRESENCE OF ARSENATE BY HGAAS

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In waters, arsenic is generally found in the inorganic forms of arsenite (As(III)) and arsenate (As(V)). The As(V) forms predominate in oxygenated waters while in deep well waters, where reducing conditions exist, the trivalent species may be present. Because these inorganic species show different toxicity, mobility, and behaviour in biological systems, their differentiation has generated considerable interest.

Many methodologies exist for the speciation of As in waters. Selective reduction procedures based on the highly pH-dependent reduction reaction between arsenic species and $NaBH_4$ to generate arsine in HG-AAS systems are relatively commonly used. In this case, for As(V) strongly acidic solutions are required ($pH \leq 1$), while for As(III) hydride formation occurs in mildly acidic solutions.

The aim of this study was to critically evaluate the most frequently used reaction media for the speciation of arsenic by HGAAS. The main attention was paid to the determination of arsenite in the presence of arsenate at different ratios. Four different reaction media has been used to achieve a selective volatilization of arsenite: 0.1 M acetic acid (pH 2.9), acetate buffer (pH 5.0), phosphate buffer (pH 7.2), and citrate buffer (pH 3.1).

In order to evaluate the As(V) interference effect, the mixtures containing 60 µg/l of total inorganic arsenic with corresponding relative contents of 1 %, 2 %, 5 %, 10 %, 20 %, 35 % and 50 % of As(III) were prepared. The percent analytical error due to the As(V) interference was calculated for each case.

Acknowledgement: The work was supported by Science and Technology Assistance Agency under the contract No. APVT-20-042002 and Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences under the contract No. VEGA 1/3561/06.

P-14

CONDENSATION IN AN AXIALLY FOCUSING CONVECTION (AFC) ETV-UPSTREAM – A NEW MODEL

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A new model is presented for analyte condensation in presence of the highly concentrated carbon evaporated from the graphite furnace of an ETV device. The numerical calculations are carried out with the parameter used with a newly constructed ETV device. The main feature of the new device is a laminar upstream released through the outlet hole in the center of the ETV graphite furnace into a vertically oriented tube where vapor condensation occurs predominantly apart from the walls owing to an Axially Focusing Convection effect (AFC). This new ETV device shows high uniformity for analyte transport efficiencies for elements of different volatility. Experimental results are presented in another paper on this conference. It is shown that carbon particles that are already found inside the furnace and in the released gas flow are crucial for the analyte condensation process and carrier formation. The particles are analyzed via scanning and transmission electron microscopy (SEM and TEM), and with energy dispersive X-ray spectroscopy (EDX).

The simple model quantifies the condensation process with coagulation of carbon particles and diffusing analyte atoms attached to the growing carbon particles based on the initial carbon density owing to the mass losses of the graphite tube and on the measured temperatures in the gas flow. The model allows the calculation of analyte losses in different parts of the ETV and tubing system and of analyte transport efficiencies for medium and high volatile analytes with and without matrix/carrier modifiers, such potassium and palladium.

Values for analyte transport efficiencies calculated on the basis on this model are compared with directly measured results.

P-15

LASER ABLATION OF POWDERED MATERIALS: PELLET PREPARATION TECHNIQUES FOR LA-ICP-OES/MS

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Application of laser ablation inductively coupled plasma optical/mass spectrometry (LA-ICP-OES/MS) is widely used for the analysis of both compact and powdered solid samples.

Laser ablation of powdered materials requires more complicated sample preparation then in the case of compact materials where the sample treatment usually involves only polishing the target surface. However, an internal standard addition or mixing with a unifying matrix is possible with powdered sample form. The unifying matrix usually serve as a binder for pressing, casting or fusion techniques to obtain compact targets exhibiting good cohesion and adequate mechanical strength with respect to the laser beam interaction. The binder selection depends on the sample origin, characteristic and composition.

Different techniques of pellet preparation were compared for powdered samples representing geological (soils) and biological (infant formula) materials. The most important factors such as hardness, cohesion and homogeneity of prepared targets were studied. UV and IR laser ablation of prepared pellets with 266 nm and 1064 nm Q-switched Nd:YAG laser was investigated. The elemental analysis using LA-ICP-OES was performed and the precision and accuracy of created methods were compared.

Acknowledgement: The authors gratefully acknowledge the Ministry of Education, Youth and Sports of the Czech Republic for bestowing the research project with RP identification code MSM0021622412.

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HEAVY METALS IN CONTAMINATED SOILS

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Total heavy metal content in soil is important parameter for specification of enviros contamination. The elements as Cd, Cr, Hg, Ni, Pb, V rank among these elements which negatively influence the environment. Monitoring these elements is important for sanitation of contaminated soils.

Aim in this paper was monitoring heavy metals in soil in dependence of depth underground bores. Samples were contaminated by petroleum compounds from old refinery area. Soil samples from six various depths were investigated (depth from 0.2 m to 9 m).

Samples were decomposed by microwave high-pressure oven with HNO_3, HCl and HF.

Content of As, Ba, Be, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sn, V, Zn, B was analysed. Atomic absorption spectrometer with graphite tube atomizer was used for determination content of Pb, Cd, total Cr, Ni and V. Content of Hg was determinated by Trace mercury atomizer TMA 254.

Decreasing of the elements content was investigated for each element in dependence of depth. Each element had specific relation of content from depth. Elements as V, Pb, Hg and Cd show slow decreasing of content and Ni and Cr show intense decreasing of content.

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DETERMINATION OF THALLIUM IN FUNGAL BIOMASS BY ETAAS

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Thallium is highly toxic element that may be immobilized in the environment by fungal biomass. Fungal strain originally isolated from locality Pezinok - Kolársky vrch (*Neosartorya fischeri*) was used for preparation of fungal biomass by static and dynamic cultivation. Prepared forms of biomass with determined weight and radius of wet pellets (dynamic cultivation) or weight of wet compact biomass (static cultivation) was used for hour's biosorption of thallium from deionized water (45 mL) enriched with 5 mL solution of thallium with concentration of 1 $mg.L^{-1}$ (5 μg of thallium) or 5 $mg.L^{-1}$ of thallium (25 μg of thallium). Solutions with desired concentrations of thallium were prepared from standard solution $TlNO_3$ (1.000 $mg.L^{-1}$ of Tl stabilized in 2% HNO_3). The analytical conditions for thallium determination in fungal biomass by electrothermal atomic absorption spectrometry were studied and optimized. The strong background interferences due to the presence of organic matrix were studied and eliminated by application of pyrolytically coated graphite tubes/platforms in conjuction with Zeeman background correction and utilizing $Pd(NO_3)_2$ and ascorbic acid as modifiers. Optimal temperature conditions for pyrolysis and atomization of thallium from aqueous standards and matrix-matched standards were selected. The precision and accuracy of thallium determination by described method for fungal biomass was acceptable. The limit of detection of thallium for the proposed method was approx. 50 $\mu g.kg^{-1}$. Dynamically prepared biomass immobilized in average 0.272 μg or 1.809 μg of thallium from systems originally enriched with 5 μg or 25 μg of thallium, respectively. Biomass prepared by static cultivation immobilized in average 3.450 μg of thallium from system originally enriched with 25 μg of thallium.

Acknowledgement: This work was financially supported by Slovak grant agency VEGA No. 1/3555/06 and VEGA No. 1/3462/06 and UK Grant No. 132.

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DETERMINATION OF LEAD IN BLOOD BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY -LONG-TERM PARTICIPATION IN EXTERNAL QUALITY CONTROL FOR LEAD IN BLOOD

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Lead is well established occupational and environmental pollutant with a broad spectrum of serious health effects. The recent research unequivocally demonstrated its irreversible effects on central nervous system in children encountered at surprisingly low blood lead levels without an apparent threshold. The most common and widespread method for lead quantitative analysis in various biological samples is electrothermal atomic absorption spectrometry (ETAAS), which is used for determination of lower and lower concentrations approaching the limit of determination. This is typical scenario when issues of accuracy and reliability of the measurement is of great interest. Our experience in this field is presented.

