XIXTH SLOVAK - CZECH SPECTROSCOPIC CONFERENCE

BOOK OF ABSTRACTS

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Preface

It is my great pleasure to welcome all of you at the XIXth Slovak–Czech Spectroscopic Conference which is held in the special facility of the Office of the National Council of the Slovak Republic in Častá-Papiernička, 12-16 October, 2008. Since 1993 up to the present time when the Slovak and Czech spectroscopic communities organized separately their conferences, this event is a joint decision to continue in their long-time tradition of common meetings.

The objective of this 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 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.

On behalf of the Organization committee I would like to thank for the interest of well-known scientists from 12 countries as well as participants from various institutions, laboratories, and commercial companies who create together very worthwhile professional program for us.

This year Conference offers a 5 day scientific program that consists of 4 honoured and 11 invited lectures, about 40 oral presentations, 60 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 should like to take this opportunity to thank all my colleagues and collaborators who have contributed towards the preparation of this Conference and I gratefully acknowledge the support of our sponsors.

I wish all of you a very enjoyable stay here in Častá-Papiernička and I hope that despite of rather busy schedule you will be able to visit some of our cultural, historical, and natural localities and to taste the typical products of this most important wine region of Slovakia

With my best regards

Jana Kubová
chair of the organizing committee

PROGRAMME

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PROGRAMME

Sunday, October 12, 2008

12.00-21.00	Registration
12.00-22.00	Installation of posters
12.30-14.00	Lunch
16.00-16.30	Opening ceremony

Chairperson: J. Kubová

16.30-17.00	**M. Matherny** Atmospheric dustiness of residential agglomeration and his element analysis
17.00-17.30	**E. Plško** Contribution of statistical methods to the evaluation of spectroanalytical results
17.30-18.00	**J. Toman** Brief insight into the history of plasma spectroscopy in the Czech and Slovak Republics
18.00-18.30	**M. Vobecký** Induced radioactivity – analytical property of activation analysis
18.30-20.00	Dinner
20.00-22.00	Get together and Welcome party

Monday, October 13, 2008

07.30-08.30	Breakfast
08.30-18.00	Registration

Chairperson: B. Dočekal

08.30-09.00	**T. Kántor** A possible new reagent in sample preparation methods – Reduction of excess nitric acid content in sample solutions by formic acid addition for use in dissolution based atomic spectrometry methods
09.00-09.20	**G. Knapp** Microwave induced combustion – a powerful sample preparation technique

09.20-09.40 **I. Hagarová** Cloud point extraction as a tool for separation and preconcentration in metal analysis: Theory and applications

09.40-10.00 **L. Macháčková** Comparison of the preconcentration procedures for element determination in waters using atomic spectrometry techniques

10.00-10.20 **F. Čacho** Electrochemical preconcentration technique for atomic spectrometry

10.20-10.50 Coffee break

Chairperson: V. Otruba

10.50-11.20 **V. Kriváň** Trace analysis of solid materials with atomic spectrometry methods: Dramatic performance improvement by direct solid sampling

11.20-11.40 **P. Török** Direct determination of selected elements in CRMs of food-stuffs by ET AAS

11.40-12.00 **U. Oppermann** The easy way for solving interferences in ICP-OES

12.00-12.20 **P. Kolečkář** ICP spectrometers and their application in the tribotechnical analysis

12.20-12.40 **M. Kröppl** Validation of ICP-OES for the determination of metals in ashes from biomass incinerators

12.40-13.00 **D. Mackových** Determination of mass concentration of sulphur dioxide from stacionary source emissions by atomic emission spectrometry with inductively coupled plasma

13.00-14.00 Lunch

Chairperson: P. Veis

14.00-14.30 **D. Günther** Laser ablation inductively coupled plasma mass spectrometry – a mature technique for direct solid analysis

14.30-14.50 **V. Kanický** Selected applications of laser ablation inductively coupled plasma spectrometry in the analysis of powdered and compact samples

14.50-15.10 **J. Čáslavský** Application of mass spectrometry on spherical ion trap for the identification of cluster boron compounds

15.10-15.30 **Š. Bova** Mass spectrometry of analogs isopropyl metylfluorphosponate and dimetyl - N,N - phosporamidates

15.30-15.50 **A. Ramsza** Some applications of ultrasonic NOVA-1 nebulizer

15.50-16.20 Coffee break

Chairperson: V. Kanický

16.20-16.50 **J. Havliš** Laser ablation process as the key point of GLIM

16.50-17.10 **P. Veis** High sensitivity spectroscopy using cavity ring-down spectroscopy and laser induced breakdown spectroscopy for trace detection

17.10-17.30 **E. Reszke** Studies in generation of toroidal plasmas

17.30-17.50 **R. Borisov** Derivatization of silsesquioxanes for structure elucidation by MALDI-ToF mass spectrometry

17.50-18.00 **L. Babej** Addressing application challenges in AA, ICP-OES and ICP-MS

18.00-18.10 **A. Povolný** HORIBA JOBIN YVON spectrometers

18.10-19.30 Dinner

19.30-22.00 Poster session with beer tasting

Tuesday, October 14, 2008

07.30-08.30 Breakfast

08.30-18.00 Registration

Chairperson: J. Majzlan

08.30-09.00 **T. Liptaj** New trends in NMR

09.00-09.20 **J. Sitek** Half a century of Mössbauer spectroscopy

09.20-09.40 **M. Miglierini** Nuclear resonance with synchrotron radiation

09.40-10.00 **Š. Krnáč** New trends in the gamma ray spectrometry – whole spectrum processing

10.00-10.30 Coffee break

Chairperson: P. Matějka

10.30-11.00 **Š. Urban** High resolution microwave spectroscopy: Rotational spectra of free radicals with resolved fine and hyperfine structures

11.00-11.20 **F. Billes** Vibrational spectroscopic study on 2-[2-(4-dipropylamino-phenyl)-vinyl]-1,3,3,-trimethyl-3H-indolium chloride

11.20-11.40 **I. Němec** Vibrational spectroscopy of hydrogen bonded materials for nonlinear optics

11.40-12.00 **M. Varga** Diamond-like carbon thin films: A Raman spectroscopy study

12.00-12.10 **A. Gába** Raman spectroscopy and new developments in combined analytical methodes: Combined Raman and FTIR, TERS-tip enhanced AFM-Raman spectroscopy

12.10-13.30 Lunch

Chairperson: F. Billes

13.30-14.00 **L. Nasdala** Spectroscopic studies of radiation damage in minerals

14.00-14.20 **P. Matějka** FT Raman and infrared spectra of coniferous needles: What effects can be elucidated?

14.20-14.40 **J. Majzlan** The local environment of Sb and As on the surfaces of iron oxide minerals: An EXAFS study

14.40-15.00 **R. Krickl** Effects of external alpha-irradiation on sheet silicates

15.00-15.30 Coffee break

Chairperson: M. Miglierini

15.30-16.00 **D. Velič** 4D structural dynamics – time resolved laser spectroscopy and spatial mass spectrometry

16.00-16.20 **P. Buček** Spectroscopic study of non-canonical DNA structures using advanced chemometrics methods

16.20-16.40 **E. Svätý** Application of standardless XRF analysis in Třinecké železárny

16.40-17.00 **D. Alexandrakis** Detection and identification of bacteria in an isolated system with near-infrared spectroscopy and multivariate analysis

17.00-17.10 **B. Bohunický** Smart spectroscopic solutions

17.10-17.20 **V. Helán** What supplies 2 THETA?

17.20-18.40 Dinner

19.00-23.00 Wine tasting in the Fugger Family Wine Cellar in Častá

Wednesday, October 15, 2008

07.30-08.30 Breakfast

08.30-12.30 Registration

Chairperson: G. Heltai

08.30-09.00 **E. Bulska** On the use of spectroscopy for the speciation analysis towards designing the functional food

09.00-09.20 **R. Koplík** Speciation of trace elements in digested cereals

09.20-09.40 **J. Machát** GC-ICP-MS technique for speciation of organotin compounds

09.40-10.00 **M. Juříček** Measurement of inorganic mercury and methylmercury in fish tissues, seafood and fish feed by HPLC/ICP-MS

10.00-10.10 **P. Krňák** Varian 820-MS – New approaches to ICP-MS technique

10.10-10.40 Coffee break

Chairperson: O. Mestek

10.40-11.10 **H. Dočekalová** In situ trace metal speciation in aquatic systems, waste-water analysis

11.10-11.30 **G. Heltai** Various fractionation procedures in study of heavy metal's mobility in the environment: Hungarian-Slovak comparative studies

11.30-11.50 **D. Remeteiová** Study of mobility of chosen elements in soils contaminated by pollutants of metallurgical industry

11.50-12.10	**V. Vojteková** The new possibilities of the alternative extraction types of environmental samples
12.10-12.30	**R. Rusnák** Comparison of single-step and BCR sequential extraction procedures of gravitation dust sediment samples
12.30-13.30	Lunch
13.45-18.30	Excursion to the Castle Červený Kameň and Falcon yard ASTUR
20.00-24.00	Conference dinner (banquet) with prizes giving

Thursday, October 16, 2008

08.00-09.00	Breakfast

Chairperson: G. Knapp

09.00-09.30	**E. Beinrohr** Trace analysis: AAS and/or electrochemistry?
09.30-09.50	**B. Dočekal** New observations in collection of hydride forming elements within miniature electrothermal devices
09.50-10.10	**J. Kratzer** In-atomizer preconcentration of hydride forming elements with AAS detection – method optimization and routine applications
10.10-10.30	**K. Elsherif** Simultaneous determination of Al, Be, Cr, and V using multi-element graphite furnace atomic absorption spectrometer (SIMAA 6000)
10.30-10.50	**H. Šoltýsová** Determination of hydrogen sulfide in emissions by AAS
10.50-11.00	**J. Vojtek** contrAA 700 – High-resolution continuum source atomic absorption spectrometer for flame, hydride and graphite furnace – A new dimensions in AAS
11.00-11.20	**V. Helán** Economy of analytical methods
11.20-11.50	Closing ceremony
11.50-13.30	Lunch

POSTER SESSION

Monday, October 13, 2008, 19.30 – 22.00

Chairpersons: M. Matherny, E. Plško, J. Toman, M. Vobecký

P-01 **V. Anan'ev** Band shapes of the electronic spectrum of anisotropic center in uniaxial crystal

P-02 **A. A. Asweisi** A new cross-shaped graphite furnace for atomic absorption spectrometry

P-03 **A. A. Asweisi** Installation of new T-Shaped graphite furnace in horizontal and vertical positions for atomic absorption spectrometry

P-04 **N. R. Bader** Optimization of quantitative AAS analysis of zinc (II) in drinking water after pre-concentration using C18 SPE columns and Schiff bases as chelation agents

P-05 **Y. Bazel'** Spectrophotemetric determination of adenosine triphospate using ion associate of Astra Phloxine FF with molybdophosphate

P-06 **Y. Bazel'** Spectrophotometric determination of some NSAIDs

P-07 **F. Billes** Spectroscopic study on fatty acid-bacterium interactions

P-08 **J. Blašková** Sono-extractive isolation of the potentially mobile element portions of environmental samples

P-09 **L. Brulík** Bioavailable fraction of trace metals in rivers of South Moravia

P-10 **M. Bujdoš** Atomic absorption spectrometry with photochemical vapor generation – recent developments

P-11 **R. Červenka** Determination of methylmercury in fish muscle by GC-AFS

P-12 **S. Dermiş** Spectrophotometric determination of montelukast sodium in tablets

P-13 **P. Diviš** Study of possible alternatives to Spheron-Thiol resin gels in diffusive gradients in thin films technique

P-14 **N. Erk** Quantitative analysis methods of the pharmaceutical preparations containing risperidone

P-15 **N. Fasurová** Synchronous fluorescence and energy dispersive spectra of soil humic substances

P-16 **D. Galusková** Determination of Si and Al in corrosion medium of sodium chloride solution by inductively coupled plasma atomic emission spectrometry

P-17 **M. Gregor** Pigments of La Tène painted ceramics from Bratislava's oppidum: X-ray diffraction and Raman spectroscopic study

P-18 **I. Hagarová** Determination of ultratrace antimony by electrothermal atomic absorption spectrometry with direct TiO_2-slurry sampling

P-19 **K.Z. Haufa** Spectroscopic and DFT studies of temperature and water content effects on the structure of 1-amino-2-propanol, 3-amino-1-propanol and aminoethanol in the liquid phase

P-20 **I. Chovancová** Determination of metals in biofuel

P-21 **J. Jampílek** Application of NIR for characterization of polymorph purity and API-excipient cocrystals

P-22 **J. Komínková** Fractionation of trace elements species in wheat

P-23 **M. Konečná** Contribution to the determination of elements using a high-resolution continuum source flame atomic absorption spectrometer

P-24 **V. Korunová** Problems encountered with the mercury and methylmercury hair analysis

P-25 **J. Kraxner** Determination of Si, Al, Ca, Mg and B in glass samples by inductively coupled plasma atomic emission spectrometry

P-26 **A. Krejčová** o-TOF ICP MS analysis of rare earth elements, uranium and thorium in the elbe river samples

P-27 **V. Kubíček** Influence of solvents on fluorescence spectra of benzimidazoles

P-28 **J. Kubová** Use of optimized BCR three-step sequential and dilute HCl single extraction protocols for the prediction of soil-plant metal transfer processes

P-29 **J. Kuta** Speciation of selenoamino acids in Se-enriched green algae by HPLC-ICP-MS

P-30 **J. Laštincová** Analysis of Cd in must and wine

P-31 **M. Lešková** Synthesis, properties and analytical application of new styryl dye 2-[(E)-2-(4-dipropylaminophenyl)-1-ethenyl]-1, 3, 3-trimethyl-3H-indolium chloride

P-32 **P. Lubal** Spectroscopic study of protonation of oligonucleotides containing adenine and cytosine

P-33 **L. Macháčková** Preconcentration of Cd from aqueous solutions using biological substrates for AAS determination

P-34 **B. Macharáčková** Content of arsenic in the fish muscle from intensive breedings

P-35 **A. Manová** Determination of arsenic in groundwaters by GFAAS

P-36 **P. Matúš** Quantitative assessment of biosorption, bioaccumulation and biovolatilization of labile aluminium and thallium species by fungal biomass using atomic spectrometry

P-37 **P. Matúš** Utilization of five different methods for the assessment of aluminium phytoavailable and/or phytotoxic fractions in acid soils

P-38 **J. Medveď** Separation/preconcentration procedure for thallium species determination in waters by ETAAS

P-39 **O. Mestek** Fractionation of trace elements species in rye seedlings

P-40 **D. Miholová** Proficiency tests and quality assurance in a trace element laboratory

P-41 **W. Misiuk** Spectroscopic study on trazodone / β – cyclodextrin inclusion interactions

P-42 **Z. Mládková** Effect of soil moisture content on the metal concentration measured by diffusive gradients in thin films technique (DGT)

P-43 **A. Mohadesi** Simultaneous determination of trace amounts of mercury and copper by derivative spectrophotometric H-point standard addition method after their separation and preconcentration on modified natural clinoptilolite zeolite

P-44 **P. Pekárková** Luminescence properties Eu(III) coordination polymers with bis(diphenylphosphino)alkane dioxides

P-45 **O. Peš** Capillary electrophoresis laser ablation inductively coupled plasma mass spectrometry for elemental speciation

P-46 **J. Polák** Immobilized metal affinity chromatography as a tool for the isolation of trace elements

P-47 **Ľ. Pospíšilová** Characterization of soil humic substances by UV-VIS and SFS spectroscopy

P-48 **Z. Poulová** The comparison of metal content in sediment and sludge after acid extraction by vapor recovery device and in microwave oven

P-49 **M. Pouzar** Novel approaches in the analysis of plant material

P-50 **J. Sikola** The new vacuum FT-IR spectrometer: Design advances and research application

P-51 **J. Šrámková** Elimination of chloride interference onto Ag and Tl determination in ETAAS using different chemical modifiers: Application to the analysis of aqua regia extracts from environmental samples

P-52 **M. Šucmanová** Determination of metal content in fine airborne particles

P-53 **M. Svoboda** Cryogenic trapping for arsenic speciation analysis by hydride generation – atomic absorption spectrometry

P-54 **J. Száková** Effect of soil sample treatment on an evaluation of trace element (Cu, Fe, Mn, Zn) mobility in soils

P-55 **L. Sztefková** Exploitation of OES ICP in laboratories of steel industry

P-56 **P. Török** Optimization of the instrumental and working conditions for determination of Zn, Pb, As and Sb in certified reference materials of soils by solid sampling – ET AAS

P-57 **J. Varga** Rotational dependence of the methyl bromide dipole moment

P-58 **J. Varga** Fine and hyperfine structures in rotational spectra of the FCO_2• radical

P-59 **J. Varga** Fine (and hyperfine) structures in rotational spectra of the FSO_2• radical

P-60 **V. Vojteková** The Z GF AAS with modulated magnetic field in the environmental analysis

P-61 **J. Zemek** Electron transport in poly[methyl(phenyl)silylene]

ABSTRACTS OF HONORARY LECTURES

pp. 13 – 16

ATMOSPHERIC DUSTINESS OF RESIDENTIAL AGGLOMERATION AND HIS ELEMENT ANALYSIS

Mikuláš Matherny, Katarína Uhrinová, Silvia Ružičková

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The atmospherical dustiness is a complicated state of the atmosphere. It is created by the direct emission sources of relevant region as well as by transported imissions from distant regions. The dust particles are partially washed out with atmospherical rainfall. The ratio of the gravitation dust sediments and flying particle is the fundamental of the studied phenomena. Beside the total gravitation dust sediments and the flying dust particles the eventual toxicity or essentiality is conditioned also by their element composition. But it is necessary to determine this element composition using optimised analytical method.

CONTRIBUTION OF STATISTICAL METHODS TO THE EVALUATION OF SPECTROANALYTICAL RESULTS

Eduard Plško

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As the introduction important scientists who contributed to the creation of mathematical statistics and to its application in different scientific branches since the oldest time till to the origin of chemometrics representing the exploitation of mathematical and statistical methods for to treat chemical data are listed.

A special interest is devoted to the author's original results obtained in the application of mathematical statistical methods on the spectroanalytical procedures.

a./ Causes leading to the broadly accepted logarithmic normal distribution of spectrochemical results are explained. In the case of logarithmic normal distribution instead of the probability range given by plus and minus standard deviation can lead to not existing negative concentration values. The range obtained by the difference between the multiple and the quotient of the geometrical mean and a special factor ($\lambda = 1 +$ relative standard deviation in proper fraction) gives more reliable probability information and it never can reach negative concentration values.

b./ Dissymmetric distributions have till now been corrected by different fully formal mathematical procedures (e.g. exponential approach) having nothing to do with the causes of their occurrence. The author described causes of negatively skewed distribution of intensity values. In order to inevitable errors in setting the maximum intensity in the optical axis of the measuring device, readings in the right, as well as in the left side are smaller than the maximum value. The same effect occurs also as consequence of excitation source (arc,spark etc.) radial wandering.

c./ Several optimization conditions were described by the author already in the beginning of sixties of the last century. For nonlinear calibration functions two addition-extrapolation procedures were elaborated and the conditions for the optimization of the additions and number of their repetition calculated. In the mentioned early time it was also determined that for to ensure optimal precision of spectrochemical results at the choice of internal reference supported by the construction of scatter diagrams the nonlinearity of analytical calibration function has to be taken in account. The reliability of photographic photometry was improved by some optimization measures too. Later also the optimization of interpolation for the determination of spectral lines wavelengths, as well as for the number and concentrations of calibration standards were discussed and determined. A simple calculation of standard deviation without the necessity of time consuming and consequently expensive repetition of analyses from a set practically in each laboratory available parallel results obtained on similar samples was proposed.

d./ In order to ensure a correct statistical treatment of quantities defined in a closed range (e.g. concentration expressed in proper fraction in: 0 – 1) the proposed so called pragmatic distribution is of good use and does not give values which do not exist (<0;>1). It is defined by the following transformation: $p = \log(c/1\text{-}c)$.

This review can serve at least as evidence that contributions to the application of statistics to spectrochemical analysis published from our country already before the worldwide chemometric boom should not be neglected.

BRIEF INSIGHT INTO THE HISTORY OF PLASMA SPECTROSCOPY IN THE CZECH AND SLOVAK REPUBLICS

Jiří Toman

Labtech, Ltd., BRNO, Czech Republic

This report is an attempt to map the spread of techniques of plasma spectroscopy during the last 30 to 40 years in the former Czechoslovakia.

During the 60s, there was a group of researchers around prof. Trunecek at the department of Physical Electronics thinking about the utilization of plasma sources for the spectrochemical elemental analysis. These attempts did not find appropriate support and the further research was directed to another field. In spite of that, the first pioneering experiments to use ICP as an analytical tool were performed by I. Kleinmann, V. Svoboda and J. Cajko (in former Institute for research, production and use of radioisotopes in Prague) during the years 1969-71. Dr I.Rubeska and coworkers (in the former Central Geological Survey in Prague) carried out the next experiments with another type of laboratory-made plasma torch and different r.f. generator.

The situation started to change after 1976, when some commercially available ICP spectrometers were acquired in Czechoslovakia. Very close co-operation between the laboratories equipped with the new instrumentation started during the first pioneering period. Former Czech Geological Institute supported then the program of co-operation between the leading laboratories in the geological branch during 1982-90. This field of interest included the comparison of different instrumentation from the viewpoint of spectral interferences also including the level of stray light, optimization of the working conditions of the source with respect to the detection limits, spectral and non-spectral interferences, especially by matrix components, and possibilities of their suppression or elimination.

In addition to these activities, specialized professional meetings and training courses have been organized on a regular basis.

ICP-MS has become an important part of these meetings since the mid 90s.

Contemporary instrumentation enables the development and use of specialized techniques in ICP spectrometry. Recently, hybrid techniques with ICP spectrometric element specific determination are starting to be developed in our research laboratories.

INDUCED RADIOACTIVITY – ANALYTICAL PROPERTY OF ACTIVATION ANALYSIS

Miloslav Vobecký

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Activation analysis may be defined as a method for determination concentrations of elements in a given sample by measuring the characteristc radiations emitted by the radionuclides resulting from selected nuclear transformations. This principle of the elemental radioactivation analysis using the low-level isotope neutron source, was first expressed and demonstrated on determination of dysprosium in inpure yttrium oxide, by George Hevesy and Hilde Levi already in 1936 [1].

A systematic development of neutron activation analysis (NAA) began only around 1950. Based on the growing availibility of research nuclear reactors and scintillation gamma-ray spectrometry the number of applications in science, geology, live sciences and industry had been rapidly increasing.

In Czechoslovakia, the beginning of routine operation of research nuclear reactor VVR-S in early sixties opened possibilities for methodical development and applications of neutron activation analysis (NAA). At that time the scientific team of the Department of Nuclear Chemistry of the Faculty of Nuclear Science and Physical Engineering developed the principle of substoichiometric separation. Later on, the replacement substoiciometry for the separation of elements with low extraction constants of their chelates was developed at Nuclear Research Institute of Czechoslovak Academy of Sciences. These discoveries were important contributions for the methodology of the radiochemical neutron activation analysis (RNAA).

The timely inland production of Ge(Li) opened new possibilities for application of high-resolution gamma-ray spectrometry in non-destructive mode of neutron activation analysis – instrumental neutron activation analysis (INAA) and for element determination using the prompt gamma rays from radiation capture of neutrons by atomic nuclei. Increasing interest in introduction of the INAA stimulated the establishment of the Task Group of Instrumental Radioanalytical Methods of the Czechoslovak Spectroscopic Society in 1971. Its main activity was concentrated on INAA methodology and processing the gamma-ray spectra measured by Ge(Li) detectors. The installation of several neutron generators in the 1970s has allowed the application of fast neutron activation analysis (FNAA) to the analysis of mineral raw materials and metallic materials. A neutron generator constructed at the Physical Institute of Slovak Academy of Sciences in Bratislava was applied also for this purpose.

Methodology investigation related to the application of gamma activation analysis (GAA) especially for the analysis of mineral raw materials were systematically performed at the Institute of Raw Materials in Kutná Hora. Since 1981, the microtron of the Faculty of Nuclear Science a Physical Engineering has been utilized for this purpose and another microtron has been installed in Kutná Hora (1989).

1. Hevesy G., Levi H., Danske Videnskab. Selskab., Matematisk-fysiske Meddelelser, XIV(1936)5

ABSTRACTS OF INVITED LECTURES

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TRACE ANALYSIS: AAS AND/OR ELECTROCHEMISTRY?

Ernest Beinrohr

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Trace concentrations of metals are usually determined by atomic spektrometry, mostly by graphite furnace atomic absorption spectrometry (GF AAS) and mass spectrometry with inductively coupled plasma ionisation (ICP MS). The superior selectivity, sensitivity and broad availability of the AAS method makes it usually the choice No 1 when seeking for a method for trace concentrations. Electrochemical methods also facilitate trace analysis of metals but cannot compete spectrometric methods owing to lower selectivity, limited number of metals measured, laborious and tedious procedures. Yet, in some cases electrochemical methods may reasonably complement or even exceed AAS:

i.) analysis of samples with high salt contents for easily evaporating elements such as Hg, Cd, Pb, etc.,
ii.) determination of some semimetals such as As, Se, Sb,
iii.) speciation analysis, e.g. As(III)/As(V), Cr(III)/Cr(VI),
iv.) on-line process analysis where atomic spectrometers could hardly be employed.

Moreover, electrochemical sample pre-treatment can significantly improve the performance of AAS in special instances:

i.) hydride forming elements can electrochemically be converted to the corresponding hydrides and measured by AAS,
ii.) metals and semimetals can be electrochemically preconcentrated on large surface electrodes and on stripping measured by GF AAS. In such a way matrix effects can be minimised and detection limits improved.

ON THE USE OF SPECTROSCOPY FOR THE SPECIATION ANALYSIS TOWARDS DESIGNING THE FUNCTIONAL FOOD

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The uptake and metabolism of elements depends on its initial form, moreover its role (be nutrient or toxic) in human organism is related to the bioactivity of particular species. Therefore speciation analysis is of great importance in supporting investigation related to the quality of life via designing the functional food towards its desired biological activity. The role of analytical methods in this field cannot be over-estimated as the knowledge on the chemical form of the element of interest in food-staff as well as in living organisms supports those investigation.

The most important task of analytical chemistry is to collect number of various information on the examined system. Nowadays, the use of single analytical technique is not sufficient for collection of multi-dimensional analytical data, therefore the effort is focused on tailoring the fit for purpose complex analytical process by using in parallel various analytical techniques.

In this presentation the advantages of using multi-techniques approach in order to collect multi-dimensional information on the sample of interest will be highlighted and exemplified by the investigation of plants, animal food-staff as well of various organs of living organisms exposed to various food. For the determination of the total content of trace elements commonly used GF AAS and/or ICP MS were applied. This allows to obtain the information on the local concentration of element of interest in various tissues. Then the LA ICP MS was used to localize the occurrence of elements in cells of plants and animals tissues. The in-vivo inspection of the cells of living organs, with high sensitivity and high spatial resolution, supports the understanding of the transport mechanism of various compounds.