Our laboratory has been participating in the international quality program "United Kingdom National External Quality Assessment Service" (UK NEQAS) ensured by Wolfson EQA Laboratory in Birmingham since 1980. The Varian SpectrAA30 atomic absorption spectrometer with Zeeman correction has been used since 1992 and GBC Avanta UZ since 2000. Two samples of blood are analysed by each participating laboratory per month.

At present we use GBC Avanta UZ equipped with the longitudinal Zeeman background correction and the transversely-heated furnace for determination of lead in blood samples. Blood samples (in duplicate) were prepared for analysis by microwave mineralization with HNO3 and H2O2. We used the standard addition method and mixed modifier (Pd, (MgNO3)2, NH4H2PO4) as a matrix modifier. The accuracy of results was verified in UK NEQAS.

Results of our laboratory in external quality control UK NEQAS from 2003 to 2005 are as follow: the concentration range in blood lead samples was from 0,10 to 3,50 µmol/l (or from 20 to 720 µg/l), average recovery factor (for GBC Avanta UZ) calculated based on results analyzed in 2003 - 2005 was 101 % and expanded uncertainty U = 9,0 % (coverage factor = 2).

The external quality control system is one of the most important tools in quality assurance. Our experience shows that the participation in an external quality control program is unavoidable. Otherwise, accuracy, reliability, and comparability of results cannot be guaranteed.

P-19

INHOMOGENEITY OF GEOLOGICAL SAMPLE QUANTIFIED BY X-RAY SPECTROMETRY AND ATOMIC ABSORPTION SPECTROMETRY. COMPARISON OF THE RESULTS

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The determination of inhomogeneity level in a solid sample is dealt with. Inhomogeneity is the characteristic of the powdered material. In connection with underestimated sample mass can lead to undesirable data scatter. Homogeneity concept takes for granted that after milling the sample the uniform particle size is achieved. Mixing sample batches must be done in a proper way. Correctly set sample weight is an assurance that in each subsample the number of particles, responsible for the element signal, is practically the same.

Inhomogeneity determination consists in measuring element responses by analytical instrumentation. The results are evaluated by mathematics-statistics.

Experiments were carried out on 15 subsamples of shale that represented 15 1kg bottles. Each subsample was analysed twice. Due to supposed small inhomogeneity effects, following inhomogeneity carriers were chosen: Mo, Pb, Rb, Cu, Ni, Cr, Mn, Zn and V. X-ray spectrometry and atomic absorption spectrometry were chosen as analytical methods and for comparison. Detailed information on sample preparation (pressed tablets for X-ray, acid decomposition for AAS) and more information on element determination are given in the contribution.

For each element 30 results were obtained. These were submitted to the ANOVA. The contribution of inhomogeneity s_{het}^2 ($s_{het}^2 = \frac{1}{2}\left(s_b^2 - s_{an}^2\right)$) was computed from the variance between samples (s_b^2). The statement[1] about sufficient sample homogeneity was based on the Fearn-Thompson approach. Element homogeneity was confirmed when inequality holds: s_{het}^2<C. $C = F_1 * s_{all}^2 + F_2 * s_{an}^2$, $F_1 = \chi^2(P, m-1)/(m-1)$, $\sigma_{all}^2 = (0.3 * \sigma_{tg})^2$, σ_{tg} is the target standard deviation. All trace elements, suspected for inhomogeneity effects, were proved to be homogeneous. Final statement was not influenced by analytical instrumentation applied, X-ray or AAS, resp. The procedure is demonstrated on nickel as an example with comments.

The general characteristic of all X-ray measurements is twofold precision over AAS measurements. This excellent method precision combined with given particle size limits inhomogeneity quantification. Effects of inhomogeneity were not observed in AAS measurements which approved itself for all elements as less precise. Comments on radiation sources, interferences and insufficiences in sample decomposition are added.

This knowledge led to adjustment of ANOVA formulae to understand the terms s_{an}, s_{het} better. Additional experiments on 1 sample were required. Modified terms are presented and discussed in a considerable extent. For existing particle size atomic absorption spectrometry turned out to be the method of choice.

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P-20

EFFECT OF GAMMA IRRADIATION ON TRICHROMATIC VALUES OF SOME SPICES

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Effect of gamma irradiation at doses of 5, 10, and 30 kGy was studied on changes of colour values L*, a*, and b*, which characterise lightness, redness, and yellowness of black pepper, oregano and allspice. From the measured trichromatic values of spice methanol extracts the value a* characterizing the redness of spices was the most sensitive to effect of irradiation. Found changes were the most sensitive and significant at used Iluminants A and C. Effect of irradiation on colour characteristics L* and b* in the studied condition of irradiation was statistically unsignificant and practically negligible. Effect of irradiation at all applied doses 0, 5, 10, and 30 kGy resulted in some significant changes of colour value a* at all spices. Redness of methanol extracts of irradiated black pepper decreased according to increased doses of irradiation. Found differences of red intensity of colour value a* remain practically unchanged during the storage of irradiated and non-irradiated black pepper. In opposite to black pepper, irradiation caused significant increase of oregano and allspice colour redness value. The biggest increase of this colour value, about 150 % at oregano, and 40 % at allspice, was observed immediately after irradiation of these spices at dose of 30 kGy. Found differences among the irradiation doses tend to reduce during the storage of oregano and allspice. Effect of black pepper storage caused small, but statistically significant, about 8 % increase of colour value a*. Four months of allspice storage caused about 50 % increase of a* value and in the case of oregano increase of this value was enormous, about 4 – 5 times bigger than initial value. These extreme changes of colour parameter, occurring during the storage of spices irradiated at doses 10 kGy (EU limit for spices and herbs) and 30 kGy (FDA limit), were not visible to the eye. These findings are well correlated with the findings of some other authors reporting about colour changes of some foods due to action of irradiation.

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APPLICATION OF ELEMENTAL ANALYSIS ON TRACING THE GEOGRAPHICAL ORIGIN OF FOOD

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The globalization of food markets and the relative ease with which food commodities are transported through and between countries and continents, means that consumers are increasingly concerned about the origin of the foods. Appreciation of qualified national products, together with a guaranteed reference for consumers, has become necessary in the field of dairy products and wine. Protected Designation of Origin (PDO) trademark has been assigned to numerous cheeses and wines. In order to receive this designation, the raw materials have to be produced and processed in the specified region from which the product gets its name.

A model for traceability of Slovakian wines according to affiliation to vineyard regions and differentiation from imported wines was proposed using of elemental markers of origin determined by atomic absorption spectrometry (AAS). For the regional segregation of Slovakian wines according the vineyard production areas the Ca, Mg, Rb, Sr, Ba and V were selected as some crucial specific markers of origin. Principal component factoring (PCF) using of Ba, Ca, Co, Cr, Li, Mg, Rb, Sr and V markers resulted in a very efficient differentiation of Slovakian wines from many European ones. According to this model the European wines differ in content mainly of Ca, Mg, Rb and Sr and the best discrimination for Portugal, Italian, Spain and partially for French wines was achieved.

Study of traceability of typical sheep cheese bryndza made in Slovakia, Poland, and Romania was realized using of some special elemental markers determined by atomic absorption spectrometry. Principal component factoring was used for elements variability determination, differentiation, and visualization of optimal data. Elemental markers Ba, Cu, Cr, Mg, and Ni enable effective identification of majority of Slovakian bryndza cheese producing areas. For the successful multiregional differentiation of Slovakian, Polish and Romanian bryndza cheese were Cr, Hg, Mn, and V found as the best elemental markers of origin.