For speciation analysis the traditional approaches of using HPLC ICP MS was accompanied by the investigation performed with the use of μ-XANES (X-ray absorption near edge spectroscopy). By this it was possible to collect essential information not only on the presence of various chemical forms in the whole tissue but also to localize the particular species within investigated cells.

It is believed that the most important challenge of analytical chemistry is to elaborate the proper designed multi-approach by selecting the set of those analytical techniques which offer the complementary information on the examined system.

IN SITU TRACE METAL SPECIATION IN AQUATIC SYSTEMS, WASTE-WATER ANALYSIS

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Diffusive gradients in thin-films technique (DGT), invented by Davison and Zhang in 1994 /1/ is nowadays successfully used in environmental analysis for sampling solute species in aquatic systems. It accumulates metals continuously on a binding layer after passage through a well-defined diffusive gel layer, usually consisting of a hydrogel. The simple plastic device can be readily deployed in situ. The accumulated metals are measured later in the laboratory 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 can be used for the determination of the concentration of metal ions in the acid eluent. The ICP MS is very useful due to its detection power in this instance. The measured amounts of accumulated metals are used to calculate the in situ concentration in solution from Fick´s laws of diffusion /2/. Like ASV, the technique discriminates metal species kinetically; only species those are labile (typically minutes) are measured. However, it also discriminates by size. Hydrogels with different pore sizes can be used, so that only smaller sized species are measured.

The lecture is focused on waste-water analysis. The total concentrations of selected metals were measured in the time period from January to April of the academic year 2007/2008. The DGT was used to measure concentrations of labile metal-species (Cu, Ni, Pb and Hg) in the waste-water from Faculty of Chemistry, Brno University of Technology. Chelex-100 with iminodiacetic groups was used for preparation of resin gels used in the DGT device for Cu, Ni and Pb measurement. The concentrations of labile metal-species found by DGT were: 0.9 – 55 $\mu g.l^{-1}$ for Cu, 2.6 – 156.1 $\mu g.l^{-1}$ for Ni and 0.4 – 10.4 $\mu g.l^{-1}$ for Pb. Copper compounds measured by DGT represent only 0.6 – 5 % of the total copper concentration and lead only 0.3 – 0.9 % of the total concentration. Nickel was found in labile forms in waste water between 20 – 50 % of the total concentration. For mercury determination the Duolite GT-73 and Spheron-Thiol with thiol groups were used for resin gel preparation. Mercury compounds measured by DGT represent only 0.01 – 2 % of the total mercury concentration.

Acknowledgement: The work was supported by Ministry of Education, Youth and Sports of the Czech Republic (KONTAKT, MEB 080813) and by Slovak Research and Development Agency (SK-CZ-044-07).

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LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY - A MATURE TECHNIQUE FOR DIRECT SOLID ANALYSIS

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LA-ICP-MS experienced significant progress within the last few years and some of the key parameters in terms of stoichiometric sampling, aerosol formation and aerosol transport as well as the atomization and ionization of laser-generated aerosols within the ICP plasma have been studied in detail. Therefore, some of the fundamental studies and figures of merit will be discussed, especially with focus aerosol formation and transport efficiency.

Few years after the introduction of 193 nm and 213 nm, IR and UV femtosecond lasers are more and more applied for element analysis and isotope ratio determinations. Non-matrix matched calibration approaches are currently applied for the analysis of various matrices and few examples for UV-ns and UV-fs laser sampling will be given (e.g. glass, gold, gems).

LASER ABLATION PROCESS AS THE KEY POINT OF GLIM

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GE-LA-ICP-MS or GLIM, as a combination of gel electrophoresis (GE), laser ablation (LA), inductively coupled plasma (ICP) and mass spectrometry (MS), is one the promising tools for speciation of metalloproteins. GE serves to separate them, LA to desorb, ICP to ionise and MS to analyse and detect. LA is the key point of the chain; it is employed as method sampling gels without previous sample manipulation, which would lead to losses of information.

To be able to ablate gels, they must be as dry as possible (to prevent water evaporation and gel breaking) and flat to properly aim laser beam. It can be achieved, among other ways such as cryo-cell, by drying the gel in commercial gel drier as it is or between cellophane foils. The study is aimed to pick up the more suitable and practical drying approach.

Next part of the study was to optimise the ablation parameters of laser ablation such as repetition rate, laser spot diameter and laser power density in respect to creation of laser-induced aerosol (number of particles and particle size distribution) as it evokes subsequent changes in analytical ICP-MS signal. Thus in this work we have studied influence of laser ablation parameters on particle size distribution of laser-induced aerosol and ICP-MS signal. Laser power density was changed in range from 15.0 MW cm^{-2} to 6.5 GW cm^{-2} for repetition rate 5, 10 and 20 Hz. These parameters were kept constant: crater size (100 μm), laser ablation rate (50 μm.s^{-1}), argon (0.6 l.min^{-1}) and helium (1 l.min^{-1}) flow-rates.

All measurements were carried out with dried polyacrylamide gel, either dried as it was or between cellophane foils. All gels were saturated by Co^{2+} solutions in different concentrations (10 mM, 0.1 mM and 1 μM) to measure comparable 59Co ICP-MS signal.

In a result, gels, prepared by means of drying as they were, are difficult to achieve in suitable constitution (rough surface, breaking of the gel), but once successfully done, it shows higher signal intensities and better S/N ratio than gels dried between cellophane foils. These are easy to handle, but signal RSD is lower than with the first type of preparation. As for the laser ablation conditions, they have shown shift towards greater amount of particles with rising frequency, whereas distribution size was mostly unaffected. When increasing laser power density, particles tend to be heavier (shift in particle size distribution). The particle amount responded with a saturation profile; starting from certain value of laser power density, the number of particles created does not increase.

A POSSIBLE NEW REAGENT IN SAMPLE PREPARATION METHODS - REDUCTION OF EXCESS NITRIC ACID CONTENT IN SAMPLE SOLUTIONS BY FORMIC ACID ADDITION FOR USE IN DISSOLUTION BASED ATOMIC SPECTROMETRY METHODS

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In the majority of atomic spectrometry methods the samples are analyzed in form of solution in which the rest of the free acid content after sample destruction is determined by the applied dissolution procedure (with consideration of the allowable degree of dilution). In the widely used microwave sample digestion procedures the concentrated nitric acid is often the primary component of the dissolution reagent. Typically, when applying 5 ml 65% (m/m) nitric acid (equivalent with 91% m/v HNO_3) to 0.2 g organic sample and filling up the resulted product to 25 ml, the sample solution contains 7-15 % (m/v) free HNO_3.

Acidification of solutions (in case of a free choice) is made often to 1% (m/v) concentration for the sake of stabilization (elimination of hydrolysis) during storage and nebulization. The "acid interferences" [1] are related to this basic level of acid concentration, which amounts about 20% decrease by 4-fold diluted nitric acid (22,8% m/v HNO_3) for ICP emission of sensitive ionic lines at compromised conditions of radial plasma viewing [1]. A more serious problem is caused by the changing acid concentration in lengthening the time required to attain steady state analytical signals (in the order of 5 min) [1]. The interference effect of nitric acid is extremely strong in case of ultrasonic nebulization combined with aerosol desolvation (that is not effective enough): 43 % decrease of line intensities of 15 elements was found at 1,5 M (9.45% m/v) nitric acid concentration of nebulized solutions (ICP-OES) [1].

The fast chemical removal of nitric acid by formaldehyde or formic acid addition was introduced in the chemical technology by Healy in 1958 [3], based on the reactions that produce CO_2, NO and NO_2 gases above 60 °C temperature of the aqueous mixture. For analytical purpose the formic acid reagent seems more suitable, it can be further purified by sub-boiling distillation (b.p. 100.7 °C).

Optimization studies were made to decompose 10 ml 10 M HNO_3 by stepwise addition (1-18 ml) of 10 M HCOOH, warming up to 60 °C and allowing reaction time of 10 min. Concentrations of about 1% of both acids were obtained with 1.5 fold excess of formic acid under these conditions.

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TRACE NALYSIS OF SOLID MATERIALS WITH ATOMIC SPECTROMETRY METHODS: DRAMATIC PERFORMANCE IMPROVEMENT BY DIRECT SOLID SAMPLING

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Graphite furnace atomic absorption spectrometry (GF AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES) applied to sample digests represent the most widly used methods for trace analysis of solid materials. However, the sample digestion unavoidable in this working mode causes an enormous worsening of the instrumental performance of these methods. Therefore, direct solid sampling techniques for GF AAS (SoS-GF AAS) and, in combination wit electrothermal vaporization (ETV), also for ICP-OES (SoS-ETV-ICP-OES) are gaining great importance. In recent years, considerable progress has been achieved in the development and commercial availability of instruments for these two methods allowing a problem-free direct introduction of solid samples and well satisfying also other instrumental requirements for successful application of these direct methods.

With SoS-GF AAS, many materials can be analysed directly without any modification. However, for some materials, the applicability and performance of SoS-GF AAS is strongly impaired by matrix effects. Nevertheless, in almost all instances of occurance of strong matrix effects, effective in situ chemical modifications for their avoidance could be developed. For all determinations, aqueous standard solutions have been used for calibration. Meanwhile, matrix-specific SoS-Gf AAS methods have been developed for more than 20 materials of different nature and the acuracy has been satisfactorily assessed. In the most cases, the achieved LODs were at the 100 and 10 pg/g level and were up to three orders of magnitude lower than those of the solution GF AAS. Typically, one analysis run requires 4 to 10 minutes.

For SoS-ETV-ICP OES, compared with nebulization of digests, a similar enhancement of the performance was achieved as in the GF AAS. In analysis of most materials, addition of a halogenating agent as modifier to the argon carrier gas proved to be essential with respect to the achievement of quantitative volatilization also for carbide forming analytes, enhanced transport efficiency and feasibility of calibration using calibration curves measured with aqueous standard solutions. Limits of detection down to the ng/g level are achievable. SoS-ETV-ICP OES provides high sample throughput, low operation costs, robustness and good accuracy.

The solid sampling technique offers the opportunity for full exploitation of the performance potential of GF AAS and ETV-ICP OES. The excellent performance, together with the most important matrix-specific aspects and remaining limitations of these direct methods are discussed and demonstrated by using selected examples of their application.

NEW TRENDS IN NMR

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Similarly as in other branches of spectroscopy there was a significant progress in development of new NMR methods and applications in the last few decades. In NMR this progress was acknowledged by the awarding 3 Nobel Prizes since 1991 and also by wide spreading of this method in the research laboratories. NMR became one of the principal research tools in many branches of natural sciences.

It would be difficult to prepare a comprehensive list of all significant developments of NMR in the last two decades as they concern with very broad variety of applications ranging from physics to medicine. Most of the new developments deal with the structure and properties determination of complex biomolecules and their exploitation usually requires a multidisciplinary approach. However, developments concerning the small or medium size molecules were also important and in this presentation we will focus on them. In particular we will discuss two specific developments: a) Implementation of so called "Residual Dipolar couplings" to the structure elucidation of small rigid molecules; b) New trends in application of NMR to the analysis of mixtures of compounds.

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SPECTROSCOPIC STUDIES OF RADIATION DAMAGE IN MINERALS

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In the past few years, research groups worldwide have increasingly applied micro-spectroscopic techniques to study minerals and their synthetic analogs that suffered from the impact of natural or artificial irradiation. Such studies are done to characterize, and quantify, radiation effects and resulting property changes in solids. Results are of exceptional relevance in the Earth sciences (e.g., potentially biased age determinations based on radioisotopes), material science (e.g., performance assessment of radioactive waste forms), and environmental sciences (e.g., stability of building materials in nuclear power stations in a worst-case scenario). Especially the combined application of several non-destructive spectroscopic and imaging techniques may provide a wealth of information on the short-range order, structural state, and growth and alteration textures of radiation-damaged solids. Examples presented in the talk include (i) the use of vibrational and emission bands to estimate the radiation-induced disturbance of the short-range order, (ii) information on the secondary alteration of rocks from the damage accumulation in actinide-bearing accessories (Fig. 1), (iii) first spectroscopic results for He^{2+}-implanted samples, to evaluate alpha-particle damage versus alpha-assisted annealing, and (iv) the use of radioactive inclusions to check for possible high-*T* color enhancement of gemstones.

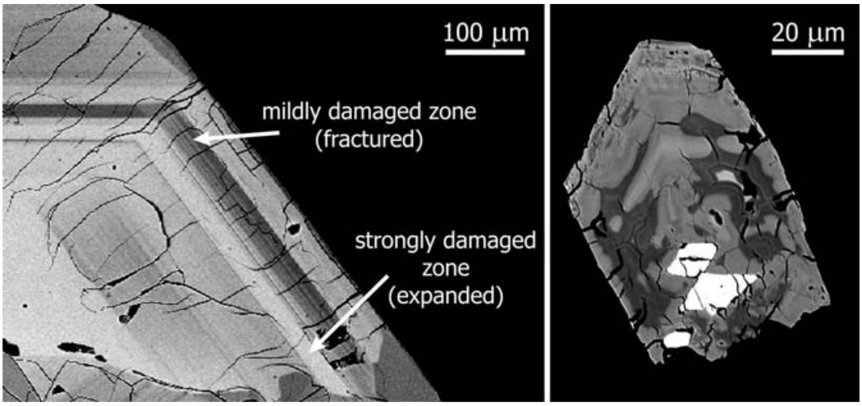

Figure 1: Left, BSE image of an unaltered zircon from Plešovice, Bohemia, showing primary growth zoning. More radiation-damaged zones appear brighter; their volume expansion has caused fracturing of neighboring zones. Right, BSE image of a zircon from La Pedriza, Spain, with xenotime inclusions (bright). Altered areas (dark) are seen near the ends of fractures, which have served as migration pathways.

HIGH RESOLUTION MICROWAVE SPECTROSCOPY: ROTATIONAL SPECTRA OF FREE RADICALS WITH RESOLVED FINE AND HYPERFINE STRUCTURES

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A new semiconductor mm/submm-wave spectrometer has been developed in the Prague laboratory during 2004-2006. This microwave spectrometer allows measurements of Doppler limited as well as sub-Doppler high-resolution spectra. The scientific program of the Prague laboratory is focused to the spectroscopy of atmospherically important species with a significant hyperfine structure of rotational levels, to the Stark measurements of molecular electric dipole moments and, recently, interesting studies are also focused to molecular free radicals.

The free radicals are defined as molecular species containing at least one unpaired electron. In this talk, two high resolution studies of free radicals will be presented – fluoroformyloxyl radical ($FCO_2\cdot$) and fluorosulfate radical ($FSO_3\cdot$). These radicals are of the atmospherical interest, for example the $FCO_2\cdot$ radical can be produced by stratospheric degradations of HCFCs and HFCs. Both radicals contain one unpaired electron that causes, above all, the fine splitting of the rotational levels into two sublevels. Beside this, there are hyperfine interactions due to 19F nucleus that can give rise to an additional hyperfine doubling of levels. The rotational spectra with these fine and hyperfine splittings were measured and analyzed.

Since free radicals are usually short-lived, it is desirable to generate them inside the cell during spectroscopic measurements. Therefore in our studies, the continuous pyrolysis of suitable precursors was used. Since spectral lines of the radical transitions are usually hidden in a redundancy of lines of other molecular species, the identification of the radical lines was simplified by using an external magnetic field which affects only the radical species by the molecular Zeeman Effect.

The radicals $FCO_2\cdot$ and $FSO_3\cdot$ were measured in the frequency regions 130 – 242 GHz and 93 – 280 GHz, respectively. From the experimental transition frequencies obtained in our laboratory, the set of rotational, centrifugal distortion, fine and hyperfine constants were calculated.

The microwave spectra of the $FSO_3\cdot$ free radical were observed, identified, and analyzed for the first time.

4D STRUCTURAL DYNAMICS –
TIME RESOLVED LASER SPECTROSCOPY AND SPATIAL MASS SPECTROMETRY

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A correlation between a structure and a function is a well defined concept in biochemistry and it is clearly relevant also for other fields of natural sciences. However, there is a third component - a time domain. This contribution represents an attempt to provide a unique overlap between the structural characterization in 3D and the dynamics in 1D time. Such 4D characterization can then provide a full picture of interacting molecular systems in space and time. Our experiments are based on two techniques, spatial distribution provided by secondary ion mass spectrometry, SIMS, and dynamics provided by laser time-resolved fluorescence spectroscopy, TRFS.

The probe fluorophore molecule of coumarin C522 is used to test a delicate balance between hydrophilic and hydrophobic interactions on montmorillonite surfaces with varying surface charge density in aqueous suspension. The interactions between adsorbate and surface are important for adsorption, desorption, and chemical reactions in confined environments. An overall negative charge is located on the layers due to isomorphous, charge non equivalent, substitutions in the structure, compensated by positively charged interlayer cations like K^+, Na^+, and Mg^{2+}. The reduced-charge montmorillonite series is prepared with 0.00, 0.12, 0.26, 0.43, 0.66, and 0.97 Li^+ molar fraction. As examples, cleavable clay minerals are selected to determine the spatial distribution of atomic species within the single layer of 1 nm thickness. Depth profiles reflect the molecular structure of clays, repeating the octahedral, [AlO,OH], and two tetrahedral, [SiO_4] units. Calculated sputter rate is estimated to be approximately 0.17 nm per scan. The fluorescence dynamics reveals biexponential dependence in the 6 ps scale. The faster component of decay time T increases linearly from 1.0 ps for Li^+ molar fraction to 3.6 ps for 0.97 Li^+ molar fraction. Two cartoons illustrating the structure of interactions between C522 and hydrophilic and hydrophobic surfaces in water are proposed and describe well the dynamics.

The spatial distribution below 1 nm and the time resolution below 1 ps are demonstrating the unique potentials of SIMS and TRFS techniques, even more the potential of their combination.

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ABSTRACTS OF LECTURES

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DETECTION AND IDENTIFICATION OF BACTERIA IN AN ISOLATED SYSTEM WITH NEAR-INFRARED SPECTROSCOPY AND MULTIVARIATE ANALYSIS

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Near-infrared transflectance spectra (700-900 nm; 0.1 nm sample thickness) of *Listeria innocua* FH, *Lactococcus lactis*, *Pseudomonas fluorescens*, *Pseudomonas mendocina* and *Pseudomonas putida* suspensions (total n = 418) were collected and investigated for their potential use in identification and classification of bacteria at species and strain level. Unmodified spectral data were transformed (1st and 2nd derivative) using Savitzsky-Golay algorithm. Principal Component Analysis was used initially to investigate the spectral data. The major outcome of this preliminary data analysis step is that the bacterial organisms studied form discrete and largely separate clusters. This strongly suggests that differentiation between the different species and strains may be possible on the basis of their near infrared spectra. Partial Least Squares Discriminant Analysis (PLS2 – DA) and Soft Independent Modelling of Class Analogy (SIMCA) were used in the analysis. Using either full cross validation or separate calibration and prediction data sets, PLS2 regression (loadings n=10) classified the five bacterial suspensions with 100% accuracy at species level. At strain level PLS2 regression (loadings n=4) classified the three *Pseudomonas* strains with 100% accuracy. In the case of SIMCA, prediction of an unknown sample set produced correct classification rates of 100% except for Listeria innocua FH (77%). At strain level, SIMCA produced correct classification rates of 96.7%, 100% and 100% for *Pseudomonas fluorescens*, *Pseudomonas mendocina* and *Pseudomonas putida* respectively. This successful study suggests that NIR technology has the potential to become a useful, rapid and non-invasive tool for bacterial identification.

ADDRESSING APPLICATION CHALLENGES IN AA, ICP-OES AND ICP-MS

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The liquid elemental analysis techniques of Atomic Absorption Spectroscopy (AA), Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) systems are used extensively in a wide range of application areas eg Environmental, Petrochemical, Pharmaceutical, Clinical etc. Each of the three techniques has issues which can create specific difficulties for user:

AA with Graphite Furnace-Method development is an area where difficulties can arise.

ICP-OES-Re analysing samples can be a problem (Unexpected Elemental Contamination).

ICP-MS-Removing potential interferences.

In this presentation we would like to highlight how recent developments in instrument design are helping to overcome these analytical problem areas.

VIBRATIONAL SPECTROSCOPIC STUDY ON 2-[2-(4-DIPROPYLAMINO-PHENYL)-VINYL]-1,3,3,-TRIMETHYL-3H-INDOLIUM CHLORIDE

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Looking at the structure ot the molecule 2-[2-(4-dipropylamino-phenyl)-vinyl]-1,3,3,-trimethyl-3H-indolium chloride (DPPVTI) the cation seems suitable for building transition metal complexes (Fig.1). This is the reason why we dealt with the vibrational spectroscopy and quantum chemical calculations of the molecule.

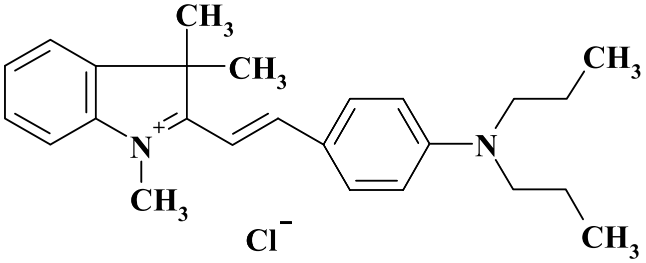

Fig. 1

The DFT Becke3P86 functional were applied with the 6-311G** basis set for the quantum chemical calculations on the cation. The results were the optimized molecular geometry, the atomic net charges, the vibrational force constants and the fundamental vibrational frequencies.

Both infrared and Raman spectra were recorded. The calculated vibrational force constants were fitted to the experimental frequencies. The yielded entries were applied for the determination of the character of the individual vibrational modes and for the simulation of both infrared and Raman spectra of DPPVTI based on the quantum chemical results. The knowledge of atomic net charges made possible to ditiguish between the complex building ability of the two nitrogens. The vibrational spectra are sensitive to the individual complex building metal ions.

DERIVATIZATION OF SILSESQUIOXANES FOR STRUCTURE ELUCIDATION BY MALDI-TOF MASS SPECTROMETRY

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A limited number of studies were devoted to the application of the derivatization techniques to structure determination and characterization of synthetic polymers by MALDI-ToF mass spectrometry. It is of interest to explore possibilities of using derivatization for end-group analysis, structure elucidation and increasing the sensitivity and signal/noise ratio. With this purpose in mind, we used for the first time the derivatization (silylation) in conjunction with MALDI-ToF mass spectrometry for molecular characterization of oligomeric silsesquioxanes, which are interesting due to probable their 3D-structure.

Silsesquioxanes were prepared from a commercially available trifunctional silane agent (3-methacryloyloxypropyltrimethoxysilane) by hydrolysis-condensation methods in a catalysed aqeous/organic solvent mixture. The analytes were derivatized in solution by using BSTFA silylating agent. Initial oligomers and the silylated products were analyzed by matrix-assisted laser desorption/ ionization time-of-flight mass spectrometry (MALDI-ToF-MS).

The molecular structure of the polysilsesquioxane plays a major role in determining the processing properties (such as solubility) as well as the properties of the final solid monolith (such as density). So the structure elucidation of silsesquioxanes oligomers is very important to clarify the reaction pathways and the improvement of reaction control and conditions. From the mechanism of polycondensation reaction follows that oligomers can possess one or more residual hydroxyl groups, and their enumeration is critical to determining their structures. As it is known from the practice of derivatization for GC/MS, the simple way to determine the number of hydroxyl groups is based on derivatization and ,in particular, silylation. In the present work, we investigated the potential of preliminary trimethylsilylation for enumeration of OH groups and molecular structure elucidation of oligomeric silsesquioxanes by MALDI-ToF-MS. It was found that silsesquioxanes under investigation readily react with excess of the silylating agent (BSTFA) to form persilylated products, except oligomers without hydroxyl groups. The mass spectra of initial polymers and their silylated products revealed the peaks for cationized sodiated molecules $[M+Na]^+$ and $[M\text{-}xH+xTMS+Na]^+$ (where x is the number of hydrogen atoms or trimethylsilyl (TMS) groups) respectively. It was found that the initial samples contained oligomers in a mass range 900u to 5000 Da, 72xn Da mass shifts (for TMS derivatives) on going from initial oligomers to silylated products were used for the determination of number of hydroxyl groups which, in turn, allowed the molecular structure of many individual oligomers to be suggested.

MASS SPECTROMETRY OF ANALOGS ISOPROPYL METYLFLUORPHOSPONATE AND DIMETYL – N,N – PHOSPORAMIDATES

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Identification of isopropyl metylfluorphosponate and dimetyl – N,N – phosporamidates next to toxic organic compounds, like sarin or VX agent, allows observation of procedure probably used for preparing this toxic chemical agent. Standard procedures prefer usage of more time consuming derivatization techniques with following gas chromatography and mass spectrometry, mainly with V agent analysis. Requirements for quick analysis and analysis in means of mobile laboratory control prefer direct measurement with minimalization of procedures necessary for sample preparation. Methods for identification conducting were optimalized within mobile laboratory with usage of gas chromatography and EI (Electron Impact) mass spectrometry, which allows quick analysis directly in extract of samples with acceptable result for purpose of quick decision making process. Interpretation of analysis result by simple comparison with databases appears like aviable and effective solution, which we confirmed in term of reproducibility and identification reliability. Identification reliability was proved by mass spectrum comparing with database and structure fragmentation prediction of observed subjects and by comparison of possible fragments mass with measurement.

SPECTROSCOPIC STUDY OF NON-CANONICAL DNA STRUCTURES USING ADVANCED CHEMOMETRICS METHODS

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The G-quadruplex having non-canonical structure has been found in telomers, with the life cycle in the cell, and in some oncogens and aptamers. These parts have been assumed as potential targets for anticancer therapies and therefore nowadays it can be observed the increase of interest in the drug development that can lead to its stabilization [1]. This work was focused on solution equilibria study of oligonucleotide BCL2 that is a 24-mer sequence which corresponds to the guanine-cytosine rich region of P1 promoter contained in *bcl*-2 human oncogene.

The molecular absorption spectroscopy in UV region was employed for oligonucleotide study in order to estimate the protonation constants and “melting points” at different pH and K^+ concentrations. Those informations threw light how the G-quadruplex is stabilized. The interaction of intercalators based on porphyrine skeleton with the G-quadruplex and its 2-aminopurine modified derviatives was studied by means of molecular absorption, fluorescence and CD spectroscopies. The experimental combined data were evaluated by MCR-ALS approach. It was found that positively charged porphyrine derivative stabilizes significantly G-quadruplex. The probable interaction mechanism is proposed.

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ELECTROCHEMICAL PRECONCENTRATION TECHNIQUE FOR ATOMIC SPECTROMETRY

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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 and Sb 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 Spectraa 400 with graphite furnace atomizer (Varian) was used to measure the preconcentrated As and Sb species. The preconcentration parameters for the electrochemical deposition of arsenic 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 As. 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.

For antimony 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 antimony. The advantage of the used preconcentration system was in an automatic and reliable matrix exchange facility. Optimum electrolyte concentrations were found to be 4 mol.dm^{-3} HCl and 2 mol.dm^{-3} HNO_3 for the deposition and stripping/AAS measurement, respectively.

We are going develop complete validation determination of antimony this methody.