P-22

STUDY OF SELENIUM HYDRIDE TRAPPING IN FILTER FURNACE ATOMIZER FOR ATOMIC ABSORPTION SPECTROMETRY

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In atomizer trapping is due to its simplicity the most convenient way of hydride collection. Until recently, the only approach to in-atomizer trapping was in-situ trapping in commercial graphite furnaces (GF). Certain drawback of the in-situ trapping in GF is trapping interferences. Recently, we investigated interferences, due to the presence of other (than analyte) hydride forming elements in the sample, observed in the trapping step. We found that the interference extent is given by a trapping capacity of the surface - the higher the capacity the lower the extent of the interference.

The aim of this work was to assess performance of the graphite filter atomizer (FF), designed by Katskov [1] for hydride trapping. FF employs a large surface area of a graphite fiber to soak the liquid sample which is subsequently subjected to a temperature program similar to that for the commercial GF. It should be underlined that the FF can be easily implemented to most of commercial GF. Until now, benefits of the FF for the liquid sample introduction have been convincingly demonstrated in a number of papers but there has not been any attempt to employ it for hydride trapping. Because of the large surface area of the graphite fiber a high trapping capacity of the FF should be expected. This is promising with respect to substantial improvement of resistance towards trapping interferences. The other potential advantage over commercial GF is that there is, in principle, no need to modify the surface.

The whole assembly of the FF consisted of the conventional transversely heated graphite atomizer (THGA) (Perkin Elmer Analyst) with the inserted filter made of porous electrographite. There was a hole made in the filter wall to improve the pattern of support gas flow through the furnace during the trapping. For the present hydride trapping experiments, there was no graphite fiber in the assembly. For the "conventional" liquid sample introduction to the FF, there was no hole in the filter and the mass of the graphite fiber wound around the filter insert was around 15 mg. Employing selenium hydride as the analyte and arsine and stibine as interferents, a preliminary evaluation of performance of FF will be discussed.

Acknowledgement: We are indebted to D. Katskov and P. Tittareli for helpful discussions and for a gift of the filter furnaces. Financial support from the Grant Agency of the ASCR (Project No. A400310507) is gratefully acknowledged.

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CALCULATION OF COMBINED UNCERTAINTY FOR MEASUREMENT OF PRESSURE CO_2 IN SPARKING WINE BY AFROMETER

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The article presents the results of calculating the combined uncertainty (U) of measuring pressure CO_2 in sparking wine. Quality of measurement need validation of the method and this require calculation of all statistical data. Program Metro 2003, version 3.04 was used. Bilantion of uncertainty was in range of pressure 0.1-0.7MPa (1-7atmosphere) as follows:, For the pressure 0.25 MPa and k=2 the combined uncertainty U=0.0046, enlarged uncertainty 0.0093, relative standard uncertainty 1.9% and enlarged relative uncertainty 3.7% was obtained. The standard manometric method using Afrometer (Fig.1) for measuring of the pressure of CO_2 was used (Reg. No.2676/1990, STN 560216 čl.62, Ú:1964). Quality Control Materials (QCMs) are used as an operational tool for the purpose of demonstrating that a measurement system is "under control". Our accredited laboratory used QCMs Hubert Club-semisweet wine and Bella Vista- dry wine to estimate the uncertainty of a measurement and/or provide an assessment of repeatability of a measurement because there is not suitable CRM of wine and this is a lower cost approach. QCMs can be used for internal and external quality control purposes, namely for quality control charts, for comparison of results of different methods within one laboratory and for inter-laboratory comparisons and estimation of bias. The inter-laboratory comparison between our laboratory and Hubert J.E laboratory is given in Table 1. The same method and process of sample preparation was used and the samples were measured three times. After correction to the 20°C very good agreement was achieved. Reliable chemical measurements in future will be depended on more RMs with direct links to the SI.

Table 1: Comparison of measuring pressure CO_2 /in MPa/ in wine between two laboratories.

	Parallel	1	2	3	1	2	3	Average at 20°C
Lab.1 Hubert Club	/at 23°C/	0,64	0,66	0,63	0,61	0,63	0,60	0,61
Lab.2 Hubert Club	/at 21°C/	0,62	0,66	0,65	0,61	0,65	0,64	0,63
Lab.1 Bella Vista	/at 23°C/	0,49	0,50	0,47	0,46	0,47	0,44	0,46
Lab.2 Bella Vista	/at 21°C/	0,45	0,47	0,49	0,44	0,46	0,48	0,46

P-24

STUDY OF THE SPECTROSCOPIC CHARACTERISTICS AND CHROMATOGRAPHIC DETERMINATION OF HYDROPHILIC ORGANIC COMPOUNDS IN DERIVATES ON THE BASIS OF THE REACTIONS OF DIAZOLINKING

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The wide spread of organic compounds use in industry and agriculture resulted in global problems connected with their remnants extraction from food, agricultural lands, environment.

The pesticides and herbicides and their remnants could be toxic for human and animals and plants. It is necessary to clean the surroundings of human and animals from residues of the chemicals.

The literature analysis provides the data about the pesticides destruction with development of chloramine, one atoms phenols, substituted indoles etc.

Direct estimation of these compounds has several methodological problems.

In this work we suggest to use of some derivate reactions for better estimation of the residues of pesticides and herbicides. The *n*-nitrodiazophenile was used as reagent.

The reaction of the reagent with prime amines resulted in development of triazenes.

The indole and its derivates provide the reaction of azolinking in position 1 with development of diazocompounds. Phenoles and their derivates develop diazocompounds with this reagent also, however joining take place mainly in the *para*-position to OH-group.

The method of the IR-spectrometry revealed the –N=N- and =NH groups. The active proton presence in =NH group of triazenes was proved by the method of spectrophotometry (the change of the absorption spectra in dependence from the solution pH). The dissociation constants of the protone (pK_a) were estimated in the range 8-10. The absorption spectra of the molecular and anionic forms of triazenes were obtained and molar coefficients (ε) of absorption were calculated in different solutions.

The effect of media pH on reaction was studied. The development of azoderivates of phenols is better in slightly alkaline media and creation of amines is better in acidic media take place. The maximum of the derivates yield was observed at 10 – 20 fold excess of diazonium cations. The kinetics of the reactions is studied. The optimum time of derivates production is from 20 to 60 min. The obtained compounds are well extracted by chloroform and dichlormethane. Some of them, particularly, azoderivates of 1-naphtylamine, indole, *o*-cresole are well soluble in diethyl ether. The compounds were isolated separately from the reaction mixture.

The analytical HPLC studies were carried out on "Perkin-Elmer" chromatograph coupled with spectrophotometric detector by isocratic elution. The stainless steel column 25 × 4.6 mm was filed by "Silasorb C_{18}". The mixture of CH_3CH + 0,05 M KH_2PO_4 was used as elution agent (v/v = 2:1). The velocity of elution agent flow was 1-1,2 ml/min.

The dependence of height and area of the chromathographic peack from the concentration of derivate is studied. This dependence is linear in the range of 0.1 – 10 μg/ml.

The methods were developed for the determination of some pesticides residues in sewage and soils on the basis of this study.

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RAMAN MICROSPECTROSCOPY AND MICROSTRUCTURAL STUDY OF ITZ IN CONCRETES REINFORCED BY PET FIBRES

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A new method, the Raman microspectroscopy mapping technique, was successfully used to study of the interfacial transition zone (ITZ) around polyethylene terephtalate (PET) reinforcement in concrete.Waste from PET bottles has been used in form of fibers as a reinforcing element in Portland cement concrete. The contact zone between the reinforcing element and the bulk is a crucial area for the development of mechanical properties of such concrete. Raman spectra represents the compositional variation of the cement matrix at the width range 5 to 65 μm from the PET fibre. The Raman bands at 3618 and 357 cm^{-1} corresponds to the vibrations of O-H bond at $Ca(OH)_2$ were used for quantitative distribution of portlandite within the ITZ area. The most intensive band of portlandite occurs at the distance from 5 to 30 μm from the PET fibre. The intensity of the spectrum decreases strongly further. Raman spectroscopy has been completed with nanoindentation and environmental electron microscopy in combination with microanalysis, and electron diffraction. The contact zone can be characterized by a higher porosity (both the air and water pores) and occurrence of newly formed mineral phases – portlandite, hydrocarbonate, ettringite, and lower Ca^{2+} saturated C-S-H gels. The structural and textural arrangements of mineral components seem to be radial or perpendicular to the plane of reinforcing elements. It was found that all microstructural factors correspond also to the micromechanical properties like elastic modulus.