Acknowledgment: This study was supported by APVV Project No. 0057-06 and by VEGA Project No. 1/0500/08.

APPLICATION OF MASS SPECTROMETRY ON SPHERICAL ION TRAP FOR THE IDENTIFICATION OF CLUSTER BORON COMPOUNDS

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Mass spectrometry is very powerful tool for the analysis of organic and organometallic compounds. Especially in the "organic" world the fragmentation rules have been worked out precisely [1] and if the library search is unsuccessful, then the compound structure could be deduced by interpretation of mass spectra. In spite of the fact than there exist similarities between carbon and boron compounds, the application of mass spectrometry in the field of cluster boron compounds in several times revealed surprisingly different behaviour of these compounds [2].

In this study we focus our attention on the tandem mass spectrometry of carboranes on spherical ion trap with electrospray ionization. The results were used for the structure confirmation of newly synthesized boranes and heteroboranes and for the identification of undesirable by-products and impurities in the reaction mixtures. Fragmentation of selected model compounds was studied in details and fragmentation routes have been described. The interpretation of product mass spectra was complicated by the multiplets resulting from the borone isotopic distribution, overlayed by peaks resulting due to non-specific sequential hydrogen losses. Inhibition of fragmentation in presence of selected cations was also observed.

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

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NEW OBSERVATIONS IN COLLECTION OF HYDRIDE FORMING ELEMENTS WITHIN MINIATURE ELECTROTHERMAL DEVICES

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Capability of simple prototypes of a miniature collection devices based on a strip of the molybdenum foil, graphite tubes and rods for collecting hydride-forming elements (As, Bi, Sb and Se) is reported. The devices were combined with a miniature hydrogen diffusion flame for detection of hydride forming elements by AAS. Influence of trapping temperature, modification of the foil surface with noble metals – Ir, Pd, Pt and Rh and the role of surface micro-structure, composition of the gaseous phase (argon-hydrogen-oxygen), mutual interference effects of co-generated hydride forming elements were studied. Using ^{73,74}As, ^{205,206}Bi, ^{125}Sb, ^{75}Se radionuclides, complementary radiotracer and radiography experiments were performed in order to determine efficiency of generation, transport and trapping, and in order to assess the spatial distribution of collected analytes within the devices.

Acknowledgement: This work was supported within the Institutional Research Plan AV0 Z40310501 and the Project No. 203/06/1441 of The Grant Agency of the Czech Republic.

SIMULTANEOUS DETERMINATION OF AL, BE, CR, AND V USING MULTI-ELEMENT GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETER (SIMAA 6000)

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Simultaneous multi-element graphite furnace atomic absorption spectrometer (SIMAA 6000) has been used for developing multi-element determinations methodology for Al, Be, Cr, and V. Firstly, the optimum experimental conditions in the case of the single-element mode have been determined (these include: pyrolysis and atomization temperature). Then, the compromised conditions for the simultaneous determination in the multi-element mode have been also determined. The setting of the compromised conditions in the case of multi-element mode has been compared with these of the single-element. The characteristic mass and detection limits for each element in the simultaneous multielement determination have been determined and compared with the single mode. To study the effect of the matrix, urine standard sample (Seronorm-LOT 0511545) has been used (the urine sample has been diluted (1:4)). The accuracy of the methods has been confirmed by analysis of different biological reference materials. The analyzed values in the simultaneous multi-element determinations were in good agreement with the certified values. Simultaneous multi-element GF-AAS provide a rapid, low cost and sensitive method for routine analysis of trace elements.

THE DC-ARC FROM SPECTROGRAPHY TO SPECTROMETRY: PROS & CONS OF VARIOUS INSTRUMENTATIONS IN SOLID-SAMPLING ATOMIC SPECTROSCOPY

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About two decades ago the DC-arc was connected with classical spectro-graphic technique that was declared to be „dead“[1]. In spite of the fact, that requirements on suitable and first of all direct solid sampling spectrochemical methods were continually higher, the logical development in instrumentation has lead besides other techniques also to comeback of the DC-arc excitation. This development has produced the commercial CID-Echelle-DC-arc-Spectrometer Atomcomp 2000 [2], as well as the totally computer-controlled DC-arc of new generation [3,4]. The new aspects of this old-fashioned spectrochemical technique have been welcomed [5] by leading spectrochemists working in the area of the solid sampling spectrochemical analysis as "The Awakening of the Sleeping Beauty".

The connection of such modernized DC-arcs to various types of spectro-meters (polychromator + photomultipliers, CID-detector) covers many new aspects in the spectrochemical evaluation. Both mentioned signal processing techniques have their positive but also negative aspects. These will be discussed in the lecture from point of view of the multielement solid sampling analyses of the environ-mentally relevant samples as biofilms, river and lake sediments. Besides the method development, the attention will be paid to the crucial point of the solid sampling methods – the analytical calibration. More calibration models will be presented and discussed, particularly in connection to the methods validation procedure.

Acknowledgement: The authors are obliged to thank the Slovak Grant Agency VEGA, as well as the DAAD for their support.

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RAMAN SPECTROSCOPY AND NEW DEVELOPMENTS IN COMBINED ANALYTICAL METHODES: COMBINED RAMAN AND FTIR TERS – TIP ENHANCED AFM-RAMAN SPECTROSCOPY

Alexandr Gába

Labimex/ HORIBA Jobin Yvon

The HORIBA Jobin Yvon (further HORIBA JY) Raman Division is the word leader in Raman Dispersive Spectroscopy, which offers many benefits to the analyst – is it a non-destructive and non-invasive technique, with no need for sample preparation. The sample is simply placed under the sampling optics. The laser energy is generally low so the sample remains intact. The performance approaches the true theoretical sub-micron limit and is not restricted by any instrumentation parameters. The HORIBA JY confocal Raman microprobe provides the ultimate in spatially resolved detail – down to the order of one mikron in X,Y and Z directions. This enables very precise microstructural characterization and forms the basis of Raman mapped imaging and depth profiling.

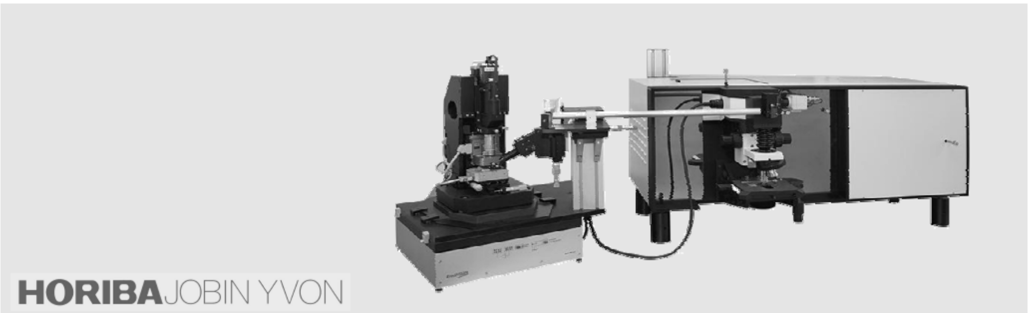
Combined FTIR and Raman:

The unique HORIBA JY instrument LabRAM IR combines both micro Raman and micro FTIR analysis upon the same instrument enabling complementary spectroscopies to be undertaken easily. This heralds the beginning of hybrid Raman analysis, where several spectroscopies can be combined to provide a wider analytical picture.

TERS Spectroscopy:

The use of Raman microscopy has become an important tool for the analysis of materials on the micron scale. The unique confocal and spatial resolution of the LabRAM instruments series has enabled optical far field resolution to be pushed to its limits with often sub-micron resolution achievable.

The next step to material analysis on a smaller scale has been the combination of Raman spectroscopic analysis with near field optics and an Atomic force microscope (AFM). The hybrid Raman/AFM combination enables nanometric topographical information to be coupled to chemici (spectroscopic) information. The unique designsdeveloped by HORIBA JY enable in-situ Raman measurements to be made upon variol different AFM units, and for the exploration of new and evolving techniques such as nanoRamanspectroscopy based on the TERS (tip enhanced Raman Spectroscopy).



CLOUD POINT EXTRACTION AS A TOOL FOR SEPARATION AND PRECONCENTRATION IN METAL ANALYSIS: THEORY AND APPLICATIONS

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Separation and preconcentration are areas of increasing interest, particularly for enhancing the inherent capabilities of analytical signals and lowering the detection limits of used detection methods. During the past years, cloud point extraction (CPE) has become one of the most preferred separation and preconcentration techniques thanks to the enormous potential, benefits and versatility.

Cloud point is the temperature above which aqueous solutions of non-ionic and zwitterionic surfactants become turbid. More specifically, the solution separates into a surfactant-rich phase of small volume, composed almost totally of the surfactant, and a diluted aqueous phase, in which the surfactant concentration is close to the critical micelle concentration. Spieces that can interact with micellar systems either as such, or after they have been derivatized, can thus be extracted and preconcentrated in the small volume of the surfactant-rich phase upon heating.

CPE consists of three main steps: I. solubilization of an analyte in micellar aggregates; II. clouding; III. phase separation for analysis (see Fig. 1).

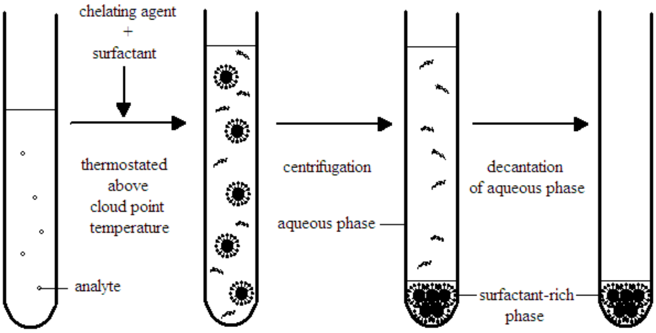

Fig. 1 Schematic representation of cloud point extraction.

The purpose of this lecture is to offer an overview of fundamentals, procedural details, and selected applications of CPE in metal analysis employing atomic spectrometric detection systems.

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ECONOMY OF ANALYTICAL METHODS

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Analytical possibilities of several instrumental methods are very similar, but their economy may differ considerably.

Both atomic absorption spectrometry with electrotermic atomization and flow-through coulometry are suitable for the determination of trace concentrations (around 1 μg/l) of heavy metals. Also the demands for place, energy, and laboratory staff are similar. But the purchase price of coulometric analyzer is 1/3 or even 1/4 of the purchase price of ETA AAS and working expenses of coulometry are 7 times lower then those of ETA AAS.

Similarly both ion chromatography and isotachophoresis / capillary zone electrophoresis are suitable for the determination of macro and micro concentrations of anions in waters. But the purchase price of fully automated ITP/CZE analyzer is 1/2 of the purchase price of IC and working expenses of ITP/CZE are 7 times lower then those of IC.

We can see that the choice of newer and less known analytical method can improve the economy of the laboratory significantly. But this decision demands some flexibility and sometimes also braveness of the responsible persons.

WHAT SUPPLIES 2 THETA?

Václav Helán

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Reference materials: certified reference materials for environmental control and hygiene, industrial, agricultural and other laboratories, setting-up standards for XRF, OES, C, S, O, N, H analysers, standard solutions, physical properties…

Sets for identification and determination of Genetic Modified Organisms in plants, agricultural products and food.

Set for taking of various gaseous, liquid and solid samples in production, environment, transport, etc.

Sample preparation: mills, shakers and press for preparation both inorganic solid samples and plant and food samples, grinders for preparation of metal samples for spectrometric analysis.

Laboratory instruments: coulometric analysers of trace elements, anions and some organic compounds, capillary electrophoresis and isotachophoresis, gel electrophoresis, photometers and spectrophotometers for chemistry and biochemistry.

Microwave mineralization units, reactors and ovens using focused microwaves.

Laboratory devices and furniture: laboratory thermostatic boxes with heating and cooling, glass-ceramic heating panel, laboratory ovens, ultrasonic cleaners, all-plastic fume hoods, furniture for wet and aggressive environment, clean boxes and rooms.

Organizes conferences and courses and issues literature for analytical chemistry, environmental control, statistics, etc.

VARIOUS FRACTIONATION PROCEDURES IN STUDY OF HEAVY METAL'S MOBILITY IN THE ENVIRONMENT: HUNGARIAN-SLOVAK COMPARATIVE STUDIES

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Mobility and bioavailability of metals and their potential ecotoxicity is strongly determined by their specific chemical forms in soils, aquatic sediments but also in airborne gravitation dusts. Due to the complexity of the system the total elemental speciation is impossible, therefore the fractionation of element content by sequential extraction procedures were developed for risk assessment caused by heavy metal contamination in practice. Nowadays mostly the BCR three-step sequential extraction scheme is used, these was originally developed for fractionation of heavy metal content in aquatic sediments. During the validation and production of CRM 601 and 701 sediment reference samples some critical points of BCR methodology have came to light (like pH-instability in 2nd step and danger of the redistribution of dissolved metals into the solid phase during the long lasting shaking). Extension of BCR-fractionation studies to airborne dust samples is particularly hindered by the above mentioned problems. In the study an attempt was made to improve the BCR methodology by acceleration the long (16 h) leaching steps using ultrasonic treatment.

The results of the BCR-proposed heavy metal fractionation were compared with the results of sequential extraction with supercritical (CO_2), subcritical (H_2O) and sub-critical mixture (H_2O+CO_2). To this comparative study three typical samples were used: a Hungarian soil sample from the control parcella of a heavy metal contamination field experiment, a contaminated lake sediment from Gödöllő and an averaged airborne gravitation dust sample collected in Košice. In addition a CRM-701 reference sample was used to control the BCR procedure. Element analysis was performed by spectrochemical methods. The total element content of solid samples before and after the extraction procedure was determined by DC-ARC-OES method. A multielement analysis of extracts was performed by FAAS, as well as by ICP-MS method.

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MEASUREMENT OF INORGANIC MERCURY AND METHYLMERCURY IN FISH TISSUES, SEAFOOD AND FISH FEED BY HPLC/ICP-MS

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A method utilizing an enzymatic extraction and HPLC / ICP-MS for the determination of inorganic mercury(II) and methylmercury(I) in fish tissues, seafood and fish feed is presented. Mercury compounds in biological tissues feature their high afinity to SH groups of proteins and peptides. Enzymatic hydrolysis and solubilization of proteins and peptides improves extraction of mercury species to the solution and also has the advantage that enzymes act only on specific chemical bonds and are not likely to alter the chemical form of the mercury species.

The enzymatic extraction by Protease type I from bovine pancreas in phosphate buffer (*pH* 7.5, 2h, temperature 37 °C) is performed for investigation of mercury species. Recieved extract is centrifugated (10 min, 6000 rpm) and filtrated through 0.45 Nylon syringe filter. The HPLC column Gemini®-NX 3µm C18 110Å (150 x 4.6 mm, Phenomenex, USA) in combination with HPLC system PerkinElmer Series 200 (PerkinElmer Sciex, USA) is used for the separation of mercury species. The 5% v/v CH_3OH-water solution containing 0.05 M CH_3COONH_4 and 0.2% w/v L-Cysteine, *pH* 6.5 (flow rate 0.8 ml min^{-1}, temperature 35 °C) serves as mobile phase. The addition of L-Cysteine to extraction solution and mobile phase is essential to eliminate adsorption, tailing and memory effects during sample preparation and separation. ICP-MS ELAN DRC-e (PerkinElmer Sciex, USA) is used for mercury species detection.

Two peaks are observed in the chromatogram. The first one for mercury(II) with retention time 2.3 minute and the second one for methylmercury with retention time 3.3 minute. Resolution of these peaks is 3, total time of the analysis is 5 minutes. The recoveries from certified reference materials (TORT-2 - *Lobster hepatopancreas*, DORM-2 - *Dogfish muscle*) are 100-107 % for mercury(II) and 98-110 % for methylmercury. The calibration curves for mercury(II) and methylmercury standards are linear in the range of 0.5-100 µg L^{-1} (R = 0.9981, R = 0.9987 respectively). The lowest measurable mercury(II) is 1.3 µg L^{-1} and this corresponds to 0.130 mg kg^{-1} in fish feed and 0.026 mg kg^{-1} in fish tissues and seafood. The lowest measurable methylmercury is 0.5 µg L^{-1} which corresponds to 0.050 mg kg^{-1} in fish feed and 0.010 mg kg^{-1} in fish tissues and seafood.

SELECTED APPLICATIONS OF LASER ABLATION INDUCTIVELY COUPLED PLASMA SPECTROMETRY IN THE ANALYSIS OF POWDERED AND COMPACT SAMPLES

Viktor Kanický, Markéta Holá, Tomáš Vaculovič, Karel Novotný, Aleš Hrdlička, Lubomír Prokeš, Veronika Konečná, Ivona Hubová, Linda Zaorálková, Hana Ovadová, Marie Pištěková, Vítězslav Otruba

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Direct analysis of solids offers several advantages over solution analysis which requires lengthy decomposition procedures in some cases and may be associated with analyte losses and sample contaminations. Analysis of solids includes two scopes of problems and tasks which emerge from compact and powdered consistence of samples. Advantages as well as limitations are associated with each of these two forms.

Powdered materials make it possible: i) to mix sample with appropriate binders and/or internal standards; ii) to apply “a standard addition method”; or iii) to spike a series of blank samples with a known amount of analytes and thus to prepare matrix-matched calibration. On the other hand, pellets pressed of powdered samples may exhibit insufficient resistance, which results in pellet cracking and excessive releasing of material. Laser micro-spot sampling of pressed pellets or cast borosilicate glass disks makes demands on preparation of homogeneous targets.

To the contrary, laser ablation-based analysis of compact materials does not require any important sample treatment, however, it is hampered by: i) a lack or at least a limited choice of standard reference materials, which are requisite for reliable calibration and accurate determination; ii) a limited choice or even impossibility to use any element as internal standard; iv) and finally by impossibility to dilute a sample with an appropriate matrix. Texture of some “compact” solids exhibits unwanted sample porosity, which keeps results far from being quantitative.

LA-ICP-MS was optimized for the analysis of compact natural materials which exhibit imperfections (porosity). These materials comprise such specimens as historic/prehistoric skeletal remainders (bones) and recent kidney stones. On the other hand, mediaeval jewelry or prehistoric obsidian and flint tools from archaeological excavations require a limited damage by laser beam. Different ablation rate in a solidified molten fluoride salt layer adhered on the wall of a reactor secondary circuit piping, and in a structural material (steel, nickel, and alloys) complicates evaluation of study of dissolution of structural material in LiF/NaF melt or penetration of the melt into the construction. Some soft materials, such as gels from PAGE technique, require optimization due to for H_2O contents. Powdered materials can be combined with a homogeneous, internal standard-enriched binder prepared by sol-gel technique. However, preparation of cast or pressed targets is lengthy and arduous.

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MICROWAVE INDUCED COMBUSTION – A POWERFUL SAMPLE PREPARATION TECHNIQUE

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In spite of the wide spread and successful use of conventional microwave-assisted wet digestion for many matrices its application leads to some drawbacks like high remaining carbon content with tough organic materials (e.g. petroleum coke), or the high acid concentrations in the digests, which may interfere with some analytical techniques. A subsequent step to remove the acid may be necessary. The determination of halogens after acidic wet digestion is just as impossible in most cases. In spite of some limitations, the use of combustion techniques as oxygen-flask and combustion bombs has been recommended for such cases. A recently developed technique, microwave assisted combustion (MIC) opens new ways to solve difficult sample preparation problems. The suitability of this technique, that combines some features of microwave-assisted wet digestion and combustion in the same system, was evaluated for the subsequent determination of non metals and metals in many sample materials. Combustion is carried out in a quartz vessel pressurized with oxygen using microwave irradiation to ignite the sample. After combustion the analytes were absorbed in a suitable solution and a reflux step, if necessary, was applied in order to obtain a complete recovery of analytes. In this system the achieved temperature during the combustion was higher than 1350 °C assuring effective matrix decomposition. Up to 500 mg of sample can be completely combusted with residual carbon content typically below 1% (eight samples can be simultaneously processed). Contrarily to combustion bomb and oxygen flask systems, the reflux step of MIC improves the washing of vessel walls and quartz holder, minimizing eventual losses due to analyte adsorption on internal parts of vessel. Recent applications of MIC technique will be discussed with main concern for tough organic materials.

ICP SPECTROMETERS AND THEIR APPLICATION IN THE TRIBOTECHNICAL ANALYSIS

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ICP-OES spectrometers (optical emission spectrometers with inductively coupled plasma) are gradually, as their parameters getting higher, more and more used for the analysis of samples with heavy matrices, if it goes here for strongly contaminated solutions, salt solutions (direct analysis of samples with 30g/l salinity) or solutions with organic matrices.

The main types of ICP-OES spectrometers available at present are as follows:

A. According to configuration

1/ The spectrometers with CZERNY-TURNER monochromator represent the lower end price group, usually with a sequential measurement, i.e. one element after another.

2/ Next group fits the category of ECHELLE spectrometers with simultaneous measurement i.e. all elements together, and represents at present the most spread type of instruments.

3/ The spectrometers with PASCHEN-RUNGE configuration are also simultaneous instruments, generally capable to measure the complete spectra.

B. According to detection elements

As the detection elements, all the above-mentioned instruments then use either photomultipliers or semiconductive sensors of CCD or CID type.

C. According to plasma viewing

According to the way of plasma viewing we divide the instruments into so called radial or axial.

The lecture in its first part gives a general and concise description of the above-mentioned principles (without mentioning the producers), in the second one then presents the measured results of oils, fuels and AdBlue that can be achieved todayas for the limits of detection, time of analysis and sample preparation are concerned.

SPECIATION OF TRACE ELEMENTS IN DIGESTED CEREALS

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Food processing somewhat changes the original species of elements present in food. Moreover some chemical changes take place during gastrointestinal digestion of food just before absorption. To investigate element speciation in digested food samples the enzyme digestion using pig's pepsin and pancreatin was performed. Our experiments were focused on rye, durum wheat and oat flakes. The 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 samples were analysed by SEC/ICP-MS using Superdex 75 column (300x10 mm) and 0.02 M Tris-HCl buffer solution (pH=7.5) as a mobile phase. Enzyme catalysed digestion is able to solubilise approx. 80 % of the sample mass. Major portion of elements is brought into solution: the percentages of solubilised P, Mn, Fe, Co, Ni, Cu, Zn and Mo element content are 81-91, 56-95, 43-57, 33-100, 36-91, 64-92, 44-86 and 63-91 respectively. Soluble portions of most elements in original samples (ascertained by pH 7.5 Tris-HCl buffer extraction) are much lower. SEC recovery of P, Fe and Mo in digested samples approaches to 100 %, while that of Cu varies from 60 to 70 % and that of Zn is approx. 10 %. Ionic species or labile complexes represent the non-recovered portion of the element. Proportions among individual element species fraction are changed as a result of enzyme digestion, e.g. a high molecular mass fraction of Cu compounds increases owing to release of originally less soluble species. On the other hand low molecular mass (<2kDa) fractions of Cu and Zn partially persist in digested samples. Therefore changes in element speciation depend on the molecular mass and character of the original species.

IN-ATOMIZER TRAPPING OF HYDRIDE FORMING ELEMENTS WITH AAS DETECTION – METHOD OPTIMIZATION AND ROUTINE APPLICATIONS

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Hydride trapping in quartz atomizers is a novel, fast and operator-friendly, approach to reach LODs at ultratrace levels by HG-AAS. Moreover, quartz traps are easy to integrate with quartz atomizers. The inlet arm of the quartz multiatomizer[1] served as the trap in the optimization study. Analyte is collected at the quartz surface using O_2 excess over H_2 in the carrier gas. Subsequently, trapped analyte is re-volatilized by H_2 excess over O_2.

Collection and volatilization conditions (surface temperature, gas composition) as well as atomization conditions (oxygen content in the atomizer that controls the hydrogen radicals amount) were optimized for all the four analytes tested (As, Sb, Bi and Se)[2,3]. Analytical methods based on in-situ trapping of Sb and Bi hydrides in the conventional quartz tube atomizer and in-atomizer trapping of As and Se hydrides in the quartz multiatomizer were developed and validated. LODs in the low $pg.ml^{-1}$ range were reached for 5 min preconcentration (20 ml of sample).

The collection and volatilization efficiency of Bi and As was verified by an independent radiotracer study. Complete Bi collection (96±5)% as well as volatilization (98±2)% was proved by ^{205}Bi isotope. ^{73}As radiotracer experiments proved the lossless retention and subsequent volatilization of arsenic from the quartz surface under the optimized conditions. However, they indicated analyte fraction lost between collection and volatilization step caused by low heating speed.

New insights into fundamental processes taking place during hydride trapping, analyte volatilization and atomization resulting from both – radiotracer and AAS investigation will be outlined. The increase of hydrogen radicals amount in the volatilization step allows to decrease the volatilization temperature. Thus, analyte losses might be avoided.

Acknowledgement: Financial supports from the Grant Agency of the ASCR (Project No. A400310507), Institute of Analytical Chemistry of the ASCR (Project No. AV0Z40310501) and the Grant Agency of Charles University (Project No. GAUK 306/2006/B-CH/PrF) are highly acknowledged.

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EFFECTS OF EXTERNAL ALPHA-IRRADIATION ON SHEET SILICATES

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Coloured aureoles surrounding radioactive inclusions are found in a number of rock-forming minerals. These so-called radiohaloes are formed by the action of alpha-particles emitted from a radionuclide bearing phase into a nominally non-radioactive host. The most popular mineral known to contain this sort of radio-induced alteration zones is biotite, where haloes often exhibit striking pleochroism (“pleochroic haloes”). However, there are only a few studies on radiohaloes in other sheet silicates. We report results of a systematic investigation of radioinduced alteration in naturally and artificially irradiated chlorite, muscovite and biotite, using modern spectroscopic techniques. Optical absorption spectroscopy showed that the changed colour in the halo is not caused by additional bands in the visible part of the spectrum but rather by the effects of an intensified absorption in the ultraviolet (UV) region. This is – as least partly – due to radio-induced ionisation of Fe^{2+} to Fe^{3+} and a resulting shift of the ligand-metal charge-transfer bands to lower wavenumbers. With increasing alpha-dose, the UV absorption edge is shifted to lower energies, therefore progressively affecting the visible part of the spectrum via its low wavenumber slope (Fig. 1).

The change in colour is accompanied by structural damage caused by the impact of the alpha-particles. Raman spectroscopic investigations of naturally and artificially irradiated chlorite and muscovite show a significant broadening of vibrational bands, as well as a decrease in intensity in the most heavily damaged areas, which is attributed to the perturbation of the short range order in the crystal structure of the sheet silicates.