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FRACTIONATION OF ALUMINIUM BY COUPLED SEPARATION AND SPECTROMETRY DETECTION TECHNIQUES

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The concentration of some individual Al species is difficult to determine directly. For that reason these species are determined in one or more fractions. Generally, these fractions are defined operationally or functionally, respectively, and they are termed according to the used separation method, e.g. the reactive species fraction, or the function of the isolated analyte, e.g. bioavailable species fraction.

In our previous papers [1-10] we dealt with the fractionation of aluminium in synthetic solutions and acid soil, sediment, rock and water samples by five different separation procedures (single and sequential extractions, membrane filtration, method based on kinetic strength discrimination and solid phase extraction with utilization of chelating ion-exchangers). The selectivity of these procedures was investigated with the relation to the Al plant availability, i.e. the relationship between the Al concentrations in the individual soil fractions and the Al concentrations in the grass stems samples was studied. The selectivity of obtained results decreases with the increased efficiency of the used methods. The concentration of Al was measured by flame atomic absorption spectrometry (FAAS), UV/VIS spectrophotometry and optical emission spectrometry with inductively coupled plasma (ICP OES).

Acknowledgement: The work was supported by Science and Technology Assistance Agency under the contract No. APVT-20-010204 and Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences under the contracts Nos. VEGA 1/2439/05 and VEGA 1/3561/06.

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APPLICATION OF A MODIFIED BCR SEQUENTIAL EXTRACTION SCHEME FOR THE ETAAS DETERMINATION OF THALLIUM IN SOILS

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Electrothermal atomic absorption spectrometry was used to the determination of extractable thallium in soils following the application of the modified BCR three steps sequential extraction scheme. The potential interferences from cations and anions commonly present in soil solutions and reagents used for leaching were observed. Optimal temperature conditions for atomisation of thallium from aqueous standards and matrix-matched standards with extractants were selected. The utilization of $Pd(NO_3)_2$ and $Pd(NO_3)_2$ + $Mg(NO_3)_2$ as a matrix modifier were investigated and compared. The precision and accuracy of thallium determination by the described method was acceptable. The limit of detection of thallium for the used method was around 50 $\mu g.kg^{-1}$. The proposed analytical procedure was applied for the determination of thallium in soils polluted by pyrite taillings (Banská Štiavnica – Šobov, Slovakia), which is affected by environmental acidification (pyrite oxidation in the open quartzite mine and mine dump).

Acknowledgement: This work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences VEGA No. 1/3555/06.

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STUDY OF PROPERTIES CHANGE OF TURBINE OILS AFTER HEAT STRESS

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The change monitoring of oil grade makes it possible define to life cycle of lubricant. The quantity of oxidothermal products designates wearing of oil. Turbine oils are exposing for them working high temperature, pressure and leakage undesirable materials from external environs.

The properties of turbine oils were evaluated in Tribotechnical laboratory VLTSU Košice whereby determination of total acid number, kinematics' viscosity and Fourier transform spectrometry.

By examination were monitored two types of oils, ASTO-555 (Aero Shell Turbine Oil 555) and MS-8P (Mineral Shell 8P). The tests were performed after heat stress in definite intervals.

The properties of samples turbine oils analyzed by laboratory methods listed above were evaluated and compared to facilities of oils monitored in the working condition.

P-29

QUANTITATIVE ^{31}P NMR SPECTROSCOPY OF SOIL AND PEAT HUMIC ACIDS

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Humic acids (HA) are complex mixtures of high molecular substances isolated from soils, peats, composts, natural waters, sediments, lignites and brown coals. The analyses of the composition of HA provide invaluable information about the character and quality of an investigated soil. Soil humic acids generally contain between 800 and 1500 mg.kg^{-1} of phosphorus of either inorganic or organic origin, in some cases the P level achieves almost 30 g.kg^{-1}. On the other hand, the typical P content in coal/oxihumolite HA is about 50 – 500 mg.kg^{-1} only. Our contribution deals with the quantitative analysis of various species (types) of phosphorus atom in humic acids by ^{31}P NMR spectroscopy. The present level of knowledge of the field makes ^{31}P NMR spectroscopy a reliable and irreplaceable tool for analyses of various phosphorus species in HA and/or alkaline extracts of soil or biomass. By following strictly defined procedures and conditions for both the isolation of HA and NMR spectra measurements, ^{31}P NMR spectroscopy provides quantitative and fully reproducible results about the content of different phosphorus species in the soil. Individual phosphorus species in HA give clearly separated NMR signals (Fig. 1) that can be easily analyzed qualitatively and quantitatively. Further investigation of phosphorus in HA will provide more accurate information on composition of individual P species, which can be helpful e.g. in the study of phosphorus transformations in various ecosystems.

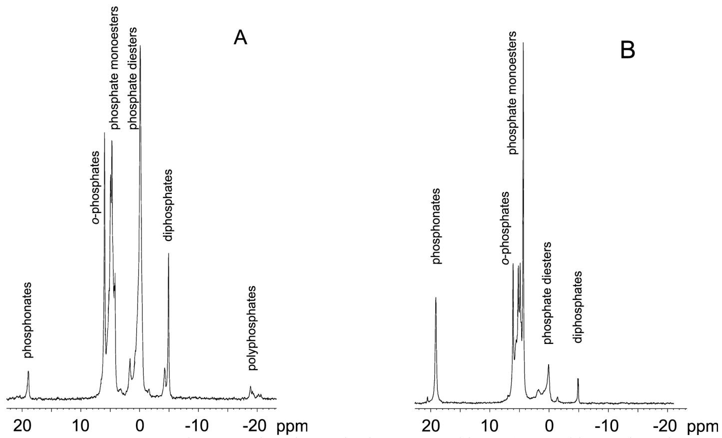

Fig. 1. ^{31}P NMR spectra of HA isolated from soil. A) Soil A-horizon in subalpine Nardus grassland (as. *Nardion* Br.–Bl. 1926) , B) horizon A_h of acidophilous mountain spruce forest soil (podzol, Bohemian Forest).

Acknowledgement: This work has been supported by the Grant GACR 206/05/0269.

P-30

THE DETERMINATION OF HAZARDOUS SUBSTANCES ACCORDING TO THE ELECTRICAL AND ELECTRONIC EQUIPMENT ACT (WEEE & ROHS)

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The guidelines for waste of electrical and electronic equipment (WEEE) [1] and the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) [2] are lately in the focus of the public interest. Most of the European memberstates have been implementing or are recently trying to implement these guidelines in national law.

In Germany the electrical and electronic equipment act (ElektroG) was introduced 24 March 2005, and public collection of electrical and electronic waste began 13th August 2005. As of 1st July 2006 hazardous substances like lead, cadmium, mercury, hexavalent chromium and polybrominated biphenyls and diphenyl ethers are banned in electro- and electronic equipment. This restriction, even though in discussion since 1991, has become more and more important from year to year because of tons of electronic waste releasing toxic substances which are accumulated in the environment, the food chain and all human beings.