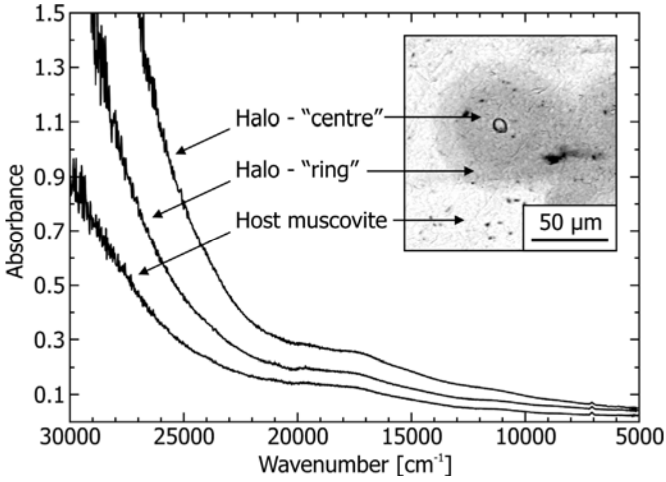

Fig. 1: Polarised optical absorption spectra obtained in different zones of a radiohalo in muscovite ($E \perp c^*$). With increasing irradiation dose – *i.e.* decreasing distance to the radioactive inclusion – the UV-absorption edge is shifted towards the visible region. The changed colour inside the haloes is mainly caused by the “tail” of this strong absorption.

NEW TRENDS IN THE GAMMA RAY SPECTROMETRY – WHOLE SPECTRUM PROCESSING

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The whole spectrum processing (WSP) in the gamma analysis includes a set of advanced algorithms based on the response operator method. These algorithms provide a complete analysis of gamma ray spectra and real incident gamma ray spectra are obtained.

The WSP algorithms of the response operator model use a matrix representation, thus, spectra are put into vectors and operators are represented in matrices. The response operator matrix is built up by SCFA (Scaling Confirmatory Factor Analysis) methodology for each of used detectors. The standard response operator describes detection processes within the detector and has been calculated from a set of several experimental calibration measurements at different energies. The operator includes full energy and efficiency calibration parameters. Therefore, no additional user's calibration measurements are needed.

The WSP system works with high level of safety with various types of detectors (semiconductor HPGe, scintillation NaI(Tl), and plastic scintillation detectors). The system needs no modification and no additional calibration, when changing detector types, only exchanging the appropriate response operator is enough.

For voluminous samples and large volume objects measurements, the additional response operators describing the detection geometry may be incorporated into the system. The geometry response operators are calculated by mathematical calibration using MCNP simulation. A result of the WSP application is demonstrated in Figs. 1 and 2.

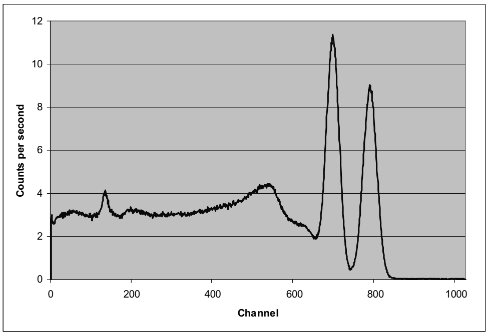

Fig. 1 Physical gamma ray spectrum of ^{60}Co acquired by NaI(Tl) detector

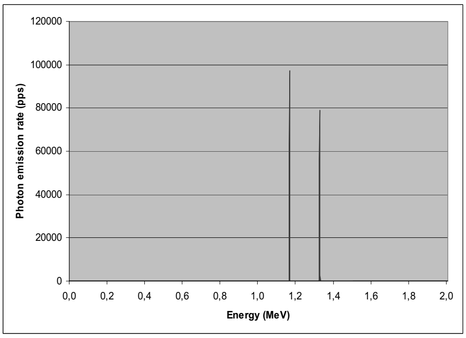

Fig. 2 Incident gamma ray spectrum of ^{60}Co obtained by WSP approach

VARIAN 820-MS – NEW APPROACHES TO ICP-MS TECHNIQUE

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Varian Inc. has launched the 820-MS model in the ICP-MS field featuring some unique technologies - 90 degree ion mirror both focusing the analyse ions into the quadrupole and removing the neutrals and photons. The collision/reaction interface (CRI) injects helium and hydrogen collision and reaction gases directly into the plasma as it passes through the orifice of the cones. These approaches result in unmatched gigahertz sensitivity (at more than 1 million counts per second for 1ng/ml) and easy and efficient suppression of the polyatomic interferences, even in the difficult samples such are blood, urine and sea water.

VALIDATION OF ICP-OES FOR THE DETERMINATION OF METALS IN ASHES FROM BIOMASS INCINERATORS

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The objective of biomass incinerators is the generation of electric power by burning organic material, such as wood chips, pellets or bark. During the incineration process the organic input material is decomposed and mostly transformed into gaseous components, while inorganic material remains as solid ash. Bottom ash is the coarse residue which is collected at the bottom of the incinerator. Smaller ash particles can leave the incinerator and are collected as fly ash in gas cleaning filter.

Since the ash contains valuable elements like Ca, K, Mg it is reasonable to recycle it to the ground where the biomass was grown, however the concentration of harmful heavy metals has to be under certain limit values given by legislation; limit concentrations for the most common elements are prescrived in the recommendation of the ministry for Agriculture "The use of plant-ashes on fields and grassland" from 1998.

For monitoring the metal amounts of ashes intended to be used in agriculture a fast and reliable method is mandatory which allows the qualitative and quantitative determination even at trace levels. ICP-OES was chosen since it offers many advantages for the given analytical task.

An analytical method consisting of an acidic microwave assisted digestion prior to the ICP-OES measurement was optimized for ashes from biomass incinerators. The elements of interest were As, Zn, Sb, Pb, Ni, Co, Cd, B, Mn, Fe, Cr, Mg, Al, V, Cu, Ti, Sr and, Ba. A validation including the following parameters was performed for each analyte: limit of determination, limit of quantification, recovery by spiking experiments, accuracy by analysing a certified reference material, wihtin-day-, day-to-day- as well as week-to-week-reproducibility, linearity, and uncertainty of measurement.

The method optimized allows the determination of all elements covered by the above mentioned regulation and represents thus an appropriate tool for monitoring flyh ashes.

DETERMINATION OF MASS CONCENTRATION OF SULPHUR DIOXIDE FROM STACIONARY SOURCE EMISSIONS BY ATOMIC EMISSION SPECTROMETRY WITH INDUCTIVELY COUPLED PLASMA

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The sulphur dioxide (SO_2) content emitting to atmosphere from ducts and stacks can be determined using ion chromatography or by titration[1]. The sample of gas is filtered and draw through hydrogen peroxide absorber solutions. The sulphur dioxide in sample gas is absorbed and oxidised to sulphate ion. The concentration of absorption solution is 0,3 % H_2O_2 up to 1000 mg/m^3 SO_2 and 3 % H_2O_2 up to 2000 mg/m^3 SO_2.

Appropriate amount of solution with absorbed SO_2 is injected directly to ion chromatograph. The concentration of SO_2 is calculated from calibration curve.

The second method is titration with a barium perchlorate solution using Thorin as indicator.

In this article we describe a new method for determination of SO_2 – Atomic Emission Spectrometry with Inductively Coupled Plasma. The solution with absorbed SO_2 is directly aspirated to the AES-ICP. Analytical signal of sulphur is calculated using calibration curve. Total amount of sulphur in the measured solution is calculated on SO_2.

In the next table is comparison of limit of quantification (LOQ) of three methods.

SO_2	Ion chromatography	Titration	AES-ICP
LOQ [mg]	3	0,5	0,1

The performance characteristics of the method AES-ICP were evaluated using certified reference material and reference method.

The AES-ICP method of determination of SO_2 is useful as alternative method.

1. EN 14791: 2005, Stationary source emissions – Determination of mass concentration of sulphur dioxide - Reference method

COMPARISON OF THE PRECONCENTRATION PROCEDURES FOR ELEMENT DETERMINATION IN WATERS USING ATOMIC SPECTROMETRY TECHNIQUES

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Metal quantification at low concentration levels comprises one of the most important targets in analytical chemistry. Nowadays, trace metals are determined in a great variety of environmental (such as water, soils, sediments) samples. It is evident that despite recent advances in analytical instrumentation, the use of separation and preconcentration procedures is still often necessary before the determination step.

The purposes of the methods for metal preconcentration are often different, depending on whether the methods are applied in environmental or another fields. The respective method needs to be efficient, give high sensitivity and selectivity, which is useful when used in combination with atomic spectrometry techniques such as Flame Atomic Absorption Spectrometry (FAAS), Electrothermal Atomic Absorption Spectrometry (ETAAS), Hydride Generation Atomic Absorption Spectrometry (HGAAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Preconcentration procedures are considerable tools in analytical processes, since their applications guarantee trace metal analyses in complex matrices and improve the performance of the analytical techniques [1]. Moreover, the preconcentration procedures exploiting the clean chemistry concept and the reduction of samples/reagents consumption are extensively used. In this contribution the brief descriptions of the methods for separation and preconcentration procedures related to precipitation, coprecipitation, electrochemical deposition, liquid-liquid extraction, solid–liquid extraction and atom trapping mechanisms are discussed, as well as some applications are presented.

Acknowledgement: Financial support from the Grant UK/324/2008 is highly acknowledged.

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GC-ICP-MS TECHNIQUE FOR SPECIATION OF ORGANOTIN COMPOUNDS

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Organotin compounds were widely used as pesticides, polyvinylchloride stabilizers and in other branches. As a result these compounds can be found in different areas of the environment. Because of their toxicological properties the contact of these compounds with non-target organisms should be avoided and suitable analytical techniques must be available for investigating their content in different environmental samples. Organotin compounds can be determined in various matrices using separation technique hyphenated to element specific detection. In this work gas chromatography with inductively coupled plasma mass spectrometry detection (GC-ICP-MS) were applied for determination of mono-, di- and tri-butyltin compounds in wood. The influence of basic detector parameters was studied as well as suitable sample preparation step. Different extraction strategies were tested and their efficiency compared. Method was applied to analysis of wood samples preserved by tributyltin-oxid based fungicide.

THE LOCAL ENVIRONMENT OF SB AND AS ON THE SURFACES OF IRON OXIDE MINERALS: AN EXAFS STUDY

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Arsenic and antimony are both toxic and undesired in the environment. We have investigated sites polluted by As and Sb (abandoned ore deposits, shooting ranges) and found distinct patterns in the migration of As and Sb. At the sites investigated, both As and Sb were ferociously scavenged by iron oxide minerals ferrihydrite, goethite, and lepidocrocite. These findings are supported by numerous wet chemical and electron microprobe analyses, X-ray diffraction studies, and results from Raman spectroscopy.

Studies of Sb(V) adsorption on synthetic iron oxides were completely absent until now. We have investigated the geometry of surface complexes of Sb(V) on the surface of synthetic iron oxide minerals by extended X-ray absorption fine-structure (EXAFS) spectroscopy at the Sb *K* edge (30.5 keV). At lower surface loading, we could distinguish a bidentate-mononuclear complex with a Sb-Fe distance of 3.1 Å and a bidentate-binuclear complex with a Sb-Fe distance of 3.6 Å. As the surface loading grows, surface precipitation was detected from the observation of Sb-Sb neighbors.

Identical Sb bonding environment was found at two shooting ranges (Losone, Lucerne, Switzerland) polluted by Pb and Sb. Here, the steel mantles of the bullets weather to produce iron oxides which adsorb Sb. Organic matter may play a role in the retention of Sb, however, the bonding of Sb to organic material was difficult to prove because of the small scattering power of C/N/O.

Using EXAFS spectroscopy on the As *K* edge (11.8 keV), we have determined the local environment of As in As-rich hydrous ferric oxide from Pezinok, Slovakia. The material contains up to 28 wt% As_2O_5. The arsenate ions attach to the iron octahedra in a bidentate-binuclear (3.3 Å) and monodentate (3.6 Å) fashion. At very high As loading, we have also detected As-As pairs at a distance of 4.0 Å.

We have also collected EXAFS spectra at the As *K* edge with a resolution of ~20 μm on individual particles from Pezinok in Slovakia. The spectra from Fe,As-rich grains look similar to the bulk spectra, probably reflecting the presence of the same surface complexes. Currently, we are reducing the data from Sb-rich grains (up to 65 wt% Sb_2O_5) where arsenic may be bound to antimony instead of iron. The goal of the study is to investigate the competitiveness of the two metalloids in phases depleted in iron and the results will be presented later.

FT RAMAN AND INFRARED SPECTRA OF CONIFEROUS NEEDLES: WHAT EFFECTS CAN BE ELUCIDATED?

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Norway spruce (Picea abies (L.) Karst.) and silver fir (Abies alba Mill.) trees dominate European forest ecosystems from Pyrenees to Carpathians, and from north of Greece to the Artic in Norway. Both survival and performance of coniferous trees depend strongly on many natural and anthropogenic factors of the ecosystems.

FT Raman spectroscopy is a method that makes possible analyses of coniferous needles performed both *in vitro* and *in vivo*. Infrared spectrometry using ATR technique allows analyzing of surface layer of needles. In last few years thousands of vibrational spectra of coniferous needles collected in specifically designed series of experiments were evaluated using various chemometric methods to elucidate the variability of several spectral features, e.g. the shape of the background, bands of waxes, water and carotenoids. Some mathematical pre-processing procedures were applied and their effects on resulting information were tested. The relation of spectral changes to various natural (model) factors was studied.

In a recent study we have used FT Raman spectroscopy to evaluate effects of several ecologically relevant groups of fungi on the composition of important compounds of spruce needles, because fungi are able to influence levels of photosynthetic pigments and nutrients in needles of coniferous hosts. Aseptically germinated seedlings were planted in model systems containing sterilized litter needles and inoculated with either individual fungi or combination of two fungal strains from different groups. The seedlings without inoculation were used as a reference. Furthermore, the data obtained have been compared with data of needles taken from natural forest area in Šumava mountains.

In another study we have performed a number of experiments using solar simulator. The effects of irradiation periods and dark intervals on stomatal waxes, carotenoids and moisture of needles were studied using both FT Raman spectroscopy and FTIR spectrometry on separated needles, twigs and small living trees. The data were supplemented by images taken using optical microscope.

Generally, the spectral information on moisture, waxes and carotenoids can be related to the state of health of needles. Various natural and anthropogenic effects can be differentiated in real conditions based on results of many model experiments.

NUCLEAR RESONANCE WITH SYNCHROTRON RADIATION

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Synchrotron radiation is a source of extremely intensive photon beams (12 orders of magnitude higher than conventional X-ray tubes) with energies up to several tens of keV. In addition, the cross-section of the beam is approximately 0.5 x 2 mm^2 and can be further focused down to several microns in either direction. Its unique properties open completely new horizons in material research including enhanced spectroscopic features. Synchrotron radiation is characterized by tunable energy, high degree of polarization, high brilliance, small beamsize, small beam divergence, and pulsed time structure. In particular, a technical possibility to achieve energy resolution of about 1 meV owing to extremely precise monochromators has enabled even nuclear transitions to be excited. On the other hand, the pulsed time structure of the beam ensures nuclear transitions to be studied in time domain. Thus, originally 'static' Mössbauer spectroscopy (in energy domain) can be converted into a time-dependent technique – the so-called nuclear resonant scattering (in time domain).

In this contribution, production of synchrotron radiation, its basic characteristics as well as applications in nuclear resonant scattering are discussed. Possibilities of an access to experiments at the European Synchrotron Radiation Facility (ESRF) [1] at Grenoble are outlined.

1. www.esrf.eu

VIBRATIONAL SPECTROSCOPY OF HYDROGEN BONDED MATERIALS FOR NONLINEAR OPTICS

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The searching for new materials exhibiting nonlinear optical properties (e.g. second harmonic generation) in combination with other desirable properties (optical transparency, thermal, optical and mechanical stability) continues to be an important research goal in nonlinear optics (NLO). Essential applications of these materials lie in the areas of optical communications and optical signal processing, as well as storage and other information processing tasks.

Quite a simple but interesting class of NLO compounds is based on salts combining a cation derived from a polarizable organic molecule with an anion (inorganic or organic) capable of forming strong hydrogen-bonded crystal structures. The bonding energy present in the hydrogen bonds can counteract the tendencies of the organic dipoles to form pairs and drive the formation of salts with both high β and high $\chi^{(2)}$-values. It is assumed that the acid part of the molecular complex thus created is responsible for favourable chemical, mechanical and thermal properties, due to strong hydrogen bond interactions which stabilize the crystal lattice and also contributes to the second-order NLO tensor coefficient (d_{ijk}) of the crystal. The organic part is mainly responsible for the nonlinear optical properties of the crystal.

Full assignment of vibrational spectra (employing quantum-chemical computational methods) of crystalline materials with promising SHG activity is very useful not only for their identification but also with respect of their nonlinear optical properties. It is very well known that the origin of polarizability and hyperpolarizabilities of molecules come from their electronic structure. However, recently particular attention has been given to the vibrational contributions to the first and second hyperpolarizabilities (β and γ) of the molecules [1-4].

In this contribution we are presenting results of study of selected salts of (i) guanidine and biguanide derivatives and (ii) cyclic heteroaromatic amines obtained by combination of the methods of vibrational spectroscopy (FTIR and FT Raman), X-ray structural analysis and quantum-chemical computations.

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THE EASY WAY FOR SOLVING INTERFERENCES IN ICP-OES

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With ICP emission spectrometry, many spectral lines are emitted for each element. The fact that spectral lines for samples containing several elements may overlap is well known asspectral interference. For this reason, it is necessary to use a spectrometer with a resolution over a certain level. Even then, spectral interference may be unavoidable.

Even if a peak is obtained at a certain wavelength, it cannot be asserted that a particular element with a spectral line at that wavelength is present. This is because it may be the spectral line of another element (co-existing element). It should be possible to say that if no peak is obtained, then that element is not present. To be precise, however, it can only be said that the element is not present in an amount greater than the lower detection limit of the instrument used for measurement. It cannot be asserted that the element is completely absent.

If a peak is obtained, another wavelength for the corresponding element is investigated. Naturally, if the element is present, a peak will be detected for the other wavelength. In order to increase the reliability of the analysis, it is necessary to check as many wavelengths as possible. Another method is to investigate the existence of possible co-existing elements. If there is no co-existing element, then there is no interference peak for that element.

This explanation probably makes qualitative analysis seem like a very complex and time consuming process, that’s why in the old days of ICP-OES operations, these procedures were carried out by experienced analysts only. With “state of the art” ICP emission spectrometers such as the ICPE-9000, however, the knowledge of experienced analysts is memorized as a database, simplifying the selection and confirmation of wavelengths, allowing high precision and interference free analytical results.

HORIBA JOBIN YVON SPECTROMETERS

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Following extensive experimentation over a period on months, using a series of single element standards for “all” elements possible on ICP-OES, comprehensive data was obtained on a range of parameters that could be used for automatic method development in ICP-OES. It is the first comprehensive ICP-OES only database to be produced. Previous wavelength tables like Fassel, Boumans were relatively small & incomplete, while MIT, Zaidel tables etc are a mixture of theoretical & spark lines.

In this talk, we will describe the use of this unique proprietary database to enable an HJY ICP user to produce a validated method with multiple lines & through a simple process of running a real sample spectrum & letting the software compare with the database. Lines are eliminated & others validated & once deemed satisfactory; a further statistical process of outlier software (SOS) enables fine “tuning” of the method. The in-built calibration validation software finishes off the process, to enable an important part of laboratory validation to be made for accreditation in fields where accreditation is demanded.

Real sample applications will be described on its use & implementation.

SOME APPLICATIONS OF ULTRASONIC NOVA-1 NEBULIZER

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A low-cost microflow ultrasonic nebulizer NOVA-1 has been manufactured (patent pending solution). It was designed using a water cooling method to improve the chemical resistance of the system and prolong the lifetime of the transducer. A very localized aerosol generation area is formed by focusing of ultrasonic energy emitted from the transducer onto the surface of quartz plate. This gives stable nebulization at sub-ml/min analyte flow rates with the high aerosol production up to 120 mg/min. At low flow analyte rates of about 30 – 100 µl/min the aerosol generated has a very low mean droplet diameter of about 2,5 µm and analyte transport efficiencies are close to 90% using “single pass” spray chamber and about 10% lower with cyclonic spray chamber.

The commercial ultrasonic micronebulizer NOVA-1 can easily adapted to existing ICP instruments. Aerosols are injected into the plasma without desolvation. The performance of this ultrasonic nebulizer in plasma spectrometry has been evaluated and compared with a standard concentric nebulizer on 2 ICP sequential spectrometer. Generally good stability, precision and reproducibility were observed for emission signals of some elements. Applying the nebulizer (after optimization of excitation parameters (like nebulizer gas flow, high frequency power and analyte flow) lowers the detection limits up to te factor 3-5 depending on the element by 10 times lower analyte consumption. The relative standard deviation was found to be less then 1,5%. The micronebulizer exhibited relative short wash-out times, similar to the concentric nebulizers. In addition to use with ICP emission spectrometry, the technique should also be readily applicable to ICP-MS and MIP-OES.

STUDY OF MOBILITY OF CHOSEN ELEMENTS IN SOILS CONTAMINATED BY POLLUTANTS OF METALLURGICAL INDUSTRY

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The atmospheric deposition (gravitation dust sediment) and waste management belong to mainly sources of the soil contamination by toxic risk elements in metallurgical regions. The metals in the soil occur in various concentration and different forms. The fractionation analysis is method, which enables classification of elements forms movable under specific soil-ecological conditions.

For the evaluation of mobility of chosen risk elements (Cu, Pb, Ni, Zn) in the four soil samples collected nearly of metallurgical plant U. S. Steel in Košice agglomeration was used of fractionation analysis. For separation of adequate elements forms was applied of single-step extractions by definite extraction reagents. The 0,1 mol dm^{-3} $CaCl_2$ and 1 mol dm^{-3} NH_4NO_3 was used for the isolation of mobile forms, which may be mobile under normal soil conditions. Extraction reagent 0,05 mol dm^{-3} EDTA was applied for separation of mobilizable forms. These forms may be mobile during of changed soil conditions caused by synchronous action of fertilisation and agricultural engineering. The solution of 2 mol dm^{-3} HNO_3 was used for isolation of maximal potential mobilizable forms of elements, which represent forms mobile during extreme changed of soil conditions (so called "environmental risk"). For the quantification of elements contents in isolated forms, i. e. in the extracts was used of flame atomic absorption spectrometry.

The results of experiments refer to increased mobility of Cu, Pb, and Ni during changed soil conditions, which are typical for agricultural soils. The highest mobility was observed in this soil, which occur nearly objects of slag-heap management. The content of elements in the most dangerous mobile forms wasn't determined or its content in the extracts occur below limit of detection of FAAS method, respectively. The content of Zn in extracts wasn't evaluation because of contamination of extracts or blank solution, respectively.

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STUDIES IN GENERATION OF TOROIDAL PLASMAS

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A new approach to generating the toroidal plasma discharges which are useful as the excitation sources will be presented. Microwave and non-microwave examples will be provided in which multipoint energizing of the plasma results in creation of the stable electrical discharges loaded by analytical samples. Applications in emission as well in mass spectrometry will be discussed in some details.

All presented solutions are patent pending.

COMPARISON OF SINGLE-STEP AND BCR SEQUENTIAL EXTRACTION PROCEDURES OF GRAVITATION DUST SEDIMENT SAMPLES

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The gravitation dust sediment as part of atmospheric solid pollutants belong to possible sources of the soil contamination mainly in industrial regions The contamination is caused by these elements forms, which will be mobile from dust particles to the soil system. The single-step extraction by definite extraction reagents is method of the fractionation analysis, which is often used for evaluation of the elements mobility in soil during given soil conditions. The BCR sequential extraction scheme was originally developed for fractionation of heavy metal from sediment. The modified BCR sequential extraction methods were applied for soils, too. For gravitation dust sediment samples it is possible to use of these extraction procedures for evaluation of mobility of elements from dust particles to the soil.

This work presents results of single-steps extractions by using extraction reagents with different extraction effect: 1 mol dm^{-3} NH_4NO_3 for isolation of mobile forms (water-soluble, exchangeable), 0.05 mol dm^{-3} EDTA for isolation of mobilizable forms (water-soluble, ion-exchangeable, organic, carbonate) and 2 mol dm^{-3} HNO_3 for isolation of all releasable forms. The content of elements in the extracts was determined by FAAS method. These results were compared with results of three-steps BCR sequential extraction procedures. In this method were applied extraction reagents with increasing extraction effect in the sequential extraction steps: 0.11 mol dm^{-3} acetic acid (1st step) for isolation of water-soluble, exchangeable, and carbonate fraction, 0.1 mol dm^{-3} hydroxylamine hydrochloride (2nd step) for isolation of reducible (e.g. Fe/Mn oxides, oxihydroxides) fraction, which may be mobile by change of redox potential, 8.8 mol dm-3 hydrogen peroxide, acid-stabilized to pH 2-3 followed by 1 mol dm^{-3} ammonium acetate adjusted to pH 2 (3rd step) for isolation of oxidizable (organic, sulphides) fraction and the aqua regia for decomposition of rest after the third step.

On the basis of obtained results it is possible to state, that:

- Differences between recoveries in the EDTA-extracts and HOAc-extracts (part of elements bounded on the organic matter) decrease in the order: Pb, Cu, Zn, Ni.
- Differences between recoveries in the HOAc-extracts and NH_4NO_3-extracts (part of elements bounded in the carbonates forms) decrease in the order: Cu, Pb, Zn, Ni.
- The recoveries in the HNO_3-extracts are approximately equal to sum of recoveries of 1st, 2nd and 3rd step of the BCR extraction.
- The content of elements in the sulphides forms decrease in the order: Cu, Pb, Zn, Ni.

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HALF A CENTURY OF MÖSSBAUER SPECTROSCOPY

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At the beginning of 1958, the basis of a new spectroscopy method, which today bears the name of its inventor, has been established. During the work on his PhD thesis, Rudolf Ludwig Mössbauer succeeded in elucidation of the physical phenomena that enabled gamma fluorescence to be observed. Only couple of days after his findings he has published in his very first scientific paper [1], R. L. Mössbauer realized that this phenomenon can be used also for spectroscopic purposes. His second paper [2] has shown how this can be achieved and demonstrated the very first (Mössbauer) spectrum (Fig. 1). Three years later, R. L. Mössbauer was awarded for his findings by Nobel Prize for physics.

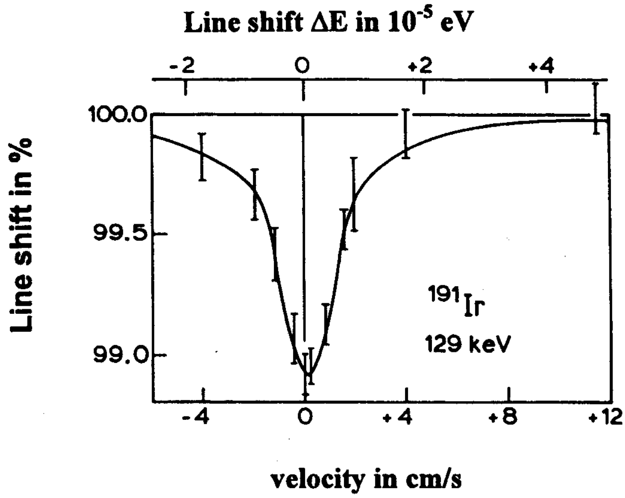

Fig. 1 First Mössbauer spectrum [2].

Today, Mössbauer spectrometry is a very well established diagnostic tool which encompasses analytical studies in all fields of human activities. This contribution will summarize the historical background, basic principles, and selected examples of the application of Mössbauer spectroscopy. It will provide also notes on present trends and perspectives.

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DETERMINATION OF HYDROGEN SULFIDE IN EMISSIONS BY AAS

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We modified a method of Hydrogen Sulfide analytical determination from samples of vapour pollutant emissions coming from waste vapours produced by stationary sources of pollution (based on STN 83 4712-3). Hydrogen Sulfide is absorbed from vapour sample in solution of Silver Sulfate, which acidity is modified by addition of Potassium Hydrogen Sulfate. The standard method is based on decomposition of Silver Sulfide precipitate by distillation without oxygen followed by photometric determination of Hydrogen Sulfide. Our modification substitutes this process by dissolving Silver Sulfide precipitate in Hydrochloric acid followed by determination of Silver by method of Atomic Absorption Spectrometry. Quantification of Hydrogen Sulfide is made by calculation from the measured concentration of Silver.

APPLICATION OF STANDARDLESS XRF ANALYSIS IN TRINECKE ZELEZARNY

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Our laboratory is equipped with new XRF analyzer ARL 9900. This spectrometer makes possible to measure samples by UniQuant method. UniQuant is highly effective for analysing samples for which no standards are available. Obviously elements from F up to Am are analysed. Elements Be to O can also be analyzed in some applications providing that the required crystals are installed on the instrument. Monitoring is used to detect any long term drift and to correct it. For monitoring of the intensities there are set nine CAL samples. Two elements for each of seven groups of channels are set up. The drift values in percent for non-monitored channels are determined by interpolation. To measure unknown samples using UniQuant in first step the Tau values have to be set up. To improve accuracy of trace analysis we evaluated necessary parameters of matrix that is as similar as possible to the analyzed materials (sludges). Special CAL sample was measured and necessary parameters and factors were evaluated. Shape of continuum and Impurity Factors are required for calculation of background by UniQuant. Background and Impurity Factors for powder samples were evaluated. The Impurity factors are needed because there are analytical channels, which are interfered by spectral impurities, anode lines for example. CAL sample was processed to find or precise Kappas. There are two kind of Kappas: the main Kappas Ki,i´s (interesting sensitivity) and the line overlap Kappas Ki,j´s (instrumental sensitivity). A Daughter calibration new Kappa List called Powder was derived from a Parent calibration.

DIRECT DETERMINATION OF SELECTED ELEMENTS IN CRMS OF FOOD-STUFFS BY ET AAS

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Graphite furnace atomic absorption spectrometry (GFAAS) is one of the most sensitive analytical techniques available. GFAAS provides sub-parts-per billion detection capability using microliter sized sample amounts. It is used exclusively for determination of metals and several non-metals at trace or ultratrace levels in a wide variety of liquid samples. It means that naturally liquid samples can be analyzed by conventional GFAAS directly or after dilution or preconcentration, but solid samples must be dissolved or digested before analysis. There is alternative way to analyse solid samples by GFAAS – the direct solid sampling technique (DSS).

Advantages of DSS over conventional sample preparation, such as wet digestion or fusion, include: reduced sample preparation time, decrease loss through volatilization in sample preparation step, reduced risk of sample contamination, increased sensitivity (digestion lead to sample dilution), elimination of hazard associated with the use of corrosive and/or toxic reagents and in the last place analysis of microamounts of sample. Direct analysis of solids can provide analysts with special information that is not obtainable by conventional techniques requiring sample dissolution. In addition, direct analysis is very important, when only small amounts of sample are available. Environmental monitoring often can be accomplished with direct solid analysis too.

Although it seems obvious that DSS GFAAS is a powerful technique it is rather limited by matrix effect of analyzed samples. Many authors reported disadvantages of these technique, such as atomizing kinetics depends on sample, increased background which requires powerful background correction system, in some cases too much sensitivity, poor precision and limited sample size introduced to atomizer.

In our work we discuss feasibility of using DSS GFAAS for determination of selected toxic and essential elements in various certificated reference materials of food-stuffs.

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DIAMOND-LIKE CARBON THIN FILMS: A RAMAN SPECTROSCOPY STUDY

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Several analytical techniques are used to characterize the diamond-like carbon (DLC) thin films: x-ray diffraction, electron energy loss spectroscopy (EELS), laser-Raman spectroscopy. Raman spectroscopy is the most frequently used analytic method because of its high sensitivity on carbon phases; it is a non-destructive and very fast method. From Raman spectra it is possible to obtain useful information about sp^3 and sp^2 content in the DLC layers which characterize the hardness, chemical composition and many other properties.

This study is focused on Raman spectroscopy investigations of differently deposited DLC layers by varying (i) Ar and/or N_2 flow rate, (ii) pulse frequency and (iii) bias voltage during the growth process. Argon and nitrogen flow rates are key factors during the deposition. They influence not only the morphology and chemical composition of the deposited DLC layer, but also its adhesion on the substrate. By changing the pulse frequency we have changed the amount of carbon atoms sputtered from target per second in vacuum chamber and hence we changed the deposition conditions for DLC layers. Also by varying bias voltage we got DLC layers with differently morphology and composition. Using above mentioned Raman spectroscopy we observed differences in spectra related to the changes in morphology and composition of various DLC layers deposited under different conditions.

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HIGH SENSITIVITY SPECTROSCOPY USING CAVITY RING-DOWN SPECTROSCOPY AND LASER INDUCED BREAKDOWN SPECTROSCOPY FOR TRACE DETECTION

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Laser induced break-down spectroscopy (LIBS) is a modern method of atomic emission spectroscopy. In our laboratory, LIBS is used for in-situ analysis of gas, liquid and solid samples. In LIBS method, high-power focused laser pulse produces the vaporizing and exciting plasma. We use Nd:YAG and Nd:YAP lasers for excitation. LIBS has an ability to detect all elements and simultaneous multi-element detection capability. Moreover, LIBS has specific advantages comparing to other AES analytical methods, because the laser spark uses focused optical radiation: simplicity, rapid or real-time analysis, no sample preparation, allows in situ measurement requiring only optical access to the sample, ability to sample gases, liquids, and solids equally well, good sensitivity to some elements (e.g. Cl, F) difficult to monitor with conventional AES methods, robust plasma that can be formed under conditions not possible with conventional plasmas. The biggest advantage of LIBS is that thanks to its simplicity it is possible to build a transportable unit for real-time analysis with comparable or better limits of detection than conventional techniques.

In order to detect trace elements, it is necessary to observe the most intensive spectral lines situated in UV and VUV range. Most of the light elements radiate in between of UV and VUV range (e.g. S, P). In our laboratory, we have a possibility to detect VUV radiation with wavelengths down to 115 nm using evacuated spectrometer.

We used LIBS for analyzing polycrystalline boron doped diamond layers and elementar analysis of pyrolysis-produced carbon. We also did fundamental studies of laser-induced plasma in argon atmosphere.

Cavity ring down spectroscopy (CRDS) is a highly sensitive and high resolution direct absorption spectroscopic technique which is based on measuring the rate of absorption rather than the magnitude of absorption of a light pulse confined in an optical cavity that is filled with the sample. This technique as such is insensitive to light source intensity fluctuations. By CRDS it is also possible to achieve extremely long effective path lengths of absorption in the sample and hence very high sensitivities.

CRDS is a very powerful tool for gas-phase and plasma analysis. It can be effectively used to measure either strong absorption of trace elements or weak absorptions of abundant species with good accuracy.

In the past few years we have been using CRDS in the near-infrared region where absorption by for us interesting molecules occurs and also off-the-shelf optical components with very good properties can be acquired without difficulty thanks to the development in telecommunication industries. We have measured absorption in plasmas and in gases and also have developed a few experimental advancements and simplifications.

CONTRAA 700 – HIGH-RESOLUTION CONTINUUM SOURCE ATOMIC ABSORPTION SPECTROMETER FOR FLAME, HYDRIDE AND GRAPHITE FURNACE – A NEW DIMENSIONS IN AAS

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High-Resolution Continuum Source (HR-CS AAS) offers completely new analytical possibilities for the entire spectral range – from the near vacuum UV to the near infrared – through the use of a single continuum radiation source.

It combines flame, hydride and graphite furnace technique in one device. For the first time the HR-CS AAS Technology becomes available for trace and ultra-trace analysis using atomic absorption with graphite furnace.

Unique flexibility of HR-CS AAS allows to measure each element from 68 available elements at any available line. As a result of this feature not only atomic absorption lines, but also molecular absorption bands are accessible, hence, a completely new analytical dimension in AAS.

The latest applications for flame, hydride and graphite furnace will be discussed.

Attention will be aimed for direct analysis of solids by AAS.

contrAA 700 Atomic Absorption Spectrometer

THE NEW POSSIBILITIES OF THE ALTERNATIVE EXTRACTION TYPES OF ENVIRONMENTAL SAMPLES

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The accumulation of heavy metals in environmental samples causes a potential risk to the human and animal health due to the transport of these elements through the individual compounds of environment. The element solubility in the aquatic media allows their uptake by plants and their subsequent introduction into the animal and human food chain [1]. The total metal content in polluted environmental samples is poor indicator of its bioavailability, mobility and toxicity. These properties essentially depend on the chemical association of the elements of the environmental samples. The use of single and sequential extraction methods provides an important experimental approach. The modified [2,3] IRMM (BCR) sequential extraction protocol and the single EDTA extraction were applied to the sediment and soil samples. The conventional single step extractions were accelerated by the alternative extraction treatment (ultrasound, microwave), in order to reduce the operating time. Single and sequential extraction procedures were applied to the samples collected from an industrially polluted region of Eastern Slovakia. A sequential extraction was applied and used as a reference extraction method. The single-step extraction with 0,05 mol l^{-1} EDTA was used in the conventional as well as alternative experimental device. Removal ability of the "EDTA extraction" was compared with the "BCR sequential extraction". As a result, good agreement was found between the elements' contents extracted into Na_2EDTA and the sum of the "acid extractable" and "reducible" extraction step of the BCR protocol for the all studied elements [4,5]. Therefore the application of the ultrasound (microwaves) by the single step extractions could be employed as a screening methods for rapid evaluation of the mobile and potentially mobile element portions in the sediments, soils, and other similar environmental matrixes. It is applicable as an economically viable choice to the BCR protocol and for fast "alarm indication" of element mobility changes in sedimentary (soil) systems.

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APPLICATION OF TXRF-SPECTROMETRY IN BIOLOGICAL RESEARCH

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Due to its excellent micro and trace analytical capability the total-reflection X-ray fluorescence (TXRF) spectrometry became a widely used analytical method in the biochemical research. In case of laboratory scale spectrometers equipped with Mo or W X-ray tubes as excitation sources the absolute detection limits change in the range of ng-pg. By application of synchrotron radiation the absolute detection limits can considerably be improved achieving the fg-range. Since the determination of low Z elements is hampered by absorption of low energy X-ray photons in the air, the development of the ATI WOBISTAX vacuum spectrometer equipped with Cr X-ray tube paved the way to analytical information from C to U.
For speciation of essential or toxic elements the X-ray techniques offer two different ways:

- Off-line hyphenated method: The biological fluids (e.g. xylem sap, urine) are introduced into a high performance liquide chromatograph (HPLC) or overpressure liquide chromatograph (OPLC) in order to separate the different species. Then the fractions of separated molecules with the eluent are transported and collected in small PTEE tubes. For TXRF (about 100-500 µl) solutions are available. In this case both the organic and inorganic species of elements can be determined since the TXRF system is only used as an element specific detector.
- K-edge TXRF-XANES: This technique delivers information about the oxidation state of medium Z-elements. It is advantageous that biological fluids can be analyzed without application of separation techniques; however, this method does not give information about the possible organic compounds of elements which are especially important for biological research.

In addition to these X-ray techniques the three-dimensional micro-X-ray fluorescence tomography offers a new powerful way to study small biological objects (less than 1 mm). It is possible to determine 2D/3D distribution of elements along an optional slice with trace level detection limits. The sample preparation methods and the analytical capabilities of X-ray techniques mentioned above are illustrated on the basis of the analysis of leaves, xylem sap, roots and hypocotyls of cucumber plants.

ABSTRACTS OF POSTERS

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P-01

BAND SHAPES OF THE ELECTRONIC SPECTRUM OF ANISOTROPIC CENTER IN UNIAXIAL CRYSTAL

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It is common knowledge that optical spectrum of an anisotropic impurity must be more easily interpreted if separate investigations are carried out with light whose electrical field vector E is polarized parallel or perpendicular to the optical axis C. It is evident that they are impossible to be carried out for a great amount of crystals whose growth sides form neither 90° nor 180° angle with C in a typical chemistry or physical laboratory. The goal of the present paper is to analyse the shapes of a single band recorded in non-polarized light in a uniaxial crystal doped with an anisotropic impurity with concentration *C* and molar absorptivities ($\varepsilon^{\perp}$, $\varepsilon^{\parallel}$).

On the basis of the analysis it can be concluded that the shape of a band due to the impurity measured in non-polarized light substantially differs from the band shape in polarized light. Figure display the theoretical absorption spectra when the “parallel and perpendicular” bands of the impurities have the half-width of the perpendicular component is twice as large as the parallel one and the bands in the two directions have the same maximum. Curves 1 (**E**||**C**) and 2 (**E**⊥**C**) illustrate the spectra with fully polarized light. It has been assumed that $\varepsilon^{\perp}/\varepsilon^{\parallel}=10$ and $\varepsilon^{\perp}\cdot C\cdot l = 1$. Curves 3, 4 and 5 represent the spectra with non-polarized light when $\varepsilon^{\perp}\cdot C\cdot l$ are equal 0.2, 1 and 5 respectively. When $A_{max} < -\lg(1-\alpha)$ (A_{max} is the optical density measured in non-polarized light in the maximum of the band; $\alpha = (\cos^2\theta+1)/2$; θ is the angle between **C** and the direction of the light beam), the band has only one maximum located between $\nu_0^{\perp}$ and $\nu_0^{\parallel}$ (the position of the band maximum in polarized light). When increasing the thickness of a crystal, e.g. $A_{max} >> -\lg(1-\alpha)$, the absorption band maximum is at $\nu_0^{\parallel}$; the number of points of inflection of the band can change from 2 to 4; two maxima of the single band due to the impurity in the difference spectrum (the difference between the spectra of a doped crystal and a pure crystal) may be observed. The availability of any band maximum position shift or the change of the number of points of inflection when spectra of similar crystals with different thicknesses are recorded in non-polarized light proves that the spectrum is due to a single band whose components have their own degrees of polarization of light but not two isotropic bands, otherwise the shift would not occur.

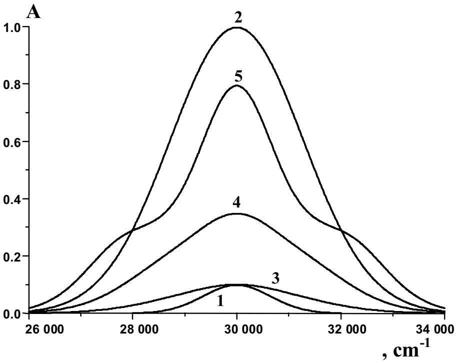

Figure. Theoretical impurity spectra in a uniaxial crystal for polarized (1– **E**||**C**, 2 – **E**⊥**C**) and non-polarized light (3-5). $H^{\perp}$ = 3 000 cm^{-1}, $H^{\parallel}$ = 1 500 cm^{-1}, $\nu_0^{\perp} = \nu_0^{\parallel}$ = 30 000 cm^{-1}.

P-02

A NEW CROSS-SHAPED GRAPHITE FURNACE FOR ATOMIC ABSORPTION SPECTROMETRY

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A new crossed graphite furnace for atomic absorption spectrometry (GFAAS) was designed and installed in heated graphite atomizer (HGA500) combined with Perkin-Elmer spectrometer (AAS1100). The analyzed sample was injected manually in one side of the cross out of the measuring zone then transferred and concentrated at the centre of it using the original inner and additional purge gas. High temperature chromatography approach using the new graphite furnace design with short time temperature program and continuous argon flow is tested for separation of analyte and background signals of highly interfering matrix such as urine.

The sensitivity and repeatability of the new system was tested for some high, middle and low volatile elements in it is standard solutions, the values of detection limit (D.L) and relative standard deviation (RSD) for measurements were comparable to that with the conventional systems. The sample in the new furnace is evaporized and atomized in a way similar to that in side-heated systems, hence good thermal conditions are expected for the sample during analysis.

P-03

INSTALLATION OF NEW T-SHAPED GRAPHITE FURNACE IN HORIZONTAL AND VERTICAL POSITIONS FOR ATOMIC ABSORPTION SPECTROMETRY

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A new T-shaped graphite furnace for atomic absorption spectrometry (GFAAS) has been designed for kinetic analysis of trace elements. It is installed in heated graphite atomizer (GFA-EX7) connected with Shimadzu AAS system (AAS6800). The new furnace is installed in two different positions vertically and horizontally between the two graphite electrodes. Good separations of analyte and matrix absorption signals were achieved for many elements with horizontal position installation. Autosampler could be used for sample injection in both cases. The separation of analyte and matrix is also possible with the vertical installation with some difficulties in sample injection process. The inner argon for continuous flow is also optimized, flow rate of 10-20 ml/min is applied for better separation of analyte and matrices for most elements.

High temperature chromatography approach using the new graphite furnace design with short time temperature program and continuous argon flow is tested for separation of analyte and background signals of highly interfering matrix such as standard urine sample (Seronorm^{TM} trace element urine LOT NO2525).

P-04

OPTIMIZATION OF QUANTITATIVE AAS ANALYSIS OF ZINC (II) IN DRINKING WATER AFTER PRE-CONCENTRATION USING C18 SPE COLUMNS AND SCHIFF BASES AS CHELATION AGENTS

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A method for pre-concentration of Zn(II) ions is proposed by using minicolumns filled with C18 silica gel modified by the Schiff's base (N,N'-Bis(salicylidene)ethylenediamine or N,N'-Bis(salicylidene)1,3-propylenediamine). The retained Zn (II) ions 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). Different experimental factors, including the pH of the sample solution, sample volume, amount of the Schiff's base has been studied to optimize the sorption efficiency for pre-concentration of Zn (II) ions. The batch-method has been tested, whereas the ligand is mixed with the water sample previously to passing it through the SPE column and then it is compared with the column method.

P-05

SPECTROPHOTEMETRIC DETERMINATION OF ADENOSINE TRIPHOSPATE USING ION ASSOCIATE OF ASTRA PHLOXINE FF WITH MOLYBDOPHOSPHATE

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The energy cycle of all living organisms involves adenosine triphospate (ATP), which captures the chemical energy released by the metabolism of nutrients and makes it available for cellular functions such as muscle contraction and transmission of nerve messages. Because of its ubiquitous presence in living matter, ATP has been widely used as an index for biomass determinations in clinical microbiology, food quality control and environmental analyses. Most commonly used methods for the determination of ATP include bioluminescent method (LOD 10^{-14} mol l^{-1}), chromatography (LOD 10^{-7} mol l^{-1}), biosensors (LOD 10^{-12} mol l^{-1}), fluorescence (LOD 3×10^{-9} mol l^{-1}) and other methods.

Hydrolysis of ATP, ADP and AMP in acid and neutral conditions has been studied, for the development of new method for ATP determination Acid hydrolysis of ATP produces three phosphate ions. The released phosphate was determined spectrophotometrically. The method is based on the formation of ionic associate (IA) between molybdophosphate with polymethine dye Astra Phloxine FF (λ_{max}= 570 nm). A linear calibration graph is obtained over the range $4.0\times10^{-8} – 1.2\times10^{-6}$ mol l^{-1} ATP with a detection limit of 3×10^{-8} mol l^{-1}. Molar absorptivity of IA is 3.3×10^{5} l mol^{-1} cm^{-1}. The effect of foreign substances on the determination of 6×10^{-7} mol l^{-1} of ATP was examined. Sucrose, leucine, glycine and starch as well as most of inorganic ions show no interference even in high ratio (up to 1:100000). The AMP and ADP are partially hydrolyzed in optimal conditions.

The proposed method was successfully applied to the determination of ATP in tablets and injections. Ternary mixtures of ATP, ADP and AMP have been simultaneously determined by application of a multivariate calibration partial least squares (PLS) method. In this study, the calibration model is based on kinetic curve of their hydrolysis in the 20-60 min time range for 20 different mixtures of ATP, ADP and AMP. Calibration matrices were containing $(0.2–1.2)\times10^{-7}$, $(0.4–3.5)\times10^{-7}$ and $(1.2–9.4)\times10^{-7}$ mol l^{-1} of ATP, ADP and AMP, respectively. This procedure allows the simultaneous determination of ATP, ADP and AMP in synthetic and real matrix samples with good reliability.

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P-06

SPECTROPHOTOMETRIC DETERMINATION OF SOME NSAIDS

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Non-steroidal anti-inflammatory drugs (NSAIDs) are a class of acidic compounds, which cover a number of different chemical types. Diclofenac (Dicl), Indomethacin (Ind), Ketoprofen (Ket) and Piroxicam (Pir) belong to the NSAIDs. These compounds are widely used in therapeutics for their anti-inflammatory and analgesic properties.

New spectrophotometric methods have been developed for the determination of Dicl, Ind, Ket and Pir. These methods based on the reaction of these NSAIDs with an analytical reagent basic polymethine dye Astra Phloxine FF (AF-FF) and the extraction of ion associate (IA). The optimal conditions for the formation and extraction of IAs with AF-FF are shown in the table 1.

Table 1. The optimal conditions for the formation and extraction of IAs

NSAIDs	pH	C (AF),10^{-4} M	C(Na_2SO_4), M	Organic solvent
Dicl	7.0 – 10.0	1.5 – 3.0	0.6 – 1.2	toluene
Pir	5.5 – 12.0	0.8 – 4.0	–	toluene
Ind	7.0 – 10.0	1.0 – 2.0	0.6 – 1.2	toluene: DChE (4.5:0.5)
Ket	3.0 – 12.0	2.8 – 5.2	0.6 – 1.3	toluene

These techniques have good metrological characteristics, high sensitivity and selectivity (table 2).

Table 2. Metrological characteristics of methods for the NSAIDs determination

NSAID	The calibration equation	λ_{max}, nm	ε, 10^4	Beers law, μg ml^{-1}	LOD, μg ml^{-1}	R
Dicl	$A=0,0195+0,1399 \cdot C_{Dicl}$	563,8	8,8	0,8 – 8,2	0,27	0,9986
Ind	$A=0,0938+0,0513 \cdot C_{Ind}$	563,0	5,8	1,0 – 18,0	0,61	0,9977
Ket	$A=0,0956+0,0789 \cdot C_{Ket}$	563,0	7,6	0,8 –16,0	0,37	0,9983
Pir	$A=0,0352+0,0736 \cdot C_{Pir}$	564,6	9,2	0,6 –17,0	0,24	0,9996

These methods can be used for the determination of diclofenac, indomethacin, ketoprofen and piroxicam in pharmaceuticals and for the control of the equipment cleaning.

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P-07

SPECTROSCOPIC STUDY ON FATTY ACID-BACTERIUM INTERACTIONS

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In the present work we studied the interactions between fatty acids and bacteria. The antibacterial property of fatty acids is a well known and investigated fact. Nevertheless, there is no reassuring explanation about the mechanism of the antibacterial activity of these compounds. The results of the mentioned interaction can be different in the case of fatty acids having various structure. Our earlier studies conduct that even small structural changes can change their behaviour towards bacteria. Our previous investigations with stearic acid (C18) pointed out, that this molecule has no effect on the bacterial growth during the first few hours of the experiment, however, after 24 hours a strong antibacterial effect was found. On the contrary, applying linolic acid (C18:2) a strong antibacterial effect was observed in the first hours but after 18 hours this effect perfectly disappeared. We applied the direct bioauthography for decovering the antibacterial effect of lipid acids, since this method allows examination of lipophilic compounds.

Vibrational spectroscopy is a good tool for the examination of the structural changes in fatty acids. Changes in the spectra of the fatty acids refer to the interaction of fatty acids with the bacteria. In this way one can conclude on the character of the happened process. We pay great attention towards the changes of double bonds, and to the methylation - demethylation processes. These spectral changes may help in the elucidation of the probable mechanisms of these interactions.

The present work is part of a greater project, dealing with study of antimicrobial properties of fatty acids and clearing of the mechanisms of the fatty acid – bacterium interactions.

P-08

SONO-EXTRACTIVE ISOLATION OF THE POTENTIALLY MOBILE ELEMENT PORTIONS OF ENVIRONMENTAL SAMPLES

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Extraction into strong chelating agents could be used for evaluating the total non-residual elemental content of sediments [1]. Single-step extraction was applied to four sediment samples collected from an industrially polluted region of Eastern Slovakia. Na_2EDTA is able to release mobile and potentially mobile metal forms associated with specific phases of sediments and soils [2,3,4]. The innovative time saving pretreatment of sediment samples - by ultrasonic extraction was investigated. Extraction conditions for a single step extraction (for soils) with 0.05 $mol.dm^{-3}$ ethylenediaminetetraacetic acid (EDTA) were optimized. The ultrasound extraction efficiency was compared with the conventional mechanical EDTA extraction and a sequential extraction procedure (SEP) as a reference extraction method [5]. The contents of elements by Na_2EDTA were in good agreement with the sum of the first three steps of the SEP for the most elements. Thus, Na_2EDTA extraction can be used for screening control of sediment and soil pollution [6]. It is applicable as an economically important, time-saving supplementary test for the recommended and attested IRMM (Institute for Reference Materials and Measurements) sequential extraction procedures and as the time saving pretreatment alternative of environmental samples. This work presents description of the sample preparation, optimisation of experiments for ultrasonic extraction of the sediments into 0.05 $mol.dm^{-3}$ Na_2EDTA and compared optimized ultrasonic extraction with the conventional 6 hours extraction into EDTA and with the optimized IRMM sequential extraction procedure.

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P-09

BIOAVAILABLE FRACTION OF TRACE METALS IN RIVERS OF SOUTH MORAVIA

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Measurements of the bioavailable metal concentrations comprise a challenge for the environmental and analytical chemists because they involve specific techniques and skills. Such as supported liquid membranes, ion exchange techniques, voltammetric techniques, diffusive gradients in thin films technique (DGT) and various biomonitoring techniques are used for sampling and measuring in natural waters in present time. The diffusive gradients in thin films technique has been established as robust in situ method for measurement of kinetically labile and free ion metal species in natural systems [1]. Because it generally accepted that the biological effects of metals in aquatic environments is related to the activity of free metal ion, it has been tempting for researchers to understand a DGT measured metal fraction as the bioavailable fraction, however only few studies compared DGT measured concentrations with the amount of metals accumulated in living organisms were done.

In this work the results from experiments in two rivers in South Moravia (Svitava River and Morava River) from 2007 to 2008 are summarized. The concentrations of Cd, Cu, Pb and Ni were monitored using different sampling techniques. Kinetically labile species were measured by DGT, total dissolved and total metal concentrations were monitored using the conventional sampling techniques. The bioavailable concentrations of trace metals were monitored by application of moss bags with Fontinalis Antipyretica aquatic moss species [2].