In order to enforce the substances ban and the limitation or substitution of hazardous components, elemental analysis is obviously the most important control measure for monitoring limiting values. This requires precise analytical systems such as X-ray fluorescence, ICP- and atomic absorption spectrometers. These instruments are able to detect trace concentrations of hazardous compounds – for example cadmium, using an atomic absorption spectrometer in the flame atomisation mode up to 0.1 mg/L, or using the digital graphite furnace technique for electrothermal atomisation even up to 0.1 µg/L. For the determination of hexavalent chromium, UV-VIS spectrometry is the method of choice and can be carried out quickly and easily using a UVmini-1240 in routine analyses. Polybrominated biphenyls as well as polybrominated diphenyl ethers are analysed using FTIR spectrometers such as the IRPrestige-21 or GCMS systems (QP2010).

The development of routine analytical methods for the accurate determination of hazardous substances like lead, cadmium, and mercury using electrothermal atomization with a digital controlled graphite furnace will be explained and advantages of flexible system configurations will be discussed.

References

[1] Guideline 2002/96/EC for Waste Electrical and Electronic Equipment (WEEE).
[2] Guideline 2002/95/EC for the Restriction of Hazardous Substances in Electrical and Electronic Equipment (RoHS).

P-31

DETERMINATION OF LANTHANIDES IN ENVIRONMENTAL SAMPLES BY SOURCE EXCITED EDXRF METHOD

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A new analytical procedure for determination of lanthanides in environmental samples after chemical separation from major matrix elements on DOWEX 50W-X8 resin followed by preconcentration with chelating agent ammonium pirrolidine dithiocarbamate (APDC) and analyses of thin targets by energy dispersive X-ray fluorescence (EDXRF) method using ^{109}Cd as the source of excitation was presented. Characteristic Lα X-ray lines of the lanthanides were used for calculations of the net peak area and mass concentrations. The influence of pH value of the solution and addition of organic matter on the complexation was investigated. Percentage of recovery of each lanthanide after separation on DOWEX 50W-X8 resin was also determined. Accuracy of the method was tested on standard reference materials and real environmental samples (red mud material). For that purpose samples of standard reference materials and red mud were prepared as thick targets and directly analyzed (without the separation step) by EDXRF method using ^{241}Am as the excitation source. In that case lanthanides concentrations were determined over their characteristic Kα X-ray lines and results were compared with those obtained after separation/ preconcentration step described above. Results showed that selected lanthanides made stable complexes with APDC in the alkaline medium with the maximum recovery at pH=8. The presence of organic matter slightly modified the complexation by means of somewhat higher recovery percentage at pH lower than 7 and approximately 20% lower recovery at pH higher than 7.

Recovery of the elements after separation on DOWEX 50W-X8 resin and preconcentration with APDC at pH=8 varied from 91.4% (Pr) to only 24.9% in the case of Dy.

Concentrations of lanthanides measured in standard reference material and environmental samples of red mud after microwave digestion, separation on DOWEX 50W-X8 resin, preconcentration with APDC at pH=8 and recalculation on the percentage of recovery were in good agreement with certified values in the case of SRM as well as with the concentrations obtained by direct determination over Kα lines using ^{241}Am excitation source in the case of red mud leading to the conclusion that presented method was applicable for the determination of lanthanides in real environmental samples.

P-32

OPTIMIZATION OF CONDITIONS OF SAMPLE PREPARATION FOR THE DETERMINATION OF METALS IN SLUDGES AND SOILS

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The content of heavy metals in agricultural soils is gradually increasing from various processes such as sewage sludge, creation of landfills, fertilizers, atmospheric fallout etc. These metals may transfer from contaminated soils into growing plants. For this purpose various leaching and other procedures are applied for estimation of them. For characterization of sludges and soils the aqua regia extraction method was in this work applied. It is a very strong acid digestion that will dissolve almost all elements that could become “environmentally available”. Elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment.

In this work, the European standard was employed for determination of heavy metals in sludges and soils. For the digestion the sample was weigh, destilated water, hydrochloric acid and nitric acid was added and it was refluxed using the vapor recovery device. The extract was filtered or centrifuging. ICP-AES was use for determination Cr, Ni and Pb. The amount of sample, the volumes of acids, the time of boiling under the reflux, filtration, centrifugation was tested. The recovery of heavy metals prepared under this conditions and the certified values in certified reference material of sewage sludge and in soil in the interlaboratory test was compared.

P-33

ANALYSIS OF METAL CONTENT AND SPECIATION OF FOODSTUFFS

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One of the main objectives of food-analysis is to determine at generally micro amount of metals being present at foodstuffs. The amount of certain metals is connected with the applied technology, thus with full knowledge of amount of metals the applicability of the technology could be determined. Physiological effects of metals are really various, there are essentials and highly toxic as well. It makes the problem more difficult, that variant combinations and oxidation states of metals have diverse effects in a different degree; even the combinations of the same metal have significant variant effects.

For this reason we have to aim at the quantitative analysis of the main species, species-groups instead of the total metal content in the food-analysis. In case of foodstuffs it is obvious to estimate the available amount for (living-organisms) humans. Researchers developed various extraction techniques for this.

The object of our study is to determine the applicability and efficiency of a number of extracting methods in case of five distinctive solid-foodstuffs. The other objective of our analysis is to carry out further examinations of the species-group in each extracting solvents especially in case of high toxic metals (Mercury, Lead and Chromium).

The investigated foodstuffs were sausage, canned oil fish, canned mushroom, biscuits and strudels. Extractions were carried out with acidic solvents, acidic-pepsin solution and acid-pepsin solution with NaCl. The metal-content of the extracts was determined by ETA-AAS. Finally, the different extracting solvents and investigated foodstuffs were compared based on the results of the experiments.

P-34

EVALUATION OF THE AVAILABILITY OF THE FAAS METHOD FOR DETERMINATION OF CD, CU, PB, AND ZN IN THE EXTRACTS OF FRACTIONATION ANALYSIS OF THE GRAVITATION DUST SEDIMENT

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The fractionation analysis is analytical process applicable for the classification of various forms of elements in the environmental samples. This process consists of isolation of elements form on the base of similar physical or chemical properties and consecutive quantification of element in the isolated fraction [1]. The fractionation analysis is often applied for soils and sediments samples. Application of fractionation analysis for the samples of gravitation dust sediments results from the requirement to monitor mobility of risk toxic elements forms from dust to the soils. For the isolation of different mobile forms of the elements in the fractionation analysis of soils is often used the single-step extraction by defined extracting reagents [2,3]. For the determination of elements content in the extracts methods of atomic spectrometry (AAS, OES) are applied.

This work is focused to the evaluation of the availability of the FAAS method for determination of Cd, Cu, Pb, and Zn in extracts of gravitation dust sediment by application of 0.05 mol dm^{-3} Na_2EDTA and 2 mol dm^{-3} HNO_3 as extracting reagents. For the evaluation limit of detection (LoD), limit of quantitation (LoQ), precision (repeatability), and robustness were calculated.

Following obtained values of chosen statistical characteristics it can be stated. The LoD and LoQ values for determination of Cd, Cu, and Pb in the HNO_3-extracts are lower than for their determination in the EDTA-extracts. The lowest LoD and LoQ values were determined for Cd in both extracts and the highest values of LoD and LoQ were calculated for Zn. The repeatability of 10 repeated measurements of analytes concentrations (RSD / %) is:in the EDTA-extracts – Zn (1.87 %), Cu (1.88 %), Pb (3.32 %), Cd (52.70 %); in the HNO_3-extracts – Cu (1.10 %), Pb (1.10 %), Zn (1.28 %), Cd (15.06 %). On the base of these RSD values it can be stated that the method of FAAS is not suitable for the determination of Cd in the both extracts.

At the testing of robustness of the FAAS method was evaluated the effect of extracting time and extracting ratio on the recoveries of Cu and Pb in EDTA and HNO_3- extracts and the effect of pH EDTA solution too. The method is few robust concerning changes of extracting time (EDTA, Cu, Pb) and changes of extracting ratio (HNO_3, Cu).