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P-10

ATOMIC ABSORPTION SPECTROMETRY WITH PHOTOCHEMICAL VAPOR GENERATION – RECENT DEVELOPMENTS

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Photochemical vapor generation is a new method for sample introduction in analytical atomic spectrometry. Nonvolatile analyte species are converted to volatile species and transferred to gas phase by means of radiation instead of the chemical reductants. The advantages of efficient matrix separation, high analyte transport efficiency, high selectivity and simple instrumentation which are connected with concentional chemical vapor generation (CVG) systems are extended by advantages of lower blanks and avoiding of hazardous chemicals. A development of new and promising vapor generation techniques for determination of mercury, selenium and other analytes using photochemical vapor generation are described.

Fig. 1 shows the laboratory-made photochemical VG device with flow-through photochemical reactor tested in our laboratory. The reactor coil is made from quartz capillary with total length of 2.0 m.

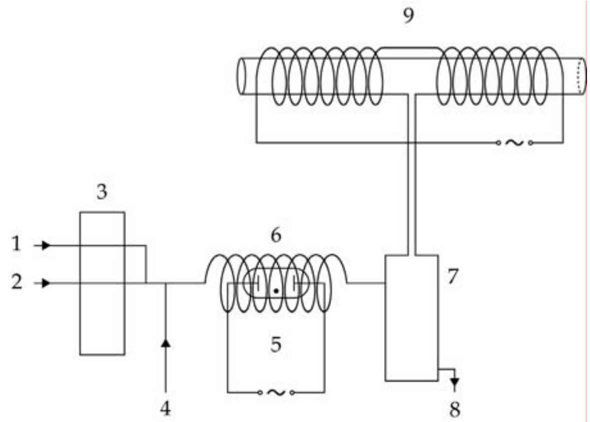

Fig. 1. Scheme of the laboratory-made photochemical vapor generation device with flow-through photochemical reactor. 1 – acid solution, 2 – sample solution, 3 – peristaltic pump, 4 – argon input, 5 – high-pressure mercury discharge lamp (254 nm) with power supply, 6 – quartz photochemical reactor, 7 – gas-liquid separator, 8 – waste, 9 – electrically heated quartz tube atomizer

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P-11

DETERMINATION OF METHYLMERCURY IN FISH MUSCLE BY GC-AFS

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The most toxic specie of mercury, the organometallic cation methylmercury (CH_3Hg^+) is formed in aquatic system and it is biomagnified in food chain from bacteria to plankton and consequently to fish. Fish is the significantly source of human methylmercury exposure. With regard to this fact the determination of methylmercury is very important. The widely used analytical method for methylmercury determination is gas chromatography (GC) with element specific detection. The analyses are based on a sequence of successive analytical steps – decomposition of the solid sample, modification of analytes through derivatization, preconcentration to the organic solvent, separation by chromatography and detection by atomic fluorescence spectrometry (AFS).

This work was focused on a comparison of two preconcentration techniques: headspace solid phase microextraction (SPME) and liquid-liquid extraction (LLE) into suitable organic solvent (as isooctane, hexane, heptane etc.). Ethylated analytes were by SPME headspace sampled with a polydimethylsiloxane-coated fused-silica fiber, by LLE extracted into toluene or isooctane phase. Both techniques are very reproducible. To detection AFS with pyrolysis of mercury species was used.

For the isolation of methylmercury, ultrasonication and microwave-assisted extractions in the presence of extraction agents, such as mixture HCl and NaCl, KOH in methanol and tetramethylammonium hydroxide were tested. Extraction efficiency of the total mercury was determined using the AMA 254 mercury analyzer, extraction yields of methylmercury using GC-AFS. During the adjustment of sample pH to 5, precipitated matter appeared and retention of methylmercury in precipitate probably caused lower extraction yields. The pH value of the sample is an important factor influencing derivatization, therefore the measurement of extraction effectivity in the range of pH from 3 to 7 was performed. The method of Association of Official Analytical Chemists (AOAC) 988.11 for determination of methylmercury was tested and its efficiency was established. Folch method extraction (chloroform : methanol, 2:1), the use of three-fold extraction by acetone were tested for increasing of extraction yields of methyl mercury. Certified Reference Material DORM-2 and real sample of fish muscle were analyzed.

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P-12

SPECTROPHOTOMETRIC DETERMINATION OF MONTELUKAST SODIUM IN TABLETS

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Montelukast sodium [1-{[(1(R)-(3-(2-(7-chloro-2-quinolinyl)-(E)–ethenyl) phenyl)-3-(2-(1-hydroxy-1-methylethyl)phenyl)propyl)thio]-methyl} cyclopropylacetic acid sodium salt] (MK-0476, Singulair®) is a potent and selective antagonist of the cysteinyl leukotriene (Cys-LT_1) receptor, used for the treatment of asthma.

Two spectrophotometric methods were proposed for the quantitative analysis of Montelukast sodium in tablets samples. Firstly, direct absorbance measurement method was used for the determination of the Related drug. This method is based on the use of the absorbances measurements at 281.6, 343.2 nm. At the above wavelenghts, two calibration graphs were obtained in the concentration range of $5x10^{-6}$ and $8x10^{-5}$ mol/L. Secondly, first derivative spectrophotometry was proposed for the determination of Montelukast sodium in tablets. This method was used as a comparison method. In the first derivative method, three calibration graphs were obtained by measuring first derivative absorbance values at 228.4, 287.0 and 339.4 nm. All the proposed methods were validated by analysing the artificial samples containing Montelukast sodium. Recovery results and relative Standard deviations were found as 100.4 % and 1.58 %; 101.4 % and 3.03 % using direct absorbance measurement and 99.6 % and 2.47 % ; 99.3 % and 1.51 % ; 100.4 % and 2.27 % using first derivative spectrophotometric method. All of the spectrophotometric methods were applied to the determination of Montelukast sodium in tablets. In application of the methods, no effect of the excipients of tablets was reported during analysis.

P-13

STUDY OF POSSIBLE ALTERNATIVES TO SPHERON-THIOL RESIN GELS IN DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE

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In our previous study a combination of agarose diffusive gel and Spheron-Thiol resin gel for determination of mercury in natural waters by diffusive gradients in thin films technique (DGT) was found to be the best choice [1]. However, Spheron-Thiol prepared by Smrž [2] is not at the market at present, therefore Duolite GT73, commercially available macro porous resin based on a crosslinked polystyrene matrix containing thiol functional group and 6-mercaptopurine functionalized Iontosorb AV resin were tested as possible alternatives to Spheron-Thiol in order to measure mercury in natural waters by DGT. The preparation procedure of resin gels containing Duolite GT73 and modified Iontosorb AV was optimized and the DGT technique verified.

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P-14

QUANTITATIVE ANALYSIS METHODS OF THE PHARMACEUTICAL PREPARATIONS CONTAINING RISPERIDONE

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In this study the aim is to suggest economic, sensitive, accurate and simple spectrophotometric methods for the determination of risperidone in pharmaceutical preparations.

The first proposed method is direct UV spectrophotometry. In this method, absorbance values of standard and sample solutions in methanol were measured at 237.5 and 278.0 nm. Linear working range of risperidone was 7.0-35.0 μg.mL^{-1}. In the calibration graphs, coefficient of correlation was 0.9997 for both wavelengths. Limit of detection and limit of quantification for 237.5 nm was 0.033 and 0.110 μg.mL^{-1}, respectively; for 278.0 nm was 0.034 and 0.112 μg.mL^{-1}, respectively.

The second proposed method in this study is first derivative UV spectrophotometry. Solutions of standard and samples' derivative absorbance values were measured at 247.9 and 286.2 nm's. In scope of this study, the third proposed method is second derivative UV spectrophotometry. This method was applied to the standard and sample solutions containing risperidone and derivative absorbance values of these solutions were measured at 246.5 and 284.4 nm. Linear working range was 7.0-35.0 μg.mL^{-1}.

The forth method that we proposed is third derivative UV spectrophotometry. Derivative absorbance values of solutions containing risperidone were measured at 283.1 nm. As a result of experiments that performed in 7.0-35.0 μg.mL^{-1} working range, calibration curve was plotted and the coefficient of correlation was calculated as 0.9958 for 283.1 nm. Limit of detection and limit of quantification for this wavelehgth were 0.119 and 0.396 μg.mL^{-1}. The accuracy of method was investigated via "% recovery" studies. Mean recovery value was found as %99.5 with a %2.16 RSD.

Spectrophotometric methods that we proposed in this study was successfully applied to the pharmaceutical preparation containig 1, 4 and 8 mg risperidone called Rispefar® that we assured from Greece; and the high performance liquid chromatographic method that we proposed was successfully applied to the pharmaceutical preparation containing 4 mg risperidone called Rispefar®.

P-15

SYNCHRONOUS FLUORESCENCE AND ENERGY DISPERSIVE SPECTRA OF SOIL HUMIC SUBSTANCES

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The aim of our work was to compare optical properties of humic substances (HS) isolated from different Czech soil matrices (Modal Chernozem, Haplic Luvisol, Eutric Cambisol). Synchronous fluorescence spectra (SFS) were measured by spectrofluorimeter Aminco Bowman at constant difference $\Delta\lambda = 20$ nm. Energy dispersive X–ray spectra (EDXS) were measured using X-ray spectrometer XEPOS. Isolation of humic acids (HA) was made according to IHSS method. Carlo Erba CHNS/O analyser for elemental analysis of isolated humic acids was used.

Alkali extracts of HS studied by SFS spectrometry showed that H. Luvisol and M. Chernozem have higher aromaticity and quality than E. Cambisol. Sample E. Cambisol had higher fulvic acids content (peak at wavelengths 359, 419 nm). All samples and Elliot soil standard have main peak at $\lambda_{em.}/\lambda_{ex.=}$ 488/468 nm (Fig.1). EDX spectra of all soil samples contained peaks of Fe, Ti, Al, Si, S and Cl.

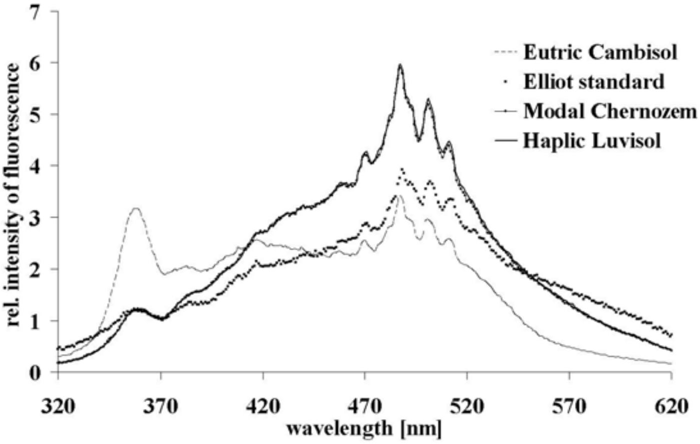

Figure 1: SFS spectra of soil humic substances

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P-16

DETERMINATION OF SI AND AL IN CORROSION MEDIUM OF SODIUM CHLORIDE SOLUTION BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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Inductively coupled atomic emission spectroscopy was used for determination of Si and Al originated from the corrosion of two most widely used structural ceramics, alumina and silicon nitride in an aqueous solution containing 0.5 mol/l NaCl at temperatures of 200 and 290 °C. The internal standardization was used as a correction technique for matrix effects. Mentioned procedure was compared with direct determination without correction of matrix effect. The method provides satisfactory precision and analytical recoveries.

P-17

PIGMENTS OF LA TÈNE PAINTED CERAMICS FROM BRATISLAVA'S OPPIDUM: X-RAY DIFFRACTION AND RAMAN SPECTROSCOPIC STUDY

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For this study were chosen the most typical shards of painted La Tène pottery from Bratislava's oppidum. The shards represent La Tène (late Iron Age) vessels with typical horizontal red to dark red and white paintings with occasionally black geometric patterns. The black, red, dark red and white pigments were studied using X-ray powder diffraction analyses - PXRD (DRON-3 diffractometer) and Raman spectroscopy (Renishaw RM 1000 spectrometer). Experimental data were compared with already published data on La Tène ceramics or with other ceramics (Rigby et al., 1989; Peréz Esteve-Tébar, 2004). A reducing atmosphere in the kiln is important for a black surface. The most common compound is usually magnetite (Maggeti et al., 1981) but the PXRD analysis did not show any minerals responsible for the black colour. Two bands characteristic for the amorphous carbon (lampblack) centred at 1350 and 1580 cm^{-1} were identified using the Raman spectroscopy.. According to the PXRD the main constituent compound of the red painting is hematite. Hematite was also identified using Raman spectroscopy with characteristic bands 293, 409, 508, 614 a 1329 cm^{-1}. Results are in good correlation with La Tène ceramics from Prunay (Rigby et al., 1989). The presence of hematite in red painting reflects strongly oxidizing atmosphere in the kiln (Maggetti, 1982). PXRD analysis of dark red pigment showed only presence of hematite. Using the Raman spectroscopy hematite (298, 411, 460, 613 cm^{-1}) and also magnetite (289, 396, 534 a 669 cm^{-1}) were identified. As the white layer is very thin, the PXRD analyses showed also impurities as quartz and feldspar coming from the ceramic body and the obtained Raman spectra didn't show any significant vibrations bands. Therefore the analysed layer consists of lime (CaO), which is a Raman inactive compound.

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P-18

DETERMINATION OF ULTRATRACE ANTIMONY BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY WITH DIRECT TIO_2-SLURRY SAMPLING

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Although ETAAS offers excellent detection limit for trace determination of antimony, ultratrace determination is impossible without using a suitable separation/preconcentration procedure. Solid phase extraction (SPE) is frequently used for this purpose. Different inorganic metal oxides can be applied as solid sorbents. Among them, TiO_2 offers a high surface area/body weight ratio and high adsorption. Generally, TiO_2 is used to adsorb metal ions as a sorbent in a column. In this case, the elution is necessary to determine these ions. However, the elution is time-consuming and sometimes results in a loss of analyte. Slurry sampling of the used sorbent is an effective mode to solve this problem.

In this work, nanometer sized TiO_2 was used for separation/preconcentration of total inorganic antimony. After antimony adsorption onto TiO_2, direct TiO_2-slurry sampling was used for injection into a graphite tube. The optimal conditions for separation/preconcentration of antimony (pH, mass of TiO_2, extraction time), effect of different valence states of antimony and effect of coexisting ions on the extraction recovery were investigated in detail. To establish a suitable temperature program for antimony determination in liquid and slurry solutions, optimization of furnace conditions was also made. After optimization, the analytical procedure for antimony extraction was used as follows. The pH of a sample solution was adjusted to 2.0 with 2 M HNO_3 and placed into a 100 ml polyethylene bottle containing 100 mg of nanometer sized TiO_2. Then, the sample solution was shaken by a mechanical shaker for 10 min and the mixture was centrifuged at 4000 rpm for 10 min. The bulk aqueous phase was decanted by inverting the bottle. Finally 5 ml of deionized water was added to prepare a slurry sample. The slurry sample was agitated for 1 min and transferred into an autosampler cup. Antimony in the slurry samples was determined in the presence of palladium nitrate using pyrolysis temperature of 1200 °C and atomization temperature of 2500 °C. The accuracy of the optimized method was checked by CRM for trace elements in riverine water SLRS-4. Finally, the method was used for ultratrace determination of total inorganic antimony in natural waters.

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P-19

SPECTROSCOPIC AND DFT STUDIES OF TEMPERATURE AND WATER CONTENT EFFECTS ON THE STRUCTURE OF 1-AMINO-2-PROPANOL, 3-AMINO-1-PROPANOL AND AMINOETHANOL IN THE LIQUID PHASE

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Two Dimensional (2D) correlation FT-NIR spectroscopy is a powerful analitical technique used to investigate the dynamics of various physico-chemical processes as for example changes in hydrogen bonds. The studies of the structure of both pure aminoalcohols and their mixtures with water are very limited so many basic questions still remain open. Here, we report new experimental results on the structure of pure liquid 1-amino-2-propanol, 3-amino-1-propanol and aminoethanol as well as their binary mixtures with water. The experimental spectra (FT-IR and FT-NIR) were analyzed by using 2D correlation approach and the chemometric methods like: principal component analysis (PCA), evolving factor analysis (EFA) and multivariate curve resolution (MCR). Besides, the energies of the most stable conformers of these aminoalcohols and their hydrates were determined by density functional theory (DFT). Based on these results we attempt to answer the following questions:

(1) Does the pure aminoalcohols have an intramolecular hydrogen bond, an intermolecular hydrogen bond or both?
(2) What is the effect of the molecular structure (of the relative position of NH_2 and OH groups) on the inter- and intramolecular hydrogen bonding in aminoalcohols?
(3) How the structure of aminoalcohols is changed upon an addition of water?

P-20

DETERMINATION OF METALS IN BIOFUEL

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Energy crisis and resource depletion in the world and increase of greenhouse gases requests to look for solution. Biofuel is one of the most important energy sources originating from renewable raw materials. Biodiesel is the most common biofuel in Europe. It is produced from vegetable oil or fats such as rapeseed, sunflower, palm oil etc. Bioethanol is blandig component of biogasoline. It is produced by fermentation of sugars derived from wheat, corn, sugar beets, sugar cane etc.

Biodiesel is mixture of diesel and fatty acid methylesters (FAME) in concentration 5% of FAME. In future biodiesel will be made with higher concentration of biocomponent (10-30 %)

Parameters of metylester strictly specify qualitative minimum standard as described in the European standard STN EN 14214. Except physical chemical indicators (ester content, density, viscosity, flash point, carbon residue, cetane number, sulphate ash, water content, contamination, corrosive properties, oxidation stability, acid number, iodine number, linolenic acid methylesters, methanol content, mon-,di-, triglycerides, phosphorus content- our laboratories have all tests accredited) content of alkali metals Na and K and content of alkali soil metals Ca and Mg is checking. Content of these metals is not allowed exceed 5 mg/kg.

Our laboratories determine content of Na, K, Mg, Ca by AAS. Standard STN EN 14538 requires metal determination by ICP OES.

Determination of these metals is performed in organic background by flame absorption spectrometry.

Aim in our contribution is describing of the metals determination, validation of the results and comparison AAS and ICP on the bases of interlaboratory crosscheck study.

P-21

APPLICATION OF NIR FOR CHARACTERIZATION OF POLYMORPH PURITY AND API-EXCIPIENT COCRYSTALS

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Optical sensing methods represent an important methodology in modern analytical chemistry. Fourier transform near-infrared (FT-NIR) spectroscopy is a fast and non-destructive analytical technique that offers many advantages for a broad range of applications [1].

Polymorphism of active pharmaceutical ingredients (API) gets more and more important physico-chemical parameter influencing stability of API and bioequivalency of generic pharmaceuticals. Besides, modern drugs possess limited solubility and/or absorption, i.e. bioavailability.

Bisphosphonates are widely used in practice. They are indicated for the treatment and prevention of postmenopausal women osteoporosis. They are powerful inhibitors of bone resorption, but their gastrointestinal adsorption is about 1% due to their high hydrophilicity [2].

Due to all the above mentioned facts various mixtures of bisphosphonates and excipients (more hydrophobic adducts) in different ratio and under various conditions were prepared. All prepared mixtures (solid compounds) and/or new entities were analyzed by means of the FT-NIR spectroscopy (diffuse reflectance method), and the results were compared with those of the FT-Raman spectroscopy, XRPD and ssNMR.

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P-22

FRACTIONATION OF TRACE ELEMENTS SPECIES IN WHEAT

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The on-line coupling of SEC and ICP-MS was used for separation and detection of zinc, copper, iron, manganese, molybdenum, nickel, phosphorous and cadmium species in various parts of wheat (*Triticum aestivum* L.) plant. The main aim of this study was to follow changes of species fractionation of phosphorous and some trace elements during growing and maturation. Analysed samples (stalks, ears, straw and grains) were collected during three growing stages. Element species were extracted by 0.02 mol l^{-1} Tris-HCl buffer solution, pH 7.5. The total contents of elements in all wheat samples, samples extract and soil sample were obtained by ICP-MS. Superdex 75 HR 10/30 column and 0.02 mol l^{-1} Tris-HCl buffer (pH=7.5) as a mobile phase were used for separation of the element species fraction. The quantitative evaluation of elements mass adherent to individual detected species fraction was achieved by post-column calibration method. The major part of element contents of all sample extracts was concentrated in low-molecular weight fractions (1-2 kDa). These fractions were isolated by preparative–scale SEC and subsequently refined by immobilized metal ion affinity chromatography. Refined samples were analysed by MALDI-MS and by IEC for the amino-acid composition as well.

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P-23

CONTRIBUTION TO THE DETERMINATION OF ELEMENTS USING A HIGH-RESOLUTION CONTINUUM SOURCE FLAME ATOMIC ABSORPTION SPECTROMETER

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In high - resolution continuum source atomic absorption spectrometry (HR-CS-AAS) the element-specific light source of classical AAS (hollow cathode lamp) is replaced by a single continuum source, a xenon short-arc lamp that ensures very high radiation density and continuous emission through the entire spectral range (190 – 900 nm). By this way it is possible to determine the elements on their base absorption lines and on all secondary wavelengths as well without any technical limitations. This technique provides to determine high number of elements simultaneously.

If macroelements are measured together in decomposed plant samples it is advantageous to measure Mg on its secondary line 202.582 nm or K on the line 404.414 nm. By this way it is not necessary to dilute the sample only the addition of ionization buffer and releasing agent is required.

With regard to large consumption of the sample during the parallel determination of a number of elements by using the typical nebulizer (7.5 ml min^{-1}) the application of special injection module called Segmented Flow Star was tested. The washing solution is continuously introduced into the flame, this flow is substituted with the sample solution only for the time as necessary for the measurements of analytes. It is advantageous for the decreasing of the sample volume required for analysis and for the continuous cleaning of the burner in the case of the samples with complicated matrix. In the case of parallel determination of 4 elements (Cd, Pb, Fe, Mn) the amount of required sample was reduced from 18.5 ml by using typical nebulizer to 2.5 ml by using injection module.

HR-CS-AA spectrometer allows not only to measure atomic, but also molecular absorption. The elements not typically determined by atomic absorption spectrometry phosphorus and sulphur were measured on the molecular PO and CS lines. For the measurement of S the rotational lines around 258 nm, P the lines around 246 and 324 nm were studied and the conditions for flame determination were optimized.

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P-24

PROBLEMS ENCOUNTERED WITH THE MERCURY AND METHYLMERCURY HAIR ANALYSIS

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The concentration of methylmercury (MeHg) in the environment is insignificant but hair can be used as a suitable matrix to estimate endogenous MeHg exposure. A validated analytical method with AMA 254 spectrometer was used for the determination of mercury species in the hair of dentists, workers in fish industry and professionally non-exposed adults.

Integral parts of the determination of MeHg are sampling and storage. Long-time stability and contamination of samples were studied using radioactive indicator ^{203}Hg.

Stability of inorganic mercury and methylmercury species in hair samples labelled with $^{203}Hg_{in}$ or Me^{203}Hg in paper and polyethylene were studied. Strong bonding affinity between mercury species and hair has been confirmed.

Ctamination of hair samples in paper and polyethylene were studied a) in laboratory room where no work with mercury takes place and b) each form separately with solution labelled with ^{203}Hg or Me^{203}Hg. The resultes of non-radioactive study not document contamination of hair from not contaminated atmosphere of laboratory during 3 month. An increase of radioactivity in hair was observed in the radioactive study with ^{203}Hg atmosphere.

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P-25

DETERMINATION OF SI, AL, CA, MG AND B IN GLASS SAMPLES BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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A comparative study of several decomposition techniques of E-glass like samples has been carried out. The samples of glass were transformed to soluble form alternatively by fusion with lithium tetraborate, by alkaline fusion with sodium peroxide, or by acidic decomposition with hydrofluoric and perchloric acids. Accuracy of analytical results was confirmed by analyzing the certified reference material of borosilicate glass (NCS DC61104). The contents of particular elements were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The obtained results and achieved precision showed that each of considered techniques is adequate for determination of specific elements. On the basis of the analytical results more than one decomposition technique needs to be applied in order to determine overall chemical composition of E-glass like samples.

P-26

O-TOF ICP MS ANALYSIS OF RARE EARTH ELEMENTS, URANIUM AND THORIUM IN THE ELBE RIVER SAMPLES

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A method for determination of Sc, Y, La, Dy, Er, Eu, Gd, Ho, Lu, Nd, Pr, Sm, Tb, Tm, Yb, Ce in biota samples using the unique spectral method o-TOF ICP MS (GBC Optimass 8000) was developed.

Using nitric and hydrofluoric acid, samples were decomposed in a microwave digestion unit. The optimisation of spectral and operation condition was performed (isotopes, internal standards and their concentrations, a proper calibration range, settings of o-TOF spectrometer). For non-spectral interference elimination, the internal standard Be was used.

The validity of the method was proved by a recovery evaluation of spiked samples and by comparison of results of determination without any internal standard, with internal standards and the standard addition technique.

Detection limits of chosen elements were in $\mu g.kg^{-1}$ and relative standard deviations up to 10 %. In fish samples, contents of elements were in tens of $\mu g.kg^{-1}$; some of elements were not detected. In case of another samples, all elements were detected in measurable concentrations. Contents of observed elements in Dreissena polymorpha samples were found from units to hundreds, in profiles and insect samples from tens to thousands $\mu g.kg^{-1}$. For benthal growth, concentrations were even bigger at one degree.

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P-27

INFLUENCE OF SOLVENTS ON FLUORESCENCE SPECTRA OF BENZIMIDAZOLES

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Benzimidazole carbamates are important anthelmintic drugs. Investigations of their pharmacokinetic action require reliable analytical methods. Methods based on fluorescence are very sensitive and efficient. Hence emission spectra of some fluorescent benzimidazoles were measured and an influence of used solvents (e. g. methanol, acetonitrile, buffered solvents) was studied in order to help to choose the most suitable solvent for fluorescence measurements or fluorimetric detection in HPLC.

Serious differences were discovered depending on the particular benzimidazole. The differences were explained with respect to the chemical structures of the studied substances.

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P-28

USE OF OPTIMIZED BCR THREE-STEP SEQUENTIAL AND DILUTE HCL SINGLE EXTRACTION PROTOCOLS FOR THE PREDICTION OF SOIL-PLANT METAL TRANSFER PROCESSES

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The prediction of soil metal phytoavailability using the chemical extractions is a conventional approach routinely used in soil testing. The adequacy of such soil tests for this purpose is commonly assessed through a comparison of extraction results with metal contents in relevant plants.

In this paper, the fractions of selected risk metals (Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Zn) that can be taken up by various plants were obtained by optimized BCR (Community Bureau of Reference) three-step sequential extraction procedure (SEP) and by single 0.5 mol l^{-1} HCl extraction. These procedures were validated using five soil and sediment reference materials (SRM 2710, SRM 2711, CRM 483, CRM 701, SRM RTH 912) and applied to significantly different acidified soils for the fractionation of studied metals. The new indicative values of Al, Cd, Cu, Fe, Mn, P, Pb and Zn fractional concentrations for these reference materials were obtained by the dilute HCl single extraction. The influence of various soil genesis, content of essential elements (Ca, Mg, K, P) and different anthropogenic sources of acidification on extraction yields of individual risk metal fractions was investigated also. The concentrations of studied elements were determined by atomic spectrometry methods (F AAS, GF AAS, HG AAS, ICP OES).

It can be concluded that the data of extraction yields from first BCR SEP acid extractable step and soil-plant transfer coefficients can be applied to the prediction of qualitative mobility of selected risk metals in different soil systems.

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P-29

SPECIATION OF SELENOAMINO ACIDS IN SE-ENRICHED GREEN ALGAE BY HPLC-ICP-MS

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Selenium is an essential nutrient and has been known to be a necessary component of the human diet. It is important e.g. for protection of cells against effects of free radicals and the normal function of immune system. Due to this the consumption of Se-enriched supplements has been very popular nowadays. Popular source of selenium is Se-enriched yeast, wherein the most dominant form of selenium is selenomethionine, it possessing higher bioavailability and lower toxicity than inorganic selenium. Se-enriched biomass of green algae *Scenedesmus* and *Chlorella* might also become an alternative source of organic bound selenium. Algal cultures are treated with sodium selenite (1-200 mg.l^{-1} as Se). The aim of this work is to develop a method for quantification of selenium amino acids in algal biomass.

Acid (4M methanesulfonic acid) and enzymatic (Protease XIV, Macerozym R-10) hydrolysis were applied for hydrolysis of proteins in algal biomass for determination of selenomethionine and selenocysteine. Determination is based on coupling of anion exchange high performance liquid chromatography (HPLC) with inductively coupled plasma mass spectrometry (ICP – MS). Both methods of hydrolysis led to recoveries of Se only about 15% (from total algal Se), the majority as selenomethionine. Extraction yield for selenomethionine was the same for acid and enzymatic hydrolysis, extraction yield for selenocysteine was 2-3 times higher for acid hydrolysis. It seems that the most dominant form of selenium in biomass could be elemental selenium, which is not bioavailable for mammals.

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ANALYSIS OF CD IN MUST AND WINE

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Cadmium is a well-known toxic element, therefore it is very important to determine it in must and vitivinicultural products. We were achieved that there is 21-50% of metals in grapes stem, 23-32% in the skin, 7-7.7% in seeds and 18-38% in the pulp of grape. Slovakian wines according to affiliation to vineyard regions are different from imported wines, therefore some heavy metals /Cd, Cu, Cr, Sr, Ba, Ca, Mg, Rb and V/ could be a markers of origin of wine(1). Concentrations of cadmium are often determined using atomic absorption spectrometry (AAS), but also stripping chronopotentiometry gives a good results (2).

Stripping chronopotentiometry consist of 2 steps. The Cd(II) ions are electrochemically deposited from the flowing sample solution in the porous working electrode: $Cd^{2+} = Cd^0 - 2e^-$

The deposition is performed by applying a suitable potential. In the next step, the deposit is stripped galvanostatically, whereas the stripping chronopotentiogram is recorded.

AAS determination was performed by atomic absoption spectrofotometer UNICAM 939/959

Flame: acethylen-air was used. The calibration curve was achieved from 8 points. The results from applying this two methods will be presented.

In this work we determine Cd in must and compare results using both techniques. The results shows, that stripping chronopotentiometry is very useful method and concentration of cadmium in must could be determine very quickly.

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P-31

SYNTHESIS, PROPERTIES AND ANALYTICAL APPLICATION OF NEW STYRYL DYE 2-[(E)-2-(4-DIPROPYLAMINOPHENYL)-1-ETHENYL]-1, 3, 3-TRIMETHYL-3H-INDOLIUM CHLORIDE

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Styryl dyes belong to the group of polymethine dyes, which are characterized by the presence of the conjugate chain–$(CH{=}CH–)_nC_6H_4$–. Dyes of this structure are mainly asymmetric styryl dyes. In depend on location of bonding of substituents can increase their solubility and change their optical, thermal or/and electronic properties. The aim of this work was synthesis and study of the spectral properties of new styryl dye 2-[(E)-2-(4-dipropylaminophenyl)-1-ethenyl]-1, 3, 3-trimethyl-3H-indolium chloride (DAET). Study of acid-basic and spectrophotometric properties have proved existence of three different forms. Ionic form R^+ is stable within the range of medium from pH 4 to 11 and the optimum analytical wavelength of this form is 550 nm (ε = $5{,}51\times10^4$ L mol^{-1} cm^{-1}). At pH > 11 is formed of hydrolyzed ROH form and the optimum analytical wavelength of this form is 340 nm (ε = $1{,}12\times10^4$ L mol^{-1} cm^{-1}). At pH < 4 is formed of protonated double-charged RH^{2+} form of reagent with absorption maximum near 370 nm (ε = $2{,}01\times10^4$ L mol^{-1} cm^{-1}). Development of this process is influenced by following factors: protonation (pKpr = 1,98) and hydrolysis (pKh = 12,27). Based on the results of NMR-spectroscopy and quantum-chemical calculations the most possible protolytic mechanism of equilibrium in solutions of DAET was elaborated.

This dye was used for the spectrophotometric determination of molybdenum. The method is based on the reaction of thiocyanate complex of molybdenum with DAET to form a colored ion associate. The influence of various factors on the formation of ion associate has been studied and optimal condition has been found: 0,1-0,16 mol L^{-1} KSCN; 0,1-0,25 mol L^{-1} HCl; 4.10-5-6.10^{-5} mol L^{-1} DAET and 0,18-0,24 % anionic surfactant OC-20. Limit of detection of this method is 0.015 µg/mL. The results obtained became the basis for the development of a new sensitive and selective spectrophotometric method for determination of molybdenum in the presence of various interferents, mainly Re, V, W.

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SPECTROSCOPIC STUDY OF PROTONATION OF OLIGONUCLEOTIDES CONTAINING ADENINE AND CYTOSINE

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Adenine (A) and cytosine (C) are important building blocks of nucleic acids taking part in the process of genetic information transfer and transfer of energy, charge and biological important compounds. Due to acidobasic properties of bioligands, the distribution of protonated species is dependent on solution pH and therefore it is important to know their protonation constants. The aim of this work was to determine the protonation constants of titled bioligands.

The protonation constants of bases (A, C) and their relevant nucleosides and nucleotides were determined by means of potentiometric titration carried on automatic titrator METROHM Titrando 835 (I = 0.15 mol.l^{-1} M NaCl, t = 25 °C) and the experimental data were evaluated by OPIUM program. In addition, the temperature dependence of protonation constants was used to estimate thermodynamic parameters for A and C ligands.

The protonation behaviour of oligonucleotides containing A and C, *i.e.* $(CAC)_3$, $A_3C_3C_3$, $C_3A_3C_3$, was followed by means of molecular UV absorption spectroscopy in pH region 2-8 and for ionic strength 0.10, 0.15 and 0.25 mol.l^{-1} adjusted by NaCl. The experimental data were treated by means of SPECIFT and MCR-ALS software and distribution diagrams of species as pH function were calculated. The influence of structural motif on protonation constants of studied oligonucleotides seems to be very important due to probable stabilization of the secondary structure of biomacromolecule.

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PRECONCENTRATION OF CD FROM AQUEOUS SOLUTIONS USING BIOLOGICAL SUBSTRATES FOR AAS DETERMINATION

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Preconcentration procedures for metal quantification at low concentration levels despite recent advances in analytical instrumentation, are often necessary before the determination step.

Solid-liquid extraction comprises metallic species retention on an adequate sorbent with a posterior desorption by using an inorganic or organic solvent. The preconcentration procedures employing solid materials as sorbents and applied to atomic spectrometry present some advantageous characteristics, such as simplicity, and higher preconcentration factors. The syntetic exchangers/adsorbers and biological substrates are classified as the most important materials for solid-liquid extraction.

Biological substrates such as bacteria, algae and fungus are materials able to accumulate metals from aqueous solutions through the biosorption process. When this process takes place on the cellular membrane, it can mainly be considered as adsorptive, because no biological activity is present. Otherwise, when live cells are used, the metallic species are firstly adsorbed on a cellular membrane and after passing through this membrane, they are absorbed into the structure. There are evidences that some phenomena such as absorption, cationic exchange, chelating take place in cellular membranes of microorganisms. The groups responsible for the adsorption processes are found from biomolecules, which contain sulphates, carboxylates and phosphates in their structure.

In the present work the preconcentration of cadmium from aqueous solutions under laboratory conditions by fungal biomass of two strains of Aspergillus niger was investigated. Strain An1 was isolated from the Eutric Fluvisols FMm (pH H_2O/KCl 7.7/7.4). Strain An3 was isolated from the stream sediment (pH H_2O/KCl 5.27/4.8) from Pezinok region (Slovakia).

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CONTENT OF ARSENIC IN THE FISH MUSCLE FROM INTENSIVE BREEDINGS

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The objective of this study was to determine the total arsenic and the species of arsenic in the Rainbow Trout muscle (*Oncorhynchus mykiss*).

Owing to the fact that there is an increased arsenic content arising from the scrap cake in the fish from the intensive breeding, the samples of feed were analysed as well. Samples were mineralized before determination of the total arsenic by the method of AAS by wet way (nitric acid 1:1 with hydrogen peroxide), then burned in a muffle furnace and reduced to As^{III} by addition of KI in the ascorbic acid. For extraction of the arsenic species, the ultrapure deionized water was used. Total arsenic was determined by hydride method of HG-AAS, species of arsenic were determined by method, which includes the combination of the method of highly effective liquid chromatography, hydrides generation and atomic fluorescence spektrometry (HPLC-HG-AFS). Concentrations of arsenic in the fish muscle were very low, they met the limit valid for the Czech Rebublic, which is stipulated by the Decree 53/2002 of the Code, where the highest acceptable arsenic volume for freshwater fish is 1 mg. kg^{-1} and for sea fish 5mg. kg^{-1}. The measurement validity was tested by certified standard material Dorm-2 (dogfish muscle), which consists of 18,0 ± 1,1 mg.g^{-1} As. Arsenobetain was detected by a method of HPLC-HG-AFS, the average content of arsenic in the samples was 65%.

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DETERMINATION OF ARSENIC IN GROUNDWATER BY GFAAS

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Arsenic, a metalloid occurs naturally, being the 20th most abundant element in the earth's crust, and is a component of more than 245 minerals. These are mostly ores containing sulfide, along with copper, nickel, lead, cobalt, or other metals. Arsenic and its compounds are mobile in the environment. Weathering of rocks converts arsenic sulfides to arsenic trioxide, which enters the arsenic cycle as dust or by dissolution in rain, rivers, or groundwater. The contamination of groundwater with arsenic has already been reported in 20 countries, out of which four major instances are from Asia [1]. These include Bangladesh, India, Inner Mongolia and Taiwan. So, groundwater contamination by arsenic is a serious threat to mankind all over the world. It can also enter food chain causing wide spread distribution throughout the plant and animal kingdoms [2]. Arsenic occurs in the natural environment in four oxidation states: As (V), As (III), As (0) and As (−III). The mobility and toxicity of arsenic are determined by its oxidation state [3], thus the behaviour of arsenic species will change depending on the biotic and abiotic conditions in water. In groundwater, arsenic is predominantly present as As (III) and As (V) [4].

Atomic absorption spectrometry (AAS) is a spectroanalytical procedure for the qualitative detection and quantitative determination of elements employing the absorption of optical radiation by free atoms in the gaseous state [5]. Graphite furnace atomic absorption spectrometry or electrothermal atomic absorption spectrometry (ETAAS) is one of the spectrometric methods, which is based on the absorption of free atoms produced from the sample deposited in a small graphite tube, which can be heated by the application of high temperatures. However, most of reported methods for arsenic detection based on GFAAS require pre-concentration in order to increase sensitivity [6].

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QUANTITATIVE ASSESSMENT OF BIOSORPTION, BIOACCUMULATION AND BIOVOLATILIZATION OF LABILE ALUMINIUM AND THALLIUM SPECIES BY FUNGAL BIOMASS USING ATOMIC SPECTROMETRY

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The biosorption, bioaccumulation and biovolatilization of labile aluminium and thallium species from synthetic solutions by compact and pelletized biomass of three strains of microscopic filamentous fungi (*Neosartorya fischeri*, *Aspergillus niger*, *Aspergillus clavatus*) were studied under laboratory conditions. The recoveries of studied processes were quantified by the techniques of atomic spectrometry (F AAS, GF AAS, ICP OES). The speciation of Al(III) and Tl(I) in synthetic solutions was obtained by computer modelling. Further the changes of pH values and the influence of biological metabolism of given fungi on the studied processes were observed and investigated.

Results showed that the highest amounts of Al were biosorbed and bioaccumulated by *Aspergillus clavatus*. The bioavailable aqua cations Al^{3+}, $Al(OH)^{2+}$ and $Al(OH)_2^+$ are the prevailing species below pH 5.0. In the pH range between 5.0 and 6.2, there is a mixture of these cations and colloidal $Al(OH)_3$ species. At pH higher than 6.2, the dominant species is $Al(OH)_4^-$.

The amounts of biosorbed, bioaccumulated and biovolatilized of labile Tl by *Neosartorya fischeri* were desribed also. The bioavailable cations Tl^+ and relatively weak neutral complexes ($TlNO_3$, TlOH) are the prevailing species at given conditions. It is assumed that dimethylthallium (Me_2Tl^+) is the main biovolatilized Tl chemical form.

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P-37

UTILIZATION OF FIVE DIFFERENT METHODS FOR THE ASSESSMENT OF ALUMINIUM PHYTOAVAILABLE AND/OR PHYTOTOXIC FRACTIONS IN ACID SOILS

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The suggested investigation deals with the separation of phytoavailable and (phytotoxic) Al fractions in soil and soil sediment samples by five different procedures (single and sequential extractions, membrane filtration, chelating solid phase extraction and kinetic strength discrimination method). The concentrations of Al in studied fractions and relevant plant materials were measured by F AAS, ICP OES and UV/VIS spectrophotometry.

Weakly efficient single extraction procedures by H_2O, dilute acetic acid, NTA, EDTA, DTPA, salicylic acid, ammonium salicylate and 8-hydroxyquinoline, chelating solid phase extraction by resins Iontosorb Oxin and Salicyl and kinetic strength discrimination method using 8-hydroxyquinoline release from the samples only small amounts of phytoavailable and phytotoxic Al by ion-exchange or complexation processes. The more efficient extractions with KCl, NH_4Cl, $CaCl_2$, $BaCl_2$, $CuCl_2$, $LaCl_3$, NH_4F and $(NH_4)_2C_2O_4$ leach approximately the same amounts of phytoavailable Al as the total Al concentrations in plant material (grass *Festuca rubra*) growing on analysed soils and soil sediments. The most aggressive leaching with $Na_4P_2O_7$, dilute HCl, $NH_2OH{\cdot}HCl$ in HNO_3 and H_2O_2/ammonium acetate in HNO_3 releases the highest amounts of Al from solid samples, approximately double to fourfold as the total Al concentrations in relevant plant material and it is unsuitable for purpose of this study.

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SEPARATION/PRECONCENTRATION PROCEDURE FOR THALLIUM SPECIES DETERMINATION IN WATERS BY ETAAS

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Thallium is a heavy, very toxic metallic element, which occurs in earth´s crust in an estimated abundance from 0.1 to 0.8 mg.kg^{-1}. In the environment, it is mainly combined with other elements (primarily oxygen, sulfur, halogens, K and Rb) in inorganic compounds. During the weathering processes it can be mobilized by aqueous media and accumulated in sediments and soils. The main sources of pollution nowadays come from anthropogenic emissions from refineries, coal-fired power stations, mining activities, metal smelters and the cement industry [1]. In natural waters, it can exist as either Tl(I) or Tl(III). Thallium content in surface waters is within the range 1.2 - 82 ng.L^{-1} [2]. Due to the low contents of thallium species Tl(I) and Tl(III) in water samples, it is necessary to combine laboratory instrumentation with preconcentration and separation techniques [3].

The scope of the presented work was to use an ion-exchange separation/preconcentration technique for thallium species in waters followed by ETAAS determination. In this method, Tl(III) was stabilized by formation of a cationic Tl(III)-DTPA complex. Tl(I) remained in its original form. The two species were separated by using a strong acid, gel-type cation exchange resin Amberlite IR120 and nitric acid as the eluent. The optimized conditions for separation/preconcentration technique and ETAAS determination were used for the determination of thallium species in acid attacked waters (acid mine drainage which is mainly a product of pyrite oxidation) from open quartzite mine in the Banska Stiavnica – Sobov region (Slovakia).

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FRACTIONATION OF TRACE ELEMENTS SPECIES IN RYE SEEDLINGS

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Fractionation of species of Cd, Cu, Mo, Ni and Zn in extracts of rye seedlings leaves and roots and rye flour was performed by on-line hyphenation of SEC/ICP-MS. 0.02 mol.l^{-1} Tris-HCl buffer solution (pH=7.5) served for the extraction and as the mobile phase as well. Superdex HR 75 column was used for the sample fractionation and PE Elan 6000 was used as the element specific detector.

Two kinds of plants were investigated; both were cultivated in a laboratory. The first ones were grown in normal fertiliser solution; the other ones were grown in Cd^{2+}-enriched medium. The sample of the rye flour was purchased on common market.

Majority of soluble Cu, Zn and Ni in all analysed samples was bound in a fraction of M_r approx. 1-2 kDa; Mo in all samples was present in a fraction of M_r 3 kDa.

The Cd content in “blank” samples, i.e. plants cultivated without Cd addition, was negligible. During five days cultivation in medium containing 30 µmol.l^{-1} Cd^{2+} the whole rye plants have cumulated 5 mg.kg^{-1} Cd (fresh material); however only 12-15 % of the total Cd was soluble in Tris-HCl buffer. A portion of 76 % of Cd content in the extract of leaves was bound into stable complexes; the portion of stable complexes of Cd in extract of roots was only 25 %. Predominant amount of complexes of Cd was involved in a fraction of M_r 3 kDa, while an only minor part was found in a fraction of M_r 20 kDa (both samples). Hence the speciation of Cd in the plants with elevated Cd content differs from that of other metals present on physiological level.

The chromatographic fractions 1-2 kDa (i.e. fraction most rich in metals) of extracts of all samples were collected and subsequently refined by immobilised metals affinity chromatography. Ligands of trace elements involved in the fraction were sorbed in column packed with Chelex-100 chelating resin in Cu^{2+} cycle and subsequently eluted by ammonia solution. Isolated ligands were hydrolysed by hydrochloric acid and analysed by IEC for the amino acid composition. Low portions of sulphur amino-acids and high amounts of acidic amino-acids were found. In parallel with amino-acid analysis the ligands were investigated by MALDI-MS. No phytochelatins were found in spectra of these ligands.

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PROFICIENCY TESTS AND QUALITY ASSURANCE IN A TRACE ELEMENT LABORATORY

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Study of the input of risk elements from the environment into food chain is impossible without analytical determination of these elements in water, as well as various biological materials. Quality assurance of the analytical information produced is a necessary pre-requisite of full-valuable work of an analytical laboratory. To asses the accuracy of data produced, analytical laboratory should regularly take part in proficiency tests (PTs).

Our Trace Element Laboratory (TEL) deals predominantly with the determination of trace elements, such as As, Cd, Cu, Cr, Hg, Ni, and Pb in animal and plant materials. TEL took part in certification analyses of CRM 12-02-01 (Bovine Liver) [1], and CRM 679 (White Cabbage) [2], and all the data supplied were accepted for the calculation of certified values. Since 1992 the laboratory had been taking part in interlaboratory analyses International Plant-analytical Exchange (IPE) organized by WEPAL (NL) for plant materials, and the agreement of our data with statistical estimates of true value published by IPE organizers was satisfactory and confirmed that procedures used in our laboratory and the whole analytical system led to accurate results for plant materials [3].

Here we wish to discuss the results of analysis of urban dust within PT organized as a part of 5th FP EU project QUA NAS. Samples of urban dust were decomposed by three methods (dry ashing with dissolution of insoluble residue with mixture of HNO_3 + HF, microwave decomposition and melting with sodium borate and sodium hydroxide). The concentrations of elements in digests were measured using ICP OES, ICP MS, flame AAS (Cd, Cr, Cu, Mn, Ni, Pb and Zn) and HGAAS (As), mercury content was determined in dry sample using AMA 254. Data obtained by the different techniques will be discussed in the poster and compared with the values derived by PT organizers.

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SPECTROSCOPIC STUDY ON TRAZODONE / β – CYCLODEXTRIN INCLUSION INTERACTIONS

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Investigations of molecular recognition have attracted much attention in supramolecular chemistry involving natural and artificial host – guest systems. Cyclodextrins (CD) are macrocyclic oligosaccharides and due to their special hydrophobic cavity structure have the unique ability to form inclusion complexes with various organic and biological molecules through non-covalent interactions. CD are widely used in pharmaceutical, cosmetics and food industries for improving solubility, dissolution rate, stability and the bioavailability of drugs. They also have analytical applications for altering the properties of quest molecule through complex formation.

The main objective of the investigation is the analysis of the complexation of antidepressant drug trazodone (TRD) by β- CD in aqueous solution and in solid state by spectroscopic methods with the aim to obtain a wide range of information to draw a complete picture of the interaction. Nuclear Magnetic Resonance (NMR, 1H, 13C and COSY, HSQC), Fourier - Transform Infrared (FT–IR) and UV spectroscopy were used to characterize the TRD/ β–CD complex. The complex formed with stoichiometry of 1:1 and the formation constant (K) was used to calculate by Benesi-Hildebrand equation, based on measuring the variation in the absorption intensity of the guest molecule as a function of growing β–CD concentration. FT-IR and UV analysis gave evidence for the formation of the TRD/ β-CD complex. The details of interaction were analyzed by 1D, 2D NMR. NMR spectra confirmed the inclusion and to provide information on the geometry of TRD inside the cavity of β-CD. It was found that the part of TRD molecule, the benzene ring entered into the cavity of β-CD.

Based on the significant enhancement of absorbance of TRD, a sensitive UV spectrophotometric method was developed for the determination of active substance in bulk solution and in pharmaceuticals using β-CD. The method has been validated and marked by good precision with RSD less than 1 % and good accuracy about 99.6–100.2%.

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EFFECT OF SOIL MOISTURE CONTENT ON THE METAL CONCENTRATION MEASURED BY DIFFUSIVE GRADIENTS IN THIN FILMS TECHNIQUE (DGT)

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In situ measurement were performed by means of the diffusive gradients in thin films technique in order to characterize the sewage sludge amended soil from one representative sampling site in the Czech Republic, included in the monitoring investigations. This technique reflects actual metal ion concentrations in soil solution, the rate of metal resupply from soil solids to soil solution, and the transport rate of metal ions through the soil. The DGT technique is likely to provide a good surrogate for a metal pool in contaminated soils, which might be available for a metal uptake by a plant root system.

Impact of soil moisture content on the DGT metal uptake of cadmium, copper, nickel and lead was studied in this work. The DGT devises were deployed in the soil aliquots with various moisture content from 33% to 100% and fluxes of individual selected metals were measured. Results of the mathematical method of regression used for calculation of distribution coefficient Kd, which is in this instance a ratio of the equilibrium concentration of metal ion in the soil pore water solution and the equilibrium concentration of the same metal in soil together with the calculation of the pool concentration of the metal in soil are discussed in the contribution.

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SIMULTANEOUS DETERMINATION OF TRACE AMOUNTS OF MERCURY AND COPPER BY DERIVATIVE SPECTROPHOTOMETRIC H-POINT STANDARD ADDITION METHOD AFTER THEIR SEPARATION AND PRECONCENTRATION ON MODIFIED NATURAL CLINOPTILOLITE ZEOLITE

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This method has been developed for the simultaneous preconcentration and determination of mercury and copper based on the adsorption of their Nitroso-S complexes on a natural clinoptilolite zeolite. The adsorbed complexes could be eluted using dimethylformamid and the concentration of mercury and copper were determined by first derivative UV-Vis spectrophotometry (FDS) at appropriate (dA/dλ) in order to work on the basis of H-point standard addition method (HPSAM). By FDS (Fig. 2), minor spectral characteristics are obtainable with better resolutions against the zero-order spectra (Fig. 1). When mercury is selected as the analyte, one pair of wavelengths showing the same dA/dλ for the copper complex will be 556 and 623 nm. Therefore these two wavelengths can apply for simultaneous determination of Hg(II) and Cu(II) by FDS-HPSAM (see Fig. 3 as one sample of the FDS-HPSAM plots). In optimum conditions, detection limits in original solution are obtained 0.1 ng/mL for mercury and 0.5 ng/mL for copper. The suggestive method is applied to determine of mercury and copper ions in plant and biological samples successfully.

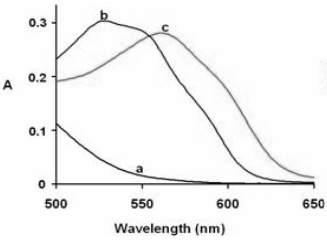

Fig.1

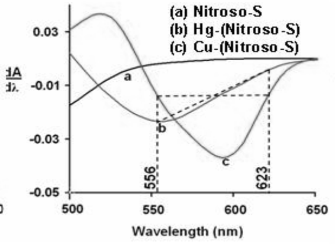

Fig.2

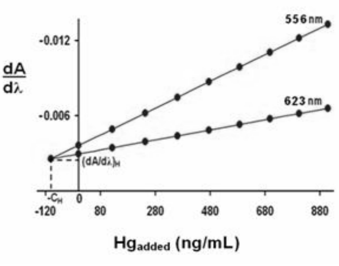

Fig. 3

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P-44

LUMINESCENCE PROPERTIES EU(III) COORDINATION POLYMERS WITH BIS(DIPHENYLPHOSPHINO)ALKANE DIOXIDES

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The luminescence properties of lanthanide(III) complexes are different to those of common organic fluorophores (sharp profiles in emission spectra, long Stokes shift, extremely long luminescence lifetimes). This behavior can be explained by "antenna effect" - the energy is absorbed by the ligand and then is transferred to the central ion. Therefore the emission from Ln(III) depends on its surroundings and emissive properties of the Ln(III) are determined by the ability with which its excited states can be populated and the non-radiative deactivation pathways are minimized [1]. The luminescence quenching is strongly dependent on the presence of –XH oscillators in the surroundings of Ln(III), such as molecules of H_2O or –NH and –CH groups [2]. The sensitization by suitable chromophoric ligands encapsulating and protecting the central ion can minimize non-radiative losses of emission and increase quantum yield as well as luminescence lifetime.

In this work, we present a study on spectral properties of lanthanide(III) coordination polymers with bis(diphenylphosphino)alkane ligands [3] where alkane is ethyl, butyl or hexyl and lanthanide salt is $EuCl_3$ or $Eu(NO_3)_3$) to find relationship between luminescence properties and structure of newly synthesized compounds. Our preliminary results have proved significant differences in luminescence lifetime for each polymer - it was observed that luminescence lifetime is in correlation with length of alkane chain (in both solid state and in acetonitrile). Differences were found also in emission spectra (mainly in ratio intensity of $^5D_0$ - $^7F_2$ and $^5D_0$ - $^7F_1$ transitions) for polymers prepared from nitrate and chloride salts. This variation is probably related to the symmetry of complexes.

Acknowledgment: This work was supported by the GAČR project (203/08/1111).

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P-45

CAPILLARY ELECTROPHORESIS LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR ELEMENTAL SPECIATION

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On-line combination of capillary electrophoresis (CE) and sensitive, element-selective, inductively coupled plasma (ICP) and mass spectrometry (MS) is commonly based on a nebulizer interface for direct linking to ICP torch, resulting in reducing the electrophoretic resolution due to pressure-induced flow caused by the nebulizer. In our approach, CE fractions are collected on a suitable target and the entire separation record is analyzed by laser ablation/desorption (LA/LD) ICP MS.