Acknowledgement: This research was supported by projects VEGA No. 1/3149/06 and APVV No. 20-0094-04.

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P-35

INTER-LABORATORY COMPARISON TESTS - THE EVALUATION OF ANALYTICAL TECHNIQUES APPLIED TO THE ELEMENTAL ANALYSIS OF WATER MATRICES

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The Water Research Institute has been organizing inter-laboratory tests in the area of special inorganic analysis of water matrices from 1994. A brief history of the organization of inter-laboratory comparison tests is mentioned and various analytical techniques (e.g. atomic and molecular spectrometry, electrochemical, etc.) as utilized by the participating laboratories are evaluated and compared over a period from 1997 to 2006. A summary of the relevant ISO, EN and STN standards is also presented.

P-36

QUANTITATIVE DETERMINATION OF PLATINUM GROUP ELEMENTS IN OMBROTROPHIC PEAT PROFILE USING IMPROVED NICKEL-SULPHIDE FIRE-ASSAY WITH ICP-MS

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Inductively coupled plasma mass spectrometry (ICP-MS) is one of the methods used to detect trace and ultra-trace concentrations in geological and environmental samples. Since the first experimental application of such spectrometers with an inductively coupled plasma at the end of 70^{th}, this method has undergone a number of improvements over the last two decades; commercial instruments have become available and this instrumentation is now well established in many geochemical laboratories. An improved traditional Ni-S fire-assay separation procedure for ICP-MS analyses of platinum group elements (PGE) has been revisited with the aim of reducing value of blank samples and application for monitoring of ultratrace concentration of PGE in peat layers. The Ni-S buttons were prepared by a modified approach according to Paukert and Rubeška (1993). The dry ashed samples (5 - 20g) were mixed with fluxes ($Na_2B_4O_7$+Na_2CO_3) and collector (Ni+S) thoroughly in a fire-clay crucible. The fusions were done in a temperature controlled (50 - 1150°C) muffle furnace. Mechanically separated Ni-S button were selectively dissolved in (i) HCl and (ii) HCl+H_2O_2 and the final solution (containing PGE) was dissolved in 1M HCl. All samples were diluted (5% v/v HCl) and then measured with using ICP-MS. The measured isotopes were selected with respect to their most abundant species, free from isobaric overlap and minimum other interferences. The three point calibration curve was prepared and ^{111}Cd and ^{205}Tl were used as internal correction standard. The detection limits (dilution factor of 10) were low and varied from 0.000030 μg/g (for Rh) to 0.00025 μg/g (for Pt). External reproducibility of this method was monitored using WMG-1 and UMT-1 reference material (CCRMP, Canada). The measured PGE data display a wide range of concentrations, from 0.00006 (for Ir in the lowest peat layers) up to 0.0080 μg/g (for Pt). Values of 0.028 for Pd and 0.048 μg/g for Pt from the upper part of the studied peat profile represent remote values and the contribution of PGE (in pollution) from near base-metal metallurgical works and/or automobile catalytic converters is not evident. Generally, the analyses of peat profile samples yielded an analytical precision of 0.5-10 % (RSD) for Ir and Pt and 1-15 % (RSD) for Ru, Rh and Pd in most cases.

P-37

HYDRIDE GENERATION FOR ARSENIC SPECIATION ANALYSIS BY ATOMIC ABSORPTION SPECTROMETRY

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The general aim of this work was to contribute to the development of a method for the speciation analysis of trivalent and pentavalent human metabolites of inorganic arsenic in complex biological matrices.

The method employed the combination of the selective hydride generation (based on the pre-reduction of pentavalent arsenic forms by L-cysteine) with the generation of substituted arsines followed by hydride trapping in a cryogenic trap (quartz tube with chromosorb, cooled by liquid nitrogen) and by subsequent separation of the trapped arsines. The detection was performed in an atomic absorption spectrometer equipped with the multiatomizer.

The main target of the work was to identify parameters controlling limit of detection (LOD). The shape of electrodeless discharge lamp was studied by screening of beam with screen. Noise of this arrangement was quantified too. These results were applied for screening with models of atomizer (tubes and screen) and noise for this models was determined. It was found that making the atomizer narrower than 6 mm was reflected by a pronounced increase of the baseline noise. Also the contribution of the deuterium background correction to the noise level has been quantified. The dominant contribution to the noise was found to be fluctuations in the atomizer caused by gas flow pulsations in the hydride generator. In contrast, measurements with the cryogenic trap increased the basic noise level only slightly. This indicates the potential of the studied speciation method (employing the cryogenic trap) for reaching extremely low LOD. The influence of fundamental experimental parameters on LOD was specified. Also the repeatability of the observed chromatograms was studied. Actual LODs corresponding to various modes of hydride generation and atomization were determined. The optimized LODs were several time lower compared to those published in the literature.

Acknowledgement: This project is supported by NIH-FIRCA project No. 1 R03 TW007057-01 (PI: M. Stýblo) and by GA ASCR grant No. A400310507.

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THE EFFECT OF AMELIORATIVE MATERIALS ADDITION ON THE DISTRIBUTION OF AS, CD, PB, AND ZN AMONG MAIN SOIL FRACTIONS DETERMINED BY SEQUENTIAL EXTRACTION PROCEDURE

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The immobilization of toxic elements in soil *via* alteration of one or more soil characteristics (soil pH, soil sorption complex, content and composition of soil humic substances and content of Fe/Mn oxides) can significantly minimize element uptake by crops planted in soils with elevated heavy metal content and improve quality of food production. Liming has been applied for long time to increase soil pH and subsequently to decrease metal uptake by plants with respect to soil characteristics and behavior of individual elements in soil. Zeolites are considered to be among the most effective mineral amendments reducing heavy metal transfer to plants; beside natural occuring zeolites (clinoptilolite, philipsite etc.), also synthetic zeolites are promising (1).

In pot experiment, the influence of the lime, limestone, and zeolite addition to three soils containing between 32 and 190 mg.kg^{-1} As, 7.1 and 58 mg.kg^{-1} Cd, 1747 and 5997 mg.kg^{-1} Pb, and 237 and 7453 mg.kg^{-1} Zn, respectively, was investigated. The ameliorative materials were added into the pots before sowing in amount corresponding with 3 g CaO, 5.36 g $CaCO_3$, 20 g of natural zeolite, and 20 g of synthetic zeolite per kg of the soil. Spring wheat, spring barley, oat, and again spring wheat were planted in pots for four subsequent vegetation periods. The standardized sequential extraction procedure (2) was applied for evaluation of toxic element distribution into exchangeable, bound on Fe/Mn oxides, organically bound and residual fractions of soil in the end of the experiment. For determination of mobile portions of elements in soil samples, aliquots of the soil samples were extracted with 0.01 mol l^{-1} aqueous $CaCl_2$ solution (3).

The results showed different response of extractable element fractions on soil amendment where substantial differences were evident among the investigated elements as well as among the individual soil treatments. Except for natural zeolite, the results suggested the ability of ameliorative materials to re-distribute cadmium and zinc from soil solution into the less mobile but labile soil fractions whereas lead mobility was less significantly affected and extractability of arsenic even increased in some of treated pots. Moreover, the mobility of arsenic seemed to be more evidently affected by different characteristics of experimental soils than by individual soil treatments. Summarizing the results, effective immobilization of Cd, Zn, and in lesser extent Pb by increased soil pH (liming) and soil sorption capacity (application of synthetic zeolite) was evident even after four vegetation periods suggesting stability of these soil treatments for more than one vegetation period. However, these treatments are not generally acceptable at multicontaminated soils as well as at all the soil types. Concerning the less mobile soil fractions determined by sequential extraction procedure the results suggested lower effect of the soil treatments where the effect of low pH of individual extraction agents should be taken into account.