CE separation fraction collection is carried out by linking a separation capillary via a liquid junction to an infusion capillary, which directs the effluent onto a target sealed in a partially evacuated (~20 kPa) laboratory-built chamber. The probe with the infusion capillary is software-operated to generate discrete fractions of effluent along the target, which is then moved into a laser ablation cell. Employment of the liquid junction allows maintaining high separation efficiency and the laser ablation manages the transport of sample to gaseous phase via ablation and/or desorption from the target surface.

Model system of Cr^{III}/Cr^{VI} was chosen to demonstrate the performance of this off-line connection of CE and LA/LD ICP MS in terms of sustaining the separation efficiency compared to on-line CE - ICP MS employing nebulizer-like interfaces. Selection of an appropriate target containing no chromium was performed, while considering following materials Al, AlMg, AlNi, Cu, PETG (polyethyleneterephtalate glycol), and glass.

Next, attention was paid to describe the deposition of samples onto these targets, sample morphology, laser fluence for sample spot complete clean-up, and to optimize overall speciation conditions. Finally, an example of CE – LA ICP MS of chromium species is shown.

Acknowledgement: This work was supported by the Czech Ministry of Education, Youth and Sports, MSM0021622411, MSM0021622412, MSM0021622415 and LC06035.

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P-46

IMMOBILIZED METAL AFFINITY CHROMATOGRAPHY AS A TOOL FOR THE ISOLATION OF TRACE ELEMENTS

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Immobilised metal affinity chromatography (IMAC) was used for the selective isolation of bioligands occurring in plant tissues. The following model ligands were tested: glutathione in both reduced and oxidized form, carbonic anhydrase, phytic acid, fumaric acid, peptides: Asp-Ala, Asp-Glu, Gly-Gly-Gly, $(\gamma\text{-Glu-Cys})_4$-Gly. Four different metal ions were utilized: Cu^{2+}, Ni^{2+}, Co^{2+} and Ga^{3+}. An apparatus consists of a peristaltic pump and a 1 ml HiTrap Chelating column packed with iminodiacetate resin. The procedure was monitored by an UV detector and by an ICP-MS spectrometer.

The main steps of the optimisation involved the selection of a proper metal ion as well as a kind of buffer solution, especially its pH value. The elution step accomplished by competition of adsobed ligand by ammonium (0.3 mol/l ammonia solution) is very effective: no irreversible sorption of all ligands occurs regardless the kind of metal ions. The only exception was phytic acid, which was bound too tightly and not eluted.

Optimum conditions allowing an isolation of the peptides with expected affinity to metal ions (containing His, Cys, Glu, Asp) with good efficiency comprise the use of Ga^{3+} ion and sample adsorption at pH=4. The adsorption on Cu^{2+} on the resin is less effective; an application of other metal ions is not suitable at all. $(Gly)_3$ was tested as a weakly chelating compound and its isolation recovery was lower than 5 %. When Ga^{3+} ions are used, the sample adsorption is not affected by the status of S-containing (thiol or disulfide) groups. This was proved by the isolation of oxidized glutathione.

Optimised procedure was applied for the analysis of real samples of rye flour extract and refined ligands of trace elements were analysed by MALDI-MS.

P-47

CHARACTERIZATION OF SOIL HUMIC SUBSTANCES BY UV-VIS AND SFS SPECTROSCOPY

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In this paper we followed UV-VIS and SFS spectral curves and indexes of soil humic subctances (HS) in Modal Chernozem, Luvic Chernozem and Gleyic Luvisol (Czech soil samples). Optical curves and indexes are able to indicate HS chemical properties, structure and quality. Correlation between HS fractional composition and optical indexes in UV-VIS and SFS ranges was studied.

Fractional composition of HS was made by short fractionation method. UV-VIS spectra were measured using Varian Cary 50 Probe with optical fiber within the range 300 – 700 nm. HS were dissolved in mixture of 0.1 M sodium pyrophosphate and 0.1 M NaOH. SFS spectra were measured in the same mixture after appropriate dilution (10 times) using Spectrofluorimeter Aminco Bowman Series 2 within the range 220 - 620nm (at $\Delta\lambda$=20 nm and temperature 20ºC, scan rate: 60 nm/min).

Results indicated the following HS quality: Modal Chernozem < Luvic Chernozem < Gleyic Luvisol. Humic acids and Fulvic acids ratio (HA/FA) decreasing together with increasing values of $Q_{4/6}$ (colour index in UV-VIS range). Highest absorbance in UV-VIS range was found for Gleyic Luvisol. Relative fluorescence was the highest in Modal Chernozem. SFS spectra showed five main fluorophore peaks at: 359, <u>469</u>, <u>489</u>, 501, 513 nm and all samples had similar fluorescence behaviour as Elliot soil humic acid standard (IHSS). Correlation between relative fluorescence index (F) and fractional composition was found.

Acknowledgement: This work has been supported by Grant Agency of the Czech Republic No. 104/03/D135 by the project NAZVA No.QH72039 and by the Research plan No. MSM6215648905 „Biological and Technological Aspects of Sustainability of Controlled Ecosystems and their Adaptability to Climate Change" which is financed by the Ministry of Education, Youth and Sports of the Czech Republic.

P-48

THE COMPARISON OF METAL CONTENT IN SEDIMENT AND SLUDGE AFTER ACID EXTRACTION BY VAPOR RECOVERY DEVICE AND IN MICROWAVE OVEN

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The content of heavy metals in agricultural soils is gradually increasing from various processes such as application of sewage sludge and sediments, 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 sediments 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 sludge and sediment. The first method for its characterization the aqua regia digestion was in this work applied. For the the sample was weigh, hydrochloric acid and nitric acid was added and it was refluxed using the vapor recovery device. The extract was filtered. The second method it is the microwave decomposition of the same samples. For the decomposition the sample was weigh, the same acids was added and it was prepared in microwave oven. The extract was filtered.

ICP-AES was use for determination Cd, Cr, Ni and Pb. The content and the recovery of heavy metals prepared under this two methods described in European standard and values in sludge and sediment in the interlaboratory test was compared.

P-49

NOVEL APPROACHES IN THE ANALYSIS OF PLANT MATERIAL

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Fast and cheap analysis of main nutrients in agrochemical plants is a very important tool for determining the adequacy of current fertilization practices and together with results of corresponding soil tests can help to tailor fertilization practices to specific soil-plant needs. Some vegetation species can be also used as a passive monitors in areas contaminated by heavy metals or as a hyper-accumulators collecting toxic elements in the process of soil phyto-remediation. Detail information on the metal content in plant tissues is necessary for pollution assessment as well as for evaluating of cleaning process efficiency.

ICP OES is the usual technique used for the elemental analysis of plant samples. The accuracy and precision of the analysis depend namely on the process of sample preparation. The cryogenic grinding of samples in the liquid nitrogen before microwave decomposition of samples was tested as a tool for improving the quality of analytical results.

Direct analysis of cryogenically ground plant samples suspended in demineralized water with Triton-X was evaluated as an alternative analytical approach. Main advantage of direct analysis of suspensions is substantial simplification and shortening of the sample preparation step.

LIBS (Laser Induced Breakdown Spectroscopy) analysis of pellets prepared from powder originated from cryogenically ground samples was proved as well. Application of LIBS leaded to radical acceleration of whole analytical process.

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P-50

THE NEW VACUUM FT-IR SPECTROMETER: DESIGN ADVANCES AND RESEARCH APPLICATION

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When the bar for research FT-IR spectrometers was set, we knew that some day we would feel obliged to raise it. For the new VERTEX 80 series Bruker Optics provides an innovative interferometer concept and a very flexible vacuum optics layout, which is the culmination of everything that have been pioneered and developed in over 30 years. The new research FT-IR spectrometer is based on the true-aligned UltraScanTM interferometer (see Fig. 1), which provides the highest spectral resolution achievable on a bench top FT-IR spectrometer. The precise linear air bearing scanner and high quality optics guarantees the ultimate sensitivity and stability.

The rugged and stable cast aluminium vacuum optics bench enables demanding experiments such as high spectral resolution (0.060 cm^{-1}), ultra fast time resolved spectroscopy (ms down to few ns temporal resolution), or ultra-violet spectral range (up to 50,000 cm^{-1}) measurements. The two optional external detector ports accommodate liquid He dewars of bolometer and/or hot electron-detectors (see beam exits OUT 2 and OUT 5 in Fig.1). In combination with the external water cooled high power Hg-arc source, the recently rediscovered terahertz spectral range is accessible (down to less than 5 cm^{-1}). The evacuated optics bench eliminates atmospheric moisture absorptions and provides extreme sensitivity and stability, especially in the far IR spectral regions. All these features make the VERTEX 80v also an ideal instrument to be adapted to a synchrotron light source with its highly brilliant infrared beam.

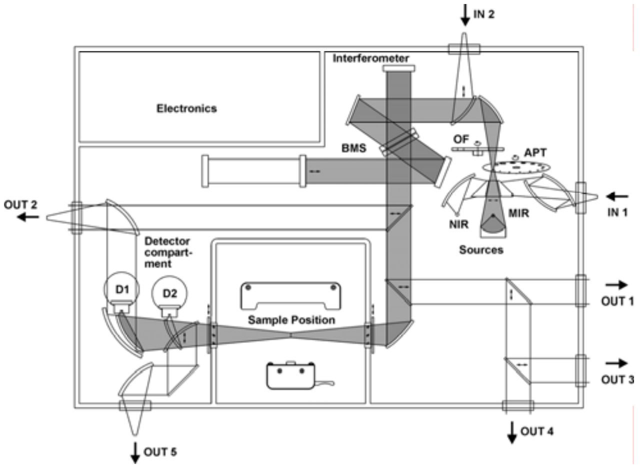

Fig. 1 Optics layout of the vacuum research FT-IR spectrometer VERTEX 80v.

In this contribution we will prove the instruments resolving power ν/Δν of better than 300.000:1 on iodine vapour absorption lines in the visible spectral range and demonstrate its excellent measurement sensitivity and stability. Furthermore, based on FT-IR-microscopy data measured with the VERTEX 80 series spectrometer and an adapted HYPERION infrared microscope, we show that the achievable lateral resolution of such a system is practically only limited by Abbe's diffraction barrier.

P-51

ELIMINATION OF CHLORIDE INTERFERENCE ONTO AG AND TL DETERMINATION IN ETAAS USING DIFFERENT CHEMICAL MODIFIERS: APPLICATION TO THE ANALYSIS OF AQUA REGIA EXTRACTS FROM ENVIRONMENTAL SAMPLES

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The influence of NaCl, $MgCl_2$ and $ZnCl_2$ matrix onto Ag and Tl determination by electrothermal atomic absorption spectrometry using instrumentation with deuterium-lamp background correction (D_2-ETAAS) was comprehensively studied. In order to remove the interference from the investigated chloride matrix, various chemical modifiers, such e.g. mixtures of Pd, Rh or Pt with citric, ascorbic and tartaric acids were suggested and tested. Regarding Ag determination, the presence of Pd with citric acid has shown the highest robustness to presence of all investigated interferent. For Tl determination, the further addition of Li had to been applied to increase the robustness of chemical modifier against strongly interfering $ZnCl_2$ matrix, probably by binding free chlorine into a more stable LiCl molecule. The amounts of individual compounds of Pd with citric acid alone or in combination with Li chemical modifier were optimized for the purpose of direct determination of Ag and Tl in aqua regia extracts from rocks, soils and sediments. The application of modifiers to the direct analysis of all types of investigated samples has enabled the use of maximum pyrolysis temperature of 1000 °C without any noticeable loss of volatile Ag or Tl species. Using optimized measurement conditions the interference of the matrix was completely removed and an accurate determination of both Ag and Tl could be performed using calibration solutions without matrix-matching. The accuracy was verified by the analysis of certified reference samples and/or by the comparison of results with those found using ICP-MS method. Characteristic masses and LODs values for the original sample, using injection of 10-µL aliquots of sample, were 4.3 pg and 0.019 $\mu g\ g^{-1}$ for Ag and 13 pg and 0.043 $\mu g\ g^{-1}$ for Tl.

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P-52

DETERMINATION OF METAL CONTENT IN FINE AIRBORNE PARTICLES

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Particulate matter (PM) is a complex mixture of particles suspended in the air. The size, chemical composition and other physical properties of particles vary depending on the sources and such factors as location, season, day, and time of the day.

Traffic contributes significantly to the production of PM emissions mainly from fuel combustion but also from mechanical abrasion processes from tyres, brakes, clutches and road surfaces. Particles with an aerodynamic diameter < 10 µm are inhaled by humans and very fine PMs penetrate deeply into the lungs. Epidemiological studies have reported associations between the long-term increases in exposure to PM and the increase in illness and death. It is expected that health problems resulting from traffic emission are largest in cities. Traffic emissions do not contribute only to outdoor PM levels, but also to the indoor levels. The major components of PM are metals, organic compounds, and materials of biological origin, ions, reactive gases and the particle core, frequently composed of elemental carbon. Several reports suggest that much of PM toxicity is related to the trace metals content .The group of transition metals may be important. These catalyze the production of reactive oxygen species (ROS). Ultra fine particles collected through autopsy from human lungs were shown to consist mainly of metals.

There are still a few data on the contents of trace metals in fine fraction. Because of small amounts of sampled fine particulates deposited on the filter and due to the low concentrations of some relevant elements, combined analytical methods consisting of high performance sample decomposition in combination with highly sensitive instrumental methods are a prerequisite for getting accurate data. We will present results of PM concentrations and metal contents in the air of localities impacted by the transport. Sampling of PM_{10}, $PM_{2.5}$, PM_1 was performed during 24 hours on streets with different traffic intensity and character. Samples were taken on pre-weighted mixed cellulose filters (Millipore, Type: RAWP) using medium volume samplers Leckel MVS 6 operated in accordance with Directive 1999/30/EC and CEN EN 12341 for sampling of PM for heavy metals analyses. The filters were weighted after 48 hours conditioning with microbalance Mettler-Toledo MX5/A, equipped with antistatic ionizing unit Haug, in an air-conditioned room at 22±1°C and 50± 2% RH. The exposed filters were digested with the mixture of 2 ml H_2O_2 + 3 ml HNO_3 + 1 ml HCl by means of microwave digestion device Multiwave (Anton Paar), equipped with a combined pressure-temperature sensor accessory for reaction control. The determination of elements Ba, Cd, Co, Cr, Cu, Ni, Mn, Mo, Pb, Pd, Pt, Sb, Sn, Sr, Ti, Zn, Zr and platinum group (Pt, Pd, Rh) was carried out by inductively coupled plasma mass spectrometry ICP-MS.

P-53

CRYOGENIC TRAPPING FOR ARSENIC SPECIATION ANALYSIS BY HYDRIDE GENERATION – ATOMIC ABSORPTION SPECTROMETRY

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

The method combines 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 (cooled by liquid nitrogen, packed with Chromosorb). After the preconcentration step, the trap is heated and arsines collected are separated according to their boiling points and released into a quartz multiatomizer. The detection is performed by an atomic absorption spectrometer.

The main target of this work was to investigate processes during the cryotrapping procedure. The arsine collection and volatilization efficiency was determined radiometrically employing ^{75}As radiotracer. 100 % efficiency was found for both collection and volatilization step. In addition, spatial distribution of arsine in the cryogenic trap was studied by image plate autoradiography. Collected arsine was proved to be located in a small spot at the upstream part of the U-shaped cryogenic trap.

A way to achieve lower concentration detection limits is to increase the sample volume. Then a trap blockage by frozen water vapour presents a serious problem. The amount of water vapour can be reduced to a tolerable extent when using a nafion tube dryer with optimized nitrogen dryer gas flow rate.

Another approach to further improving detection limits is to replace atomic absorption detection by atomic fluorescence. Preliminary comparison of detection limits obtained for arsine, methylarsine and dimethylarsine by the both detection methods will be presented and discussed.

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P-54

EFFECT OF SOIL SAMPLE TREATMENT ON AN EVALUATION OF TRACE ELEMENT (CU, FE, MN, ZN) MOBILITY IN SOILS

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Various soil extraction procedures were developed and tested for determination of plant-available, mobile, and potentially mobilizable pools of trace elements in soils without agreement of authors which extractant is the most suitable to estimate individual element portions. Moreover, the effectiveness of individual extractants to predict the plant-available elements depends on soil physicochemical parameters and contamination levels (1). In our experiment the extractability of Cu, Fe, Mn, and Zn with various extracting agents as well as the effect of sample pretreatment were evaluated at eight soil samples differing in their physicochemical parameters.

Among the strong extractants used the extractability decreased in order 2 mol.l^{-1} HNO_3 > 0.05 mol.l^{-1} EDTA > Mehlich III > 0.43 mol.l^{-1} CH_3COOH whereas the extractability of individual elements in order Zn > Cu > Mn > Fe. In the case of mild extraction procedures (0.01 mol.l^{-1} $CaCl_2$, water) the released portions of elements were lower and affected more significantly by differing physicochemical parameters of individual soils and also in behavior of individual elements.

Three sample pre-treatments before extraction were compared: i) air-dried samples; ii) fresh samples; iii) samples freezed for 14 days and than air-dried. The results showed significant response of elements on individual sample pre-treatments as well as the influence of extraction agent applied. Whereas the water extractable portions of elements decreased in order air-dried soil > freezed+air-dried soil > fresh soil completely opposite behavior of extractable elements were observed in 0.01 mol.l^{-1} $CaCl_2$ extracts where the air-dried soils were the lowest. The sample pre-treatment and/or storage before extraction can affect the composition of soil solution which is related to element mobility in soils (2).

Element concentrations in soil solution represent the element portion determining directly the plant-availability of these elements. However, there are different approaches of sol solution collection. We tested i) centrifugation of saturated soil and ii) the application of suction cups. Slightly higher Fe and Zn concentrations were obtained by centrifugation method whereas Cu and Mn concentrations were lower. However, fairly good correlations between these sampling methods were calculated for Cu (r=0.74), Mn (r=0.94), and Zn (r=0.57). For Fe high variability of the data due to very low element concentrations limited the statistical evaluations of the analytical data.

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P-55

EXPLOITATION OF OES ICP IN LABORATORIES OF STEEL INDUSTRY

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Utilization of the OES ICP spectrometry has been started in Chemical Laboratory Department of Trinecke zelezarny, a.s. in 1992. This laboratory provides large amount of analyses of raw materials for steel and iron production process as well as for associated processes such as foundry, refractory materials production and also secondary raw materials and waste processing technologies. The review of materials analyzed by OES ICP method and also the share of OES ICP analyses in total number of classical analytical tests are presented in this paper.

Sample preparation methods of analyzed materials are described. The instrument and analytical program settings as well as obtained results are presented. The parameters of method validation such as repeatability, reproducibility and accuracy evaluated on the base of CRM analyses are demonstrated.

The confidence intervals on the 95% probability level were calculated for different materials (matrices).

P-56

OPTIMIZATION OF THE INSTRUMENTAL AND WORKING CONDITIONS FOR DETERMINATION OF ZN, PB, AS AND SB IN CERTIFIED REFERENCE MATERIALS OF SOILS BY SOLID SAMPLING – ET AAS

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Direct analysis of solids can provide analysts with special information that is not obtainable by conventional techniques requiring sample dissolution. In addition, direct analysis is very important, when only small amounts of sample are available. Environmental monitoring often can be accomplished with direct solid analysis. Although it seems obvious that direct solid sampling analysis with graphite furnace atomic absorption spectrometry (GFAAS) is a powerful technique, it is rather limited by matrix effect of analyzed samples.

In the present work our intention was to develop analytical method for direct determination of selected essential (zinc) and toxic (lead, arsenic, antimony) elements in three certified reference materials (CRMs) of soils by graphite furnace atomic absorption spectrometry in concentration intervals for Zn 63.7-119 μg g^{-1}; Pb 18.9-41.3 μg g^{-1}, As 9.36-14 μg g^{-1} and Sb 1.92-4.58 μg g^{-1} in soils. The undecomposed matrix components from solid samples can influence the atomization of the analyte, so the optimization of analytical parameters and the selection of suitable matrix modifiers is very important.

By the selection of the optimal working conditions it is possible to achieve independence atomization kinetics from matrix components and under suitable conditions it is possible to determine the analyte by using aqueous calibration curve. At optimized experimental conditions, effective in-situ analyte/matrix separation was achieved and calibration could be performed using calibration curves measured with aqueous standard solutions. In solid sampling ET AAS for determination of Zn and Pb the modifiers of Pd/$MgNO_3$ were used. For determination of As the platform was covered with iridium before sampling and then also the modifiers Pd/$MgNO_3$ were used. For the measurements of Zn, Pb, As and Sb were used the resonance lines 307.6; 205.3; 197.2 and 231.2 (206.8) nm respectively and achievable limits of detections for Zn, Pb, As and Sb in soils were 5.18; 1.24; 0.5 and 0.81 μg g^{-1} for maximum used weight, respectively. The results obtained by this method are compared with certified values of the determined elements by application of t-test (at 95% confidence level), which confirmed that the difference in results is not statistically significant and the achieved results are correct.

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ROTATIONAL DEPENDENCE OF THE METHYL BROMIDE DIPOLE MOMENT

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A Stark cell has been developed for Stark spectrum measurements. The Stark electrodes, which are made from stainless steel plates, are 150 cm long, 8 cm wide and 1 cm thick. The electrodes are distanced 1 cm by special quartz blocks which are equally distributed between the plates. A high voltage stabilized power supply (Statron 4209) make possible to provide an electric field up to 3 kV/cm. The corresponding voltage is measured by a precise digital voltmeter (Agilent 34401A). The final values of the electric field intensity between the electrodes are obtained by a voltmeter calibration to precisely measured Stark transitions.

The rotational dependence of the methyl bromide dipole moment was measured for rotational transitions with J" = 3, 8, and 12 in frequency regions of 70, 172 and 249 GHz, respectively. Several different voltages were used in this study. The first, a low voltage (45-80V) when the Stark splitting does not mix different transitions and when the individual Stark components are not resolved were used to obtain the estimation of the dipole moment values for individual rotation transitions. The other voltages used were in interval 500-800V when the individual Stark components were separately assigned.

The standard rotational, Stark and hyperfine matrix elements were used to built up the Hamiltonian matrix in $||J, K, F, m_F\rangle$ basis. The Stark energies were calculated by the direct diagonalization of the Hamiltonian matrix.

A significant increase of the molecular dipole moment with the increasing rotational quantum number J has been observed.

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FINE AND HYPERFINE STRUCTURES IN ROTATIONAL SPECTRA OF THE FCO_2• RADICAL

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The fluoroformyloxyl radical $FCO_2\cdot$ belongs to the atmospherically significant molecules as a product of stratospheric degradation processes of HCFCs and HFCs.

Rotational spectra with resolved fine and hyperfine structures were measured by Prague millemeterwave spectrometer. Fluoroformyloxyl radical was produced by low pressure pyrolysis of bis(fluoroformyl)peroxide at temperature about 570 K. Spectral lines of other molecular species (for example COF_2 molecule) were also observed in our spectra. Therefore the identification of the radical lines was simplified using an external magnetic field affecting only radical lines by the molecular Zeeman effect that causes line intensity reduction.

Previous study of the radical[1] was now extended by more than 160 transitions of both the isotopologues $FC^{16}O_2\cdot$ and $FC^{18}O_2\cdot$from the frequency region 154 – 260 GHz and the new sets of rotational, centrifugal distortion, fine and hyperfine constants were calculated. In addition to molecular parameters, the accurate geometry of this radical was obtained.

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FINE (AND HYPERFINE) STRUCTURES IN ROTATIONAL SPECTRA OF THE FSO_3• RADICAL

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Rotational spectra of the $FSO_3\cdot$ radical were measured in the region 93 – 280 GHz using the Prague millimeterwave spectrometer. The fluorosulfate radical was produced by a low pressure pyrolysis of bis(fluorosulfuryl)peroxide at temperature about 440 K. The measurements were performed using the frequency modulation with accuracy about 10 kHz in the cases of well developed lines.

The assignment of the $FSO_3\cdot$ radical lines was carried out for the first time. Only transitions corresponding to the rotational levels with K = 0, 3, 6, 9 … were unambiguously assigned and this fact indicates the $^2A_2$ ground electronic state. The measured rotational spectra were analyzed in terms of the matrix elements of the rotational, fine and hyperfine Hamiltonians and the corresponding set of precise rotational, centrifugal distortion, fine and hyperfine parameters was derived for the first time.

An interesting feature observed in the fluorosulfate radical rotational spectra was a significant A_1-A_2 splitting that is manifested by a measurable doubling of K = 3 transitions. Both the h_3 splitting constant and its N-dependence were also determined.

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THE Z GF AAS WITH MODULATED MAGNETIC FIELD IN THE ENVIRONMENTAL ANALYSIS

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The Zeeman effect has been known for a long time [1]. The Z GF AAS is also old as a technique itself [2]. The modulation of the magnetic field strength brings new analytical capabilities and the higher engineering comfort of the routine analysis. The introduction of the "three field mode" allows the sensitivity adaptation for higher analytical concentrations. At the last generation instrument device, the magnetic field strength can be freely selected within the given interval. It allows the switching cycle of three magnetic field phases (H_{zero} , H_{med} , H_{max}) and intensity evaluation at the medium and maximum field strength. In this way, the calibration range limited by the roll-over effect is shifted to the higher concentrations. The 3-F switch mode enables the combined evaluation of intensities of the 2-F and 3-F mode. This combined evaluation, termed as the dynamic – D-mode, allows the simultaneous measurement and calculation of analytical curves of different sensitivities. In this way, the concentration range can be expanded over 3 orders of magnitude [4, 5, 6, 7]. The Z GF AAS methods for element determinations of the water and sludge samples were developed. There are presented calibration data (expanded over two orders of magnitude), furnace and digestion programs, and accuracy control of the obviously monitored elements in the environmental samples. The acceptable detection limits (3σ criterion) for this technique and elements were obtained. Study presents the methods of simultaneous determination of the samples with the different element concentration range and the different matrix, as an useful information for an analyst working in the area of the spectro-analytical, hydro-analytical and eco-analytical research.

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ELECTRON TRANSPORT IN POLY[METHYL(PHENYL)SILYLENE]

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Thin films of aryl-methyl-substituted polysilane chain, poly[methyl(phenyl)-silylene], (PMPSi), were prepared by casting from benzene solution under He protecting atmosphere in a small preparation chamber attached to a photoelectron spectrometer and were characterized by X-ray and UV-induced photoelectron spectroscopy. The inelastic mean free path of electrons, the basic parameter for the quantitative analysis using electron spectroscopy [1], has been determined from the measurements and calculations of the elastic electron backscattering probability. Monte Carlo calculations utilize the theoretical model of the electron transport, accounting for the multiple elastic scattering events in the analyzed films. In the present work, calculations were performed using the software packet EPESWIN [2]. The inelastic mean free path values have been determined in the energy range 200 – 1600 eV and compared to the predictive TPP-2M formula [3] and to the quantitative structure-property relationship [4].

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