Acknowledgement: Authors thank for financial support of GACR project No. 526/06/0418.

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P-39

MOBILITY OF IMPORTANT TOXIC ANALYTES IN URBAN DUST AND SIMULATED AIR FILTERS DETERMINED BY SEQUENTIAL EXTRACTION AND GFAAS/ICP-AES METHODS

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The modified BCR three step sequential extraction procedure has been applied to homogenized urban dust samples (APM) and to simulated air filters (acetyl cellulose, diameter of 47 mm and pore size 0.45 μm) loaded with APM using a wet deposition process developed in IAEA in Vienna [1]. The homogeneity of both bulk APM and the loaded filters and total analyte concentrations were carried out using several analytical methods (INAA, PIXE, GFAAS, ICP-AES and ICP-MS). Chemical fractions were analysed by ICP-AES and GF AAS. Investigated trace elements were selected according to their adverse effects on human health: As, Cd, Cr, Mn, Ni, Pb.

Comparisons were done between extracted portions of analytes in individual fractions from urban dust and simulated air filters loaded by that urban dust. Leaching portions of most elements in simulated air filters increased in mobile fractions and decreased in residual fraction F4. Thus in exchangeable fraction F1, Cd, Mn and Pb increased in the range of 25-40 %, in fraction F2, As, Cr, Mn, Ni increased in the range of 11-20 % and in fraction F3 the significant increase of As (43 %), Cr (25 %) and Ni (32 %) was observed. More experiments were then done with urban dust when Triton X-100 was employed in extraction procedures to verify the idea of increasing mobility of analytes in filters due to the presence of surfactant Triton X-100 [2]. It was added into the APM water suspension in deposition process when loaded filters were prepared [1]. The influence of filter impurities on the reliability of results of some analytes is discussed as well.

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P-40

PLANT UPTAKE OF PESTICIDES

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Nowadays, the bioavailability of pesticides represent a serious problem as this information is required for environmental risk assessment studies, especially for foodstuff plants. Farmed produce, organic crops are grown in soils that may be contaminated with persistent organic chemicals from the applications of agrochemicals.

The objective of this study is to model the plant uptake of pesticides in - one of the most important agriculutural plant - wheat *(Triticum aestivum)* samples, in order to acquire information regarding ″biologically utilized″ amounts of examined pesticides. The bioavailability and the extent of plant uptake were investigated for 3 different types of soil and 3 pesticides. Pesticide residues from the plants, the roots and aerial parts were analyzed separately in order to determinate the plant uptake.

In this experiment three different types of soil samples (sandy, browny and floodplain soil) were treated in 3 series in parallel with 5 distinctive concentrations of Simazine, Chloropyriphos, and Acetochlore. The pesticide treatments were calculated using the recommended field doses. One of the sets of soil samples was the control series, the other series - to determinate plant uptake - was sowed with wheat. We also determined a complete series of samples in order to exclude the effect of microbiological activity. The pesticide concentration of the control series was measured at the same times as wheat sowing, and harvesting.

Wheat were germinated in a culture dish by placing them on a filter paper and stored at room temperature for 3 days. One hundred pregerminated seedlings with seminal leaves were transplanted to pots containing 100 g pesticide amended-soil. At the termination of the cultivation period, wheat plants were harvested and soil samples collected.

Soil samples were extracted by 80% methanol, acetate-buffer and humic acid, solutions to determinate their extraction efficiency. The pesticide amount were determined by GC-MS QP2010S technique.

In case the investigation of modeling the bioavailable amount of simazine from floodplain soil there was hardly any difference among the extracting solvents. The most amount of simazine could be extracted from the soil with 80% methanol, while acetate-buffer and the two different concentrations of humic acid solutions have a bit less, but the same efficiency. According to the results of the control series the one quarter of the original pesticide concentrations is present in wheat at the time of harvest.

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MULTIELEMENT ANALYSIS OF THE AIR-POLLUTION-CONTROL (APC) RESIDUES FROM A SECONDARY LEAD SMELTER - COMPARISON OF THE DECOMPOSITION METHODS

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Three types of decomposition methods were tested on four samples of air-pollution-control (APC) residues from the secondary lead smelter (Kovohutě Příbram a.s., Czech Republic). Furthermore these methods were verified on two standard reference materials (NIST 1633b-Coal Fly Ash and EnviPT 1). Solution prepared by acid decomposition in open and closed systems and alkali sintering were analysed using FAAS (Al, As, Ba, Be, Bi, Ca, Cd, Co, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Si, Zn) and ICP MS (Sn). The all studied residue samples contain both silicates phases (quartz, muscovite, cristobalite) and Pb-bearing phases, mainly Pb chlorides and sulphates (e.g. $PbSO_4$, Pb(OH)Cl, $KCl.2PbCl_2$, $PbCl_2$, $Na_3Pb_2(SO4)_3Cl$) [1].

Standard acid digestion in open system (Pt dish) consists of sample dissolution with HF and $HClO_4$, evaporation to near dryness and final dissolution in 2 % v/v HCl. The closed system of acid decomposition was performed in Savillex® PTFE vessels using HF and $HClO_4$ acid mixtures. The prepared solutes were stabilized with H_3BO_3. The alkali sintering procedure was done in Pt crucibles – 0,2 g of sample with 0,6 g mixture of Na_2CO_3 + $NaNO_3$ (12 : 1) sintering agents. All the methods described e.g. Šulcek and Povondra [2]. Matrix-matched calibration was used for solutions analysis prepared by sintering. Standard reference materials were used for recovery control of decomposition methods.

APC residues (containing Pb-phases and Pb concentration about 40-60 wt. %) have to be decomposed with preventing precipitation of Pb-salts. Low solubility of $PbSO_4$ during simple acid digestion and the observed precipitation of Pb-chlorides ($PbCl_2$) in stock solution show the limitation of traditional acid digestion. Alkali sintering provide significantly higher recoveries for a part of analysed elements in APC residues. The simple acid digestion in open system may be used for determination of As, Be, Bi, Ca, Cd, Co, Cu, Fe, K, Mg, Mn, Na, Ni, Sn, Zn, alkali sintering for Al, Ba, Cr, Pb, Sb. The closed system was applied for determination of Si. As a result, a combination of open and closed acid digestion and sintering were found to be a suitable decomposition method for multielement analysis of Pb-sulphate and Pb-chloride bearing APC residues from metallurgy.

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STUDY OF PHOTODECOMPOSITION PRODUCTS AND KINETICS OF DISTINCTIVE PESTICIDES

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Transformation of pesticides in the environment is a highly complex process affected by different factors. Both biological and physical-chemical factors may play a role in the degradation, whose ratio depends on the actual environmental conditions.

Our study aims to reveal specific details of photolytic degradation of pesticides as important soil contaminants. Significance of these studies is enhanced by the fact that pesticide decomposition may contribute to soil degradation, and harmful biological effects by degrading to toxic products. The toxicity of the examined pesticides is well known, however very little information is available regarding their natural degradation processes, the quality, structure and biological impact of the degradation products.

The photolytic degradation of frequently applied pesticides of distinctive types (simazine, chlorphyriphos, acetochlore, carbendazime, EPTC) was investigated. A special, immerseable UV-light source was applied in order to carry out photodegradation. The degradation processes were followed by TLC, GC and GC/MS techniques. Following the irradiation of the sample, the degradation products were isolated by SPE column chromatography. EI mass spectrometry was used to identify the degradation species.

All five of the different pesticides studied underwent photolytic decomposition, and the detailed mechanism of photolytic transformation was established. At least four degradation species were detected in each case, and for three pesticides two parallel ways of degradation could be observed. Typical decomposition patterns were found to be at the first stage of photodegradation the loss of thio-methyl group, cleavage of the alkyl-groups, breaking up of chloro-group. These steps are followed by cleavage of ester-bonds, destruction of N-alkoxy and N-alkyl groups, as well as breaking up of the hydroxyl-groups. Deamination occurred at the last stage of decomposition.

The kinetic aspect of photodegradation was also revealed completely by GC technique. The kinetic behaviour of the pesticides' degradation displayed significant differences in each case, e.g.: decomposition may even be 10 times faster in a certain interval of irradiation when comparing simazine and carbendazime.

The research on revealing the exact reaction mechanisms of photolytic degradation of pesticides contributes not only to the proper understanding of environmental behaviour of pesticides, but also points out the possible environmental risk factors by identifying possibly toxic degradation products.

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GC-MS INVESTIGATION OF INTERACTION OF PESTICIDES WITH SOIL WITH REGARD TO PLANT UPTAKE

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Determination of the bioavailability of widely used pesticides is necessary for environmental risk assessment and proper agricultural application, as well as for reducing human toxicological problems.

During our studies we developed and adapted experimental systems to model and compare bioavailability of different pesticides, and determine maximally available amounts of pesticides for plants.

The two pesticides examined were simazine (triazine herbicide) and carbendazim (benzimidasole fungicide). For the examination a sandy and a browny soil were used. After the sorption of the pesticides to different type of soils, their desorption was examined with seven kinds of model system. The extracted amount of the pesticides was determined by GC-MS and HPLC technique.

The studied extracting solvents showed diverse efficiency in extracting pesticides. For further investigations we chose 80% methanol, acetate-buffer and humic acid solutions to model the bioavailable amount of pesticides.

In case of the investigation of modeling the bioavailable amount of simazine from sandy soil there was hardly any difference among the extracting solvents. With aqueous methanol extracted the more simazine from the soil, acetate-buffer and the two different concentrations of humic acid solutions have the same efficiency. With humic acid solutions the largest amount of simazine could be extracted from the browny soil. We extracted with aqueous methanol more simazine than with acetate buffer. Extraction solvents had almost the same efficiency in extracting carbendazim from sandy soil. Aqueous methanol and acetate-buffer were found to be slightly more efficient extractants than $CaCl_2$ solution and humic acid solutions. During our experiments, in general, the studied extracting solvents extracted more pesticide from the sandy soil than from the browny, because of the different sorption properties.

Out of the studied extracting solvents 3 proved to be suitable to model the bioavailable amount of pesticides in case of different type of soils, namely: aqueous methanol, acetate-buffer and humic acid solution (1.). In our further investigations we want to study the adaptability of these methods for real soil-samples.

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EVALUATION OF THE MOBILITY OF FE AND MN IN INDIVIDUAL PARTS OF ENVIRONMENT

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Extraction into strong complexing agents could be used for evaluating the non-residual elemental content of sediments and soils. Assessment of the extractability of iron and manganese oxides provide information about the majority of elements associated with this environmentally important sedimentary phase. Changes in the release of iron into a water solution allows the trace element mobility changes and a change in the water's potential for aquatic life to be assessed [1,2]. The extraction and determination of iron and manganese using ethylenediaminetetraacetic acid serves as a fast additive screening for actual contamination and mobility changes in sedimentary and soil systems.

Single and sequential extraction procedures were applied to sediment and soil samples collected from an industrially polluted region of Eastern Slovakia. A sequential extraction procedure (SEP) recommended by the Institute for Reference Materials and Measurements (IRMM) was applied and used as a reference extraction method. The single-step extraction (for soils) with 0.05 mol L^{-1} ethylenediaminetetraacetic acid (EDTA) was slightly modified for this study. The ability of "Na_2EDTA extraction" to remove elements was compared with the SEP recommended by the IRMM. After optimization, the content of the elements extracted by Na_2EDTA were in good agreement with the sum of the first, second and third steps of the SEP for Fe and Mn. Therefore, Na_2EDTA can extract a majority of elements associated with the reducible sedimentary phase - bound to Fe and Mn oxides.

With respect to the realised experiments and mentioned facts [3,4], it is possible to state that a single-step leaching procedure into a strong chelating agent like Na_2EDTA (after optimisation of extraction conditions based on regional geological particularities) is able to release mobile and potentially mobile metal forms associated with specific phases of sediments and soils. Specifically, in the case of Fe and Mn in the known conditions, it is possible to evaluate the extractability changes of the other contaminating elements present in the soils and sediments on the basis of the changed extractability of iron and manganese.

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DETERMINATION OF VANADIUM AFTER FRACTIONATION OF SOILS AND SLUDGES BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Owing to vanadium essential and toxic nature for biological systems there has been considerable interest in the determination of its content in environmental samples. Its toxicity seems to increase as the valence and the solubility of its species increase. Vanadium presence in soils is not neutral for the plants and its influence on the plants depends on the concentration.

To study the distribution of the metal in a solid phase, the methods most widely used are based on extraction techniques with different chemical extractants. Sequential extraction is now a well-established approach for the fractionation of trace metal content in soils, sediments and sludges. As a part of a recent attempt to harmonize methodology for extraction tests, European Community has developed a BCR-three stage sequential extraction protocol, in which metals are divided into soluble/exchangeable, reducible and oxidizable fractions.

The BCR sequential extraction scheme was applied to Slovak reference materials of soils of various origin, and Slovak reference materials of sludges from city water treatment, in order to assess potential vanadium mobility and the differentiation of vanadium in various soil and sludge fractions. The content of vanadium in the fractions of the studied reference materials of soils was dominant in the residual fraction, the content of vanadium in the fractions of the studied reference materials of sludges was differentiated into the fractions, represent vanadium bound to organic matter and sulfide, reducible fraction and residual fraction. Total concentration of vanadium was determined after decomposition by the acid mixture of HNO_3-$HClO_4$-HF in open system. Residual fraction remaining after sequential extraction was digested similarly.

The internal check of accuracy was performed on the results of the sequential extraction by comparing of the total amounts of vanadium removed in the procedure with the results of the total digestion of original samples. The amount of vanadium extracted in the sequential extraction procedure was in good correlation with the total content of vanadium in the samples.

Acknowledgement: This work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic VEGA/1/2466/05 and Slovak-German Scientific Project DAAD No.13/2004.

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FRACTIONATION OF MOLYBDENUM IN SOILS AND SLUDGES AND THE DETERMINATION BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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The frequent low concentrations of molybdenum in environmental samples require highly sensitive techniques, such as ETAAS. The importance of molybdenum lies on its duality both as an essential trace metal for plants, animals and humans and also as a potential toxic.

Chemical speciation strongly influences the mobility of metals in soils and sludges. Operational methods of speciation, such as the use of single or sequential extraction are commonly applied. The BCR sequential extraction scheme was applied to Slovak reference materials of soils of various origin, and Slovak reference materials of sludges from city water treatment, in order to assess potential molybdenum mobility and the differentiation of molybdenum in various soil and sludge fractions. The content of molybdenum in the fractions of the studied reference materials of soils was dominant in the residual fraction, the content of molybdenum in the fractions of the studied reference materials of sludges was predominant in the fraction, represent Mo bound to organic matter and sulfide.

The internal check of accuracy was performed on the results of the sequential extraction by comparing of the total amounts of molybdenum removed in the procedure with the results of the pseudototal digestion of original samples.

Pseudototal molybdenum content in soils and sludges was determined by digestion with aqua regia. This dissolution procedure was compared with two another decomposition methods, decomposition with acid mixture HNO_3-$HClO_4$-HF at atmospheric pressure and decomposition with HF and HNO_3 at elevated pressure. The interfering effects of major and minor concomitants of soils and sludges on Mo signals were evaluated. The mixture of $Pd(NO_3)_2$+$Mg(NO_3)_2$ was selected as chemical modifier.

Acknowledgement: This work was financially supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic VEGA/1/2466/05 and Slovak-German Scientific Project DAAD No.13/2004.

